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TALANTA REVIEW

PLASMA EMISSION SOURCES IN ANALYTICAL SPECTROSCOPY—III*

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Summary—The development and properties of inductively coupled plasma sources are discussed and their applications to spectrochemical analysis are reviewed. Comparisons are made with other types of plasma source.

HIGH-FREQUENCY, ELECTRODELESS, INDUCTIVELY COUPLED PLASMAS

In 1942 Babat published the results of his researches into the properties of electrodeless discharges.[1] These researches became widely known when he published a later paper, in English,[2] in which he described capacitive electrodeless discharges excited by the electric field, and eddy electrodeless discharges excited by the alternating magnetic field, and drew a distinction between them. The first type, in which the elementary conductance currents are not closed and are continued by dielectric currents, he termed "E discharges": the second type with elementary conductance currents in the form of closed curves he termed "H discharges". He considered this distinction could be justified only if the wavelength of the exciting oscillations exceeded the dimensions of the cell containing the plasma; otherwise it was without meaning. Babat made a number of other points which are of interest. The higher the frequency of the generator the lower the current and power consumption required to form a stable plasma. The higher the inductive leakage resistance between the inductor and the "gaseous turn" then again the lower the current and power consumption for stability. (It is presumed that this means tight inductive coupling).

This paper was followed in 1961 by one by Reed[3] describing an inductively coupled plasma torch (ICPT) operating at atmospheric pressure on argon alone or mixed with other gases and powered by a 10-kW H.F. heating unit operating at a frequency of 4 MHz. The torch consisted of a quartz tube, with a brass base having a tangential gas entry, placed within the work coil of the generator. A pilot plasma was first formed by the insertion of a carbon rod into the torch, thus producing thermal electrons by the Joule heating effect of the alternating magnetic field. This provided the initial ionization of the argon, enabling coupling to occur and a plasma to form. Reed thought that a tangential gas entry was necessary in order to create a vortex which would cause some of the plasma to flow counter-current to the gas flow and so maintain the plasma. The equivalent circuit of this H discharge approximated to that of a transformer with the secondary closed by the gas discharge.

Reed followed this paper by another[4] in 1961 in which he described a torch with three concentric tubes with a centre powder feed which he used for crystal growing. There followed a paper[5] in 1962 describing many of the physical properties of these plasmas and suggesting their possible application as spectral sources for solids.

Reed made only passing mention in these and in a subsequent patent[6] of an annular plasma, finding that a doughnut plasma was formed at a frequency of 100 MHz and implying that this was undesirable. Although he claimed to inject solid particles into the plasma it would seem likely from the reviewers' experience that most of the material went round the outside of the plasma, forming a broad tail-flame.

A patent application was made in 1963 (issued later as U.K.[7] and U.S.[8] patents) by Greenfield and his colleagues for a torch adapted for use as a spectroscopic source. This consisted of three concentric tubes. The two outer quartz tubes were used to contain the plasma, and the inner tube, of borosilicate glass, was used to inject an aerosol through the plasma once this was formed. The torch was concentric with the work coil of the generator, which in this case was a 2·5-kW 36-MHz generator. Argon was fed tangentially into the inner quartz tube, the H.F. field applied by the work coil and a pilot plasma produced by a Tesla coil or graphite rod. Once the plasma formed, argon was introduced tangentially into the outer tube to stabilize the plasma and keep it off the walls of the cell. A hole was then punched through the flattened base of the plasma by the introduction,

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through the injector, of an aerosol in argon. The aerosol entered the torch, passed through a tunnel of plasma, and a long narrow tail-flame resulted: it was this tail-flame which was used as a spectroscopic source.

This device was described in a paper[9] published in 1964 which constitutes the earliest reference to the actual use of this type of cell with an annular plasma and the utilization of the emission from the tail-flame remote from the intense continuous emission from the plasma. The same group recently stated that this cell was so successful that despite trying many other designs in the intervening decade they found no reason to change.[10] The particular merits of this torch stem from the annular shape of the plasma which, as discussed later, gives enhanced stability and sensitivity.

Orders of magnitude for detection limits[9] (D.L.) indicated that the source was capable of high sensitivity; no actual optimized D.L. were given. It was also established that the source exhibited freedom from matrix effects. The well-known interference of phosphorus and aluminium with the emission from calcium was completely eliminated. The introduction of gases, vapours, aerosols, liquids, powdered solids and slurries was accomplished.

This paper was followed in 1965 by an account[11] by Wendt and Fassel of an ICPT with laminar flow for which was claimed the advantage of less turbulence and perhaps greater stability than was obtained with vortex flow. This torch was used with a 3·4-MHz, 5-kW generator. It was further claimed that whereas tangential entry of the gases tended to cause sample particles to be thrown onto the walls of the cell, laminar flow did not. This is understandable for the solid type of plasma which they studied, where the sample aerosol flows round the outside of the plasma. In their torch the emission from a part of the plasma not in contact with the atmosphere was viewed through the quartz tube, and it was suggested that this reduced the N_2^+ radiation. D.L. were quoted and were very low. In view of the solid type of plasma employed it is probable that the use of an ultrasonic nebulizer contributed greatly to these low detection limits.

Greenfield *et al.*[12] described the effect of gases, gas-flows and power on the emission from their system. They found that the intensity decreased with the injector gas in the order $Ar > N_2 > air > O_2$. Oxygen had the advantage of removing C–C bonding. It was found that the intensity decreased with the plasma gas in the order $Ar\text{-}N_2 > O_2\text{-}Ar > He > Ar$, but that only a limited quantity of a diatomic gas, which requires to be dissociated, could be used with the power available (2·5 kW). It was concluded that a bigger generator was desirable to enable a plasma to be run on nitrogen alone.

High-speed cine films of the plasma demonstrated that, without smoothing in the rectification circuit, the plasma was extinguished in every half-cycle of the mains frequency. This effect could be used instead of a chopper to allow a.c. amplification in a simple filter photometer. It was suggested that several of these instruments could be grouped around a plasma, allowing simultaneous determination of a number of elements. A further suggestion was that a stroboscope could be used to select one stage in the growth of the plasma and possibly select a particular source temperature.

Later, in 1965, Greenfield *et al.* published[13] some exploratory work on a larger (6·0 MHz, 25 kW) generator using a cell and plasma configuration similar to that previously used. It was shown that the spectra changed from those expected from a flame to those obtainable from a spark as the power in the plasma was increased up to 6·4 kW, measured by a calorimetric method.[14] D.L. were given for a number of elements, and were one or two orders of magnitude better than those obtained with a d.c. arc. The need to find the correct observation height in the tail-flame in order to obtain maximum emission was noted. Practical analyses with the plasma torch were reported for the first time: these were the determination of aluminium in a phosphate rock with a 3-kW, 36-MHz generator and an Optica CF4N1 spectrophotometer, and the determination of phosphorus in phosphate rock with a 25-kW, 6-MHz generator and a Hilger and Watts Large Quartz Spectrograph. Coefficients of variation (COV) of 5% for aluminium at a level of 0·9% and 2·75% for phosphorus at a level of 15% were quoted.

Dunken and Pforr[15] used a three-tube torch similar to that of Greenfield[12] with a 1–2-kW, 40-MHz generator and an ultrasonic nebulizer. Liquids and solids were introduced into the plasma by means of an argon blast but it was not clear if the plasma was annular in shape. The atomic and ionic lines of the elements introduced were found in the spectrum and showed very good signal-to-background ratios.

The torch described by Britske *et al.*[16] consisted of a single tube having side-arms with quartz windows, powered by a 4-kW, 40-MHz generator. This torch had the disadvantage of fixed viewing positions and therefore any optimization of position would be fortuitous. The plasma was described as a long filament (15 cm) surrounded by a weak glow; when the power was reduced the filament disappeared and the glow filled the tube uniformly. Only easily excited lines were observed in the glow, while lines with high excitation energies were excited in the filament. This discharge differs markedly from most ICPT and was later[17] compared with a capacitive discharge. The stability was reported good, with only 1–2% fluctuation, but the analytical sensitivity was low.

An ultrasonic nebulizer with a facility for sample changing was used in conjunction with a 2·5-kW, 36-MHz generator and plasma torch of three-tube design, by Hoare and Mostyn.[18] The top of the outer tube was cut at an angle of 45° and it was claimed that this improved the stability of the gas-flows and led to more effective viewing of the emission. The authors also described a powder-injection system.

Using solution techniques, they determined boron and zinc in nickel alloys. The powder system, whilst very effective for qualitative work, was not very successful quantitatively. Freedom from matrix effects was reported.

A practical application of the plasma torch about this time, was to the determination of wear metals.[19] The oils were injected, in a solvent, by means of a motor-driven syringe and a pneumatic nebulizer. Aluminium, iron and nickel naphthenates were used as standards.

A two-tube torch was used by Mermet and Robin,[20] who demonstrated that greater sensitivity was obtained when an aerosol was injected into the plasma by means of a water-cooled injector, than when fed into the plasma gas stream. They found that with a low injector-gas velocity, the aerosol was entrained on the periphery of the plasma, while at higher velocities it penetrated the discharge to give a darker zone at the centre. Thus it seems at these higher velocities to be an annular plasma. They also found that the amount of aerosol influenced the electrical properties of the plasma so that the power dissipated in it was dependent on the rate of generation of aerosol. The reviewers would not have expected this if the aerosol passed through the tunnel of an annular plasma. There are two observations which might explain the anomaly. The first is that the frequency used (1·6 MHz) is unusually low, so that the skin-depth is unusually large; the tunnel therefore may not be electrically screened. The second observation is that with an injector-gas flow-rate of less than 0·8 l./min, the aerosol all flowed round the outside of the plasma. At 1·0 l./min, the dependence of power on aerosol uptake was very marked, but at 1·5 l./min it was much less so. It might be, therefore, that with these injector-gas flow-rates, only part of the aerosol traverses the tunnel and the rest flows round the outside and that a higher injector-gas flow-rate would be required to ensure that all the aerosol traversed the tunnel. The authors also commented on the relative efficiencies of ultrasonic and pneumatic nebulizers and the effect of changing the gas-flow through them.

Veillon and Margoshes[21] were the first to report the presence of matrix effects. They used a two-tube torch similar to that of Fassel[11] but omitting the central injector, which they claimed did not affect the performance of the torch. Clearly the significance of an annular plasma was not appreciated. It seems to the reviewers that the most likely explanation of the matrix effects is that the electrical properties of the discharge were modified by the sample aerosol flowing round it, thereby altering the power dissipated and hence the temperature. It is also possible that the temperatures encountered in this external path were insufficient to dissociate refractory species.

The axial distribution of temperature, electron concentration and argon continuum was studied along with the analytical lines and detection limits of aluminium, calcium, cobalt, chromium, iron and silicon by Bandyukova *et al.*[22] They used a single-tube torch operating on argon, with a 4-kW, 40-MHz generator.

An account of the ultrasonic nebulization of molten metal into the (previously described) torch was given by Fassel and Dickinson,[23] now using a variable-frequency generator operating at 30 MHz, 2·5 kW (nominal). With this equipment the authors determined arsenic and copper in tin-base solders.

In 1969 Dickinson and Fassel[24] published an account of their continuing investigations into the analytical applications of plasma torches. They now clearly recognized the importance of an annular plasma and suggested that increasing the frequency of the generator would produce an annular plasma because of the skin-depth effect. It was also suggested that introduction of material into the plasma produced a mismatch between the plasma and generator, thus decreasing the amount of power transferred to the plasma. The use of a coupling unit was advocated. This enabled them to get three times as much material into the plasma as was possible with their previous equipment. These authors commented on the matrix effects reported by Veillon and Margoshes and suggested that these were due to the experimental conditions used by these workers. These comments were expanded recently by Larson *et al.*[25] who also extended the work of Greenfield *et al.*[9] on freedom from matrix effects.

A new departure was that of Kleinmann and Svoboda[26] who used a low-power (120–220 W) generator at 40 MHz to power a single-tube torch with separate vaporization of the sample. In a later paper[27] it was demonstrated that this low-power plasma was not in local thermodynamic equilibrium, the electron temperature (11,400 K) being much higher than the gas temperature (about 2200 K). The electron density was $4 \times 10^{14}\ \mathrm{cm}^{-3}$.

Two papers by Truitt and Robinson[28,29] described the introduction of organic material into a torch similar to that of Wendt and Fassel[11] but with a long outer tube. They also described a number of plasma conditions and claimed this torch gave a lower continuum and greater freedom from band structure than that of Greenfield *et al.*[9] This was disputed by the latter workers[30] (with experimental evidence in the form of recorder tracings of spectra recorded with torches of various lengths) who suggested that the plasma conditions described by Truitt and Robinson were probably peculiar to the equipment used. The plasma did not appear to be annular and it was reported that the torch burned if power above 1·7 kW were used, a consequence of its length, no doubt. In the earlier paper, 3064 Å OH bands, Balmer series H_2 lines, 2800 Å OH, N^{2+}, N^-, N^+, NO and N_2^+ were found in the spectra. In the later paper, following the introduction of typical hydrocarbons, four molecular fragments were found in the spectra. These were C, H, C_2 and CN. Under their experimental conditions the point of introduction of the sample made no difference to the emission. The addition of nitrogen increased the CN and decreased the C line intensity. Oxygen diminished CN and C_2 band intensities (because of oxidation to CO or CO_2). When CO or CO_2 was added their emission bands were not noticed. As well as the expected increase in emission from C and Ar, the intensities of the CN and C_2 band systems increased with power (this is undoubtedly peculiar to the particular system used, since increased power usually causes increased dissociation).

In 1970, Pforr and Aribot[31] determined calcium, magnesium, titanium, iron and aluminium in quartz, using a powder-injection system. Borms *et al.*[32] compared an ICPT with flame emission. They had difficulty in operating their ICPT owing to lack of stability, but reported D.L. of 0·01–1 ppm for a number of elements. They also reported that their analytical curves were linear over three orders of magnitude, that 1000 ppm of aluminium, sodium and phosphate did not interfere and that a 1000-fold excess of calcium gave enhancement.

In a short review on plasma sources Greenfield[33] gave a table of spectra observed with a plasma torch operating with nitrogen, argon and oxygen coolant gases. He also listed the relative exposure-times to give comparable background in parts of the spectrum free from banding; these were, for the different coolant gases, nitrogen 60 sec, oxygen 30 sec and argon 7·5 sec. Under favourable conditions COV of the order of 0·3% were obtainable.

A demountable, laminar-flow torch was used by Dagnall *et al.*[34] to experiment with the injection of powders into an annular plasma. Nitrogen was used in the coolant. They found that only one direction of winding of the work coil (the opposite to that of the gas vortex) would allow coupling with the H.F. field.

Kleinmann and Polej[35] reviewed capacitively coupled and inductively coupled high-frequency plasma torches and microwave torches, from the point of view of the requirements of a source and the type of discharge. In commenting on tangential and laminar flow torches they, like Fassel,[11] overlooked the fact that particles are not thrown onto the torch walls by vortex flow if they are fed through the centre of an annular plasma.

Triché *et al.*[36] introduced powders into a single-tube torch. The system was not quantitative and they had difficulty in penetrating the solid plasma. An attempt was made to predict the position of maximum emission according to the ionization potential of the element under examination. They found that they had to take into account the excitation potential as well. In a later paper[37] Triché and his colleagues examined the effect of mass transfer on the emission.

A 6·6-kW, 5·4-MHz generator with a three-tube torch and a water-cooled metal injector was used by Souilliart and Robin[38] to determine rare earths in an iron matrix; they also gave tables of D.L.

The extreme sensitivity and versatility of the ICPT was demonstrated in a paper by Greenfield and Smith,[39] who in 1972 showed that determinations at the ppm level could be carried out on microlitre quantities of sample. Limits of detection for barium, $1{\cdot}7 \times 10^{-10}$ g, and aluminium, $1{\cdot}1 \times 10^{-9}$ g, were obtained with precisions between 3 and 5%.

In 1972, Boumans and de Boer[40] compared an ICPT with an argon-separated nitrous oxide–acetylene flame and gave D.L. for an argon plasma. They found the stability of the plasma to be comparable with that of the flame. Theoretical reasons were given for their choice of a free-running oscillator rather than a crystal-controlled generator. They pointed out that the lowest D.L. was not always associated with the operating conditions that gave the highest line-to-background ratio. A compromise must be sought in both the choice of the carrier-gas flow and the observation height when different elements are examined simultaneously. For some elements it was found that both line-to-background ratio and noise level tended to decrease if the observation zone was chosen lower in the tail-flame. Since a decrease in line-to-background ratio and a decrease in noise level have opposite effects on the D.L., it transpired that D.L. of the elements considered did not vary markedly with the location of the observation zone. These authors also defined limits of detection, representing the curve in the vicinity of the D.L. as a straight line. The authors of this review take leave to doubt the universal validity of this assumption at very low D.L.

By using a monochromator with a nitrogen path between it and a plasma torch, Kirkbright *et al.*[41] were able to obtain D.L. of 1·7 ppm for sulphur at a wavelength of 182·04 nm and 0·15 ppm for phosphorus at a wavelength of 214·91 nm. The linear range for these two elements extended over five orders of magnitude, to above 1000 ppm. Soil extracts were analysed for phosphorus and COV of 3–7% were obtained.

Fassel[42] reviewed "Electrical Flames" and concluded that the D.L. which could be obtained with ICPT were, with few exceptions, comparable with, or greatly superior to, the best which could be obtained with flame atomic absorption, emission or fluorescence. He also confirmed that a plasma similar in configuration to his own and that of Greenfield[9] was free from the matrix effects experienced by Veillon and Margoshes.[21]

In an extension of their previous work,[41] Kirkbright *et al.*[43] determined iodine, mercury, arsenic and selenium. They reported some spectral interferences and also some chemical interferences occurring in the nebulizer.

Alder and Mermet,[44] using a demountable three-tube torch, observed all the expected ArI lines but no ArII lines. The highest energy-level from which radiation was observed was about 15·4 eV. When methane was injected, atomic C and H were observed, together with C_2 and CN, but no emission from CO or CH (see refs. 28, 29). C_2 was seen in cooler regions of the tail-flame but not in the hot regions (see ref. 13) indicating decomposition of the molecule. They commented that since the bond strength of C_2 is 6·25 eV and that of CH 3·47 eV they may be too unstable to form. No enhancement of zirconium or hafnium emission was found in an argon-methane plasma compared with one of pure argon; this implies that reduction of the oxides by atomic carbon does not take place and that the temperature and enthalpy of the plasma are sufficient to break strong oxide bonds. Similarly when lanthanum was introduced into an argon plasma, no bands due to lanthanum oxide were observed. Sulphur dioxide, hydrogen sulphide, sulphur hexafluoride, bromine, chlorine and phosphorus were also introduced into the plasma, but the system was not suitable for determining sulphur or the halogens.

Boumans *et al.*[45] considered the design of a generator and torch in a paper which is referred to in the section on oscillators.

Scott *et al.*[46] used a three-tube torch with vortex stabilization without a "plasma gas" in what is described as a compact system. The aerosol was produced by a pneumatic nebulizer and desolvation was not used. They hoped to replace the single-channel spectrometer used, by a thirty-channel instrument. With an input power of 1·3 kW one might presume a power in the plasma of between 650 and 900 W. Temperatures of 5000 K, at 18 mm above the load coil, were reported. Linear calibration curves were obtained over concentration ranges of five orders of magnitude.

Using a similar generator to Boumans and de Boer[40] and a horizontal configuration of a similar three-tube torch with a wide-tube injector, Kornblum and de Galan[47] measured the radial distribution of temperature. They found that desolvation of the aerosol was mandatory as a 2-kW plasma could not be sustained with a high input of molecular compounds. This is so much at odds with the observations of other workers[10] that the geometry of their cell and injector must be at least a contributory factor in this phenomenon. The reviewers suspect the use of the wide-bore injector.

Dreher and Frank[48] describe a demountable torch operating at atmospheric pressure in argon, which they used for emission spectroscopy in the vacuum ultraviolet. The source was totally enclosed, with no gas flow. The power was very low (250 W) and the cell had to be dismantled and cleaned after each exposure.

Kirkbright and Ward[49] constructed ideal models for an ICPT and for a flame. They concluded that the self-absorption effects were much less in a plasma than in a flame and that the sensitivity was much higher. As a consequence of the former the plasma had a greatly extended linear working range. Other deductions made were that the maximum energy supplied to the analyte particles was 2·3 and 0·001 J for the plasma and the flame respectively, that a plasma can handle a concentration range of five or six orders of magnitude against three for the flame and that concentration ranges for the plasma can be increased by reducing the sample-uptake rate. Cu, Fe, Mg, Mn, Ti and Zn were determined in aluminium alloys with a flame and with a plasma. Non-linear calibration curves were obtained when using a flame without dilution. Precisions of the order of 5% were obtained with the plasma, as against 10% with a flame. Kirkbright reported this work at a later date in lecture form.[50]

Fassel and Kniseley[51] published a re-assessment of emission spectroscopy with ICPT as against flame-excited atomic absorption, fluorescence and emission spectroscopy, and concluded that ICPT were superior on most counts. They agreed with Boumans and de Boer[40] that the ICPT–optical emission spectrometer system "constitutes a most promising excitation source for simultaneous multi-element analysis of solutions".

Such a system, which has been in everyday use for practical analysis for four years, was described[10] in February 1975. The authors give details of an ICPT coupled to a 30-channel direct-reading spectrometer with fully automatic sequential sampling and read-out. The read-out is processed by an off-line computer. With this equipment they are able to do simultaneous multi-element analysis at both trace and assay levels on each exposure.

Some important points in its design are discussed.

Low-pressure inductively coupled plasmas

Papers have appeared describing ICPT operating at low pressure. One of these[52] describes a plasma, powered by a 42–60-kW, 0·54-MHz generator, which discharges into a vacuum chamber. In action it appears to be akin to an ICPT version of a plasma jet. The authors measured the electron density, excitation temperature and the gas temperature in the jet region and in the jet nozzle. The gas temperatures were substantially lower than the excitation temperature, indicating divergence from LTE, which is, of course, difficult to achieve at low pressure.

Runser and Frank[53] designed what they call a "radio-frequency electrodeless differential pressure cell" for studying the emission spectra of organic molecules. (All frequencies from 0·01 up to 30,000 MHz are radio-frequencies. Most ICPT operate in the range 3–50 MHz and are more aptly described as high-frequency ICPT.) Pressure, power and flow-rate studies as well as gas measurements were made with this cell. Low and medium resolution spectra of aromatic and non-aromatic chlorinated hydrocarbons and chlorinated pesticides were discussed.

Inductively coupled plasmas in atomic-absorption spectroscopy (AAS)

Wendt and Fassel[54] first reported the use of an ICPT as an atom reservoir in AAS. They used a multi-pass system with their previously reported torch.[11]

Low backgrounds were reported and some matrix interferences were also removed, such as the effect of phosphorus and aluminium on the absorption spectrum of calcium.

In 1967, Britske *et al.*[16] briefly mentioned the use of their single-tube torch as an atomizer in AAS.

Bordonali and Biancifiori,[55] also in 1967, described an ICP for use as an atomizer in AAS. Powered by a 10-kW, 5-MHz generator, the cell consisted of a single tube with a branch tube having water-cooled quartz windows. They claimed temperatures up to 20,000 K, the possibility of varying the high-temperature lifetimes of atoms, control of gases in the plasma and independence of maximum temperature with the composition of the gases. These authors published another paper in 1968 on the same subject[56] and in 1969 Bordonali, Biancifiori and Donato[57] described the determination of ytterbium in rare earths. These authors with Morello[58] also determined Zn, Mn, Pb, Cr and Cu in ferrous metals. A U.S. patent was granted to Bordonali *et al.* in 1970.[59]

Greenfield *et al.*[60] designed and used a T-shaped torch as an atomizer in AAS. They claimed this to be a simpler method of achieving a long path-length than the use of multi-pass systems. They also used an ICP as a source in AAS. Some experimental results were given for copper in the atomizer mode and calcium, magnesium and copper in the source mode.

Robin[61] determined Al, La, Mg, Nb, Ta, Ti, Zn and W by an ICP used in the AAS mode. He reported that satisfactory results were obtained for aluminium and magnesium but that better results were obtained with a nitrous oxide–acetylene flame in AAS or by an ICP in emission mode. An ICP in emission mode was also better than a flame in AAS mode. Souilliart and Robin[38] also reported results obtained by an ICP in the AAS mode.

The authors of the present review can, from their own experience, see little, if any, advantage in the use of an ICP in atomic-absorption spectroscopy.

THE HIGH-FREQUENCY GENERATOR

Type of oscillator

The choice of oscillator lies between a free-running oscillator, an oscillator with capacitive tuning and a crystal-controlled oscillator. In the first type, the frequency of the oscillator is fixed by the values of the components in the tank circuit, which includes the work-coil. These values are modified by any changes in plasma impedance and in the coupling of the plasma to the work-coil. Variation of these parameters affects the frequency of operation but has only a small effect on the power transfer. No tuning is necessary. With the second type, the output circuit containing the work-coil must be tuned by a variable capacitor to the frequency of the tank circuit. If there is a change in impedance in the plasma any self-compensating change in frequency may be less than in the case of the free-running oscillator, depending on the degree of coupling of the two circuits. In the third type, the oscillator valve is driven, by a crystal, at a fixed frequency and any change in impedance of the plasma will produce a serious loss of power unless the output circuit is retuned.

Some workers[10,40] in this field argue in favour of a free-running oscillator whereas others[46] favour a crystal-controlled unit. By arcane reasoning Bouman and his colleagues[45] claim that the free-running generator which they use is self-compensating for small changes in impedance.

Dickenson and Fassel,[24] using a crystal-controlled oscillator, find that the introduction of sample material changes the electrical character of the plasma and therefore the effective impedance of the load-coil. This results in mismatching, causing instability or extinction of the plasma unless the output circuit is retuned. On the other hand, Greenfield *et al.*[10] offer circumstantial evidence for believing that there is no change of impedance when aerosols are injected through an annular plasma in their system, and practical evidence that there is little change in the frequency of their free-running oscillator. (Thorpe[62] has also commented that the addition of an injector gas through an annular plasma did not change the plate power or the grid current, indicating that the plasma was not affected.) Unlike Scott *et al.*[46] with a crystal-controlled oscillator, they need no complicated starting procedures for the equipment nor do they have the difficulty sometimes[24] experienced in injecting large amounts of liquids and do not need to desolvate except to improve sensitivity. Boumans *et al.*[45] with a free-running oscillator, also seem to experience little difficulty in starting or in running the apparatus, but they desolvate the aerosol. It can be no more than conjecture, but it is possible that other factors, such as the amount of power in the plasma and the design of torch, may be the cause of these discrepancies between workers of experience in this field, rather than the type of generator used. It must be said however, that, all other conditions being equal, complicated tuning procedures are not desirable if the equipment is ultimately to be operated by technicians.

Power

A study of Table 1 shows that most workers have used generators of between 2 and 5 kW (nominal). (50–70% of this power will find its way into the plasma, depending on the coupling efficiency).[2,3,10,62] There has been a recent trend by at least two groups of workers[40,46] towards low-powered (1–2 kW) compact generators, on the grounds of convenience in use. Greenfield *et al.*[10] work with a large (15 kW) generator and cite a number of advantages more cogent than easy availability[46] or licence to work inefficiently.[63] Amongst these advantages are greater sensitivity, frequent improvement in precision, elimination of band spectra and elimination of chemical interferences. To these advantages may be added the fact that higher powers enable diatomic gases to be used with more

Table 1. Typical generating equipment, torches and operating parameters

Ref.	Generator	Power, *kW* (nominal)	Frequency, *MHz*	Type	Nebulizer	Coolant gas and flow, *l./min*	Plasma gas and flow, *l./min*	Injector gas and flow, *l./min*	Flow pattern	Type of plasma
9	Radyne S.C. 15	2·5	36	Free running	Pneumatic	Ar 17	Ar 5	Ar	Vortex	Annular
11	Lepel T-5-3-MC-J-S	5·0	3·4		Ultrasonic	Ar 22	Ar 0·4	Ar 0·5	Laminar	Column
13	Radyne	25·0	6	Free running	Pneumatic	Ar 10–33	Ar 23–43	Ar	Vortex	Annular
18	Radyne S.C. 15	2·5	36	Free running	Ultrasonic	Ar 18	Ar 3	Ar 0·5	Vortex	Annular
19		1–2·0	40		Pneumatic	Ar 8–13	Ar 0·25–1·3		Vortex	
21	Taylor-Winfield	5·0	4·8		Pneumatic with desolvation	Ar 30	Ar 1·7	Sample introduced with plasma gas	Laminar	Column
24	Lepel T-2·5-1 MC2-J-B	2·5	30	Frequency variable with coupling unit	Ultrasonic with desolvation	Ar 17	Ar 0·75	Ar 1·7	Laminar	Annular
34	Radyne S.C. 15	2·5	36	Free running	Powder injection	N_2 7·5	Ar 7·5	Ar 0·5	Laminar	Annular
30	Radyne R.D. 150	15	7	Free running	Pneumatic	N_2 64	Ar 15	Ar 3·2	Vortex	Annular
38	STEL	6·6	5·4		Ultrasonic with desolvation	Ar 7–20	Ar 7	Ar 2	Vortex	
40	Philips 131202/01	2	50–70	Free running	Ultrasonic with desolvation	Ar 15	0	Ar 1·2–1·5		Annular
41	Radyne H30/P	5	36	Free running	Pneumatic	Ar 15·0	0	Ar 3	Laminar	Annular
44	STEL 5060	6	5·4		Ultrasonic with desolvation	Ar 7–22	Ar 7	Ar 1·5	Vortex	Annular
10	Radyne R.D. 150	15	7	Free running	Ultrasonic with desolvation and pneumatic without	N_2 20–70	Ar 10–35	Ar 2–3	Vortex	Annular
16	LG 4	4	40		Pneumatic	Ar single gas flow			Laminar	Column
20	STEL	5	1·6		Pneumatic and ultrasonic		Ar 20	Ar 0·8	Laminar	Column
76		15	15		Powder injection	Water-cooled	Ar 15–20	Ar	Laminar	Column
46	International Plasma Corp. Model No. 120–127	2·0	27	Crystal-controlled	Pneumatic	Ar 10	0	Ar 1·4	Vortex	Annular

freedom in the torch; furthermore the torch is not easily extinguished when high material loads, such as powders, are put through it. A disadvantage is that these generators are expensive and large, although the use of solid-state electronics may reduce their size.

Frequency

It now seems to be accepted by the principal workers in the field that it is desirable to use an annular plasma. Production of an annular plasma is often attributed[24,40,45,46] to the skin-depth effect whereby, as the frequency increases, the current is confined to a thinner skin on the circumference of the plasma. Thus it is claimed that frequencies of the order of 30–50 MHz are desirable.

Greenfield *et al.*[10] have shown that the central hole can be produced as easily in a plasma at 7 MHz as in one at 36 MHz and have shown photographs demonstrating that the two resultant annular plasmas are very similar. These authors are of the opinion that the tunnel effect is more a function of injector gas-flow than of skin-depth, and that since it is easier and cheaper to obtain high powers (which they favour) at lower frequencies, the optimum frequency is probably quite low, perhaps in the range 5–10 MHz. Some discussions of the optimum frequency (*i.e.*, the frequency at which a specified temperature is obtained with the minimum power) are referred to in the section on temperature. In any case, the frequency chosen should be high enough for the skin-depth to be substantially smaller than the plasma radius,[5] both to ensure that the tunnel of an annular plasma is electrically screened so that the sample will cause only minimal variations in the plasma impedance, and to keep the volume over which the power is dissipated reasonably small so that the power density required to sustain the discharge does not demand excessively high power inputs. An optimum ratio of plasma radius to skin-depth has been suggested,[46] but doubts have been expressed on the validity of the assumption of the plasma's similarity to a metallic cylinder[64] and on the validity of the expression for the magnetic field appropriate for a very long coil when applied to a short one.[10] The application of the optimum ratio to torch design has sometimes led to an unstable plasma.[10] Table 1 shows some of the generator frequencies which have been used, along with other experimental details.

INTRODUCTION OF LIQUIDS AND SOLIDS INTO THE PLASMA

The plasma

There is ample attestation[4,42,62,65,66] to the impenetrable nature of plasmas and the tendency for injected streams of material to by-pass rather than penetrate them. This tendency to deflect injected flows has been explained[67] in terms of excess of magnetic pressure inside the plasma.

Measurements of the radial distribution of the magnetic field in the plasma, by means of magnetic probes, have shown it to be at its greatest near the tube walls, falling to a low value in the centre.[68,69] Similarly the magnetic pressure exhibits this drop towards the centre. Chase[67] has pointed out that this drop from the boundaries to the axis will lead to an inward radial flow of plasma by "magnetic pumping". This will build up the kinetic pressure at the axis and cause an axial flow of plasma to both ends from whence it will return to the outer boundaries. In this way vortex rings will be formed, superimposed on the main axial flow and the thermal expansion of the gas.

Chase[70] later described how he had measured the pressures in and around a vortex-free plasma by means of probes and a micromanometer. He also obtained flow visualization and gas velocities by photographing injected solid particles; the thrust calculated from a model of the plasma was in agreement with the measurements. He concluded that in order for the injector flow to penetrate the plasma, the velocity must exceed the magnetohydrodynamic (MHD) thrust velocity. For an argon plasma at 10 kW a jet of velocity of 15 m/sec completely penetrated the plasma, whereas with a velocity of 3 m/sec it was completely deflected. Once the injector velocity is greater than the MHD thrust velocity an annular or tunnel plasma is formed and the injector stream passes through the tunnel, forming a long narrow tail-flame. It thus becomes possible to view the emission from the tail-flame remote from the intense continuum of the plasma. This gives increased sensitivity. In addition, since the sample particles flow through a tunnel which is electrically screened, they do not influence the plasma impedance. This leads to improved stability. Since this principle was first established[9] it seems to have been recognized[24,40,42] as the system giving the greatest sensitivity and freedom from matrix effects. The existence of the MHD thrust velocity may vitiate the assumptions on which some estimates[46,49] of residence times of sample atoms in the plasma have been based. In particular it would be expected to decrease the residence time in the tail-flame.

Plasma cell

It has been suggested[10] that it becomes easier to form an annular plasma by the introduction of a second gas stream which flattens the base of the ellipsoidal plasma and facilitates the entry of the injector stream. The torches used by most workers have two concentric silica tubes with a central injector. The gas streams in the outer and inner tubes have become known, respectively, as the coolant and plasma gases, although the demarcation between them is slight, since either can be turned off without extinguishing the plasma and both must contribute to the plasma process. Indeed, Scott *et al.*[46] appear to have dispensed with the plasma gas-flow although retaining its tube.

Greenfield *et al.*[10] found that most of the dimensions of the cell are unimportant as the gas velocities can be changed by altering the flow-rates. However, they emphasize that the bore and position of the injector are important. If the jet is too large or placed too far away from the plasma the resulting "fan" will not penetrate the plasma. They stress the greater importance of the dynamics of the gas flow rather than that of the skin-depth in the production of an annular plasma. This view is supported by Thorpe.[62]

Nebulizers

Most, if not all, workers introduce liquids into the plasma in the form of aerosols. These aerosols are produced either by the ultrasonic breakdown of the liquid surface or by use of pneumatic forces. In the former case the liquid may be directed onto the surface of an ultrasonic transducer[40] or the ultrasonic radiation may be focused through the liquid on to its surface.[11] A pneumatic, venturi nebulizer of the scent-spray type can be arranged to spray directly through an annular plasma,[7] or to spray into a separate chamber (often a cyclone chamber to remove the heavy droplets) and the aerosol piped to the injector in the plasma torch.[39,71] Direct injectors have to be of all-glass construction with long, fine, capillary tubes and are somewhat delicate and prone to damage.

There is little doubt that ultrasonic nebulizers give finer aerosols than do the pneumatic type and more material is conveyed to the plasma in unit time.[20] This is evidenced by the markedly superior limits of detection which can be obtained with these nebulizers. However, they have one marked disadvantage: sample-changing is difficult[20] and generally necessitates washing out the cell after each sample. This precludes automatic operation. Attempts have been made to overcome this problem by the use of pumps to change the sample.[33,45,72] Another approach was that of Hoare and Mostyn[18] who used a multicell sample vessel.

As might be expected, if the solvent water molecules are removed by the use of a heated desolvator, an increase in sensitivity results. Ultrasonic,[11,40,72] and pneumatic[73] nebulizers have been built with desolvators. Some workers[45] have found it essential to desolvate, otherwise the plasma may be extinguished, since energy is removed by the dissociation of the water molecules. Others[10] find no such difficulty and are able to introduce relatively large quantities of solvent molecules. The reason for this discrepancy may lie not only in the power available, but in the geometry of the injector and the cell. Several[10,40,46] workers have reported on the possibility of memory effects resulting from the use of desolvation techniques. Greenfield and Smith[39] have demonstrated that it is possible to inject 1–25 μl of solution from a micropipette or a syringe into a pneumatic nebulizer and for the resultant plug of aerosol to be injected into the plasma. They determined aluminium, chromium and copper at the ppm level in 25-μl

samples of oil, diluted 1:2 with xylene, and aluminium and magnesium in organophosphorus compounds. They also demonstrated the presence of ppm quantities of metals in μl samples of blood. Subsequently, Kniseley[74] also determined metals in blood by this technique.

A useful review of nebulizers is given by Mavrodineanu and Boiteux.[75]

Introduction of solids

The main difficulty in introducing powdered solids into a plasma is that of ensuring a constant, uniform feed of the material. It is doubtful whether this problem has been solved in a completely satisfactory manner. Another difficulty is that of ensuring that all the material goes through the plasma and at such a rate that it is all volatilized. These problems are not critical in crystal-growing, a field in which powder-feed to a plasma is successfully used.[4]

Greenfield *et al.*[9] used a direct pneumatic nebulizer to inject powders and slurries through an annular plasma and reported the tail-flame as being intense and the plasma stable. They did not carry out any quantitative work. Hoare and Mostyn,[18] using a similar torch, injected powders into what may have been an annular plasma from an agitated cup by upward gas displacement. The method was reported as qualitatively successful but it seems that quantitative results were not entirely satisfactory, in that the preparative history of the sample influenced the results obtained. Pforr[31] also used a powder system similar to that of Hoare and Mostyn. Lifshits *et al.*[76] fed iron and aluminium oxides into a plasma, *via* a central tube, in a stream of argon. They claimed a precision of 5–10% for the determination of impurities in these oxides.

Dickenson[77] injected powders into an annular plasma from a fluidized bed and this work was reported upon by Fassel.[42] Later, Dagnall *et al.*[34] used this technique and obtained COV of 6·5 and 10%, respectively, for twenty 10-ppm additions of beryllium and boron oxides to a magnesium oxide matrix. They also used a swirl cup similar in principle to that of Hoare and Mostyn.[18]

All the methods of introducing powders into plasmas suffer from segregation effects to varying degrees, because of the different densities and particle sizes of the powders under investigation. They also suffer from agglomeration and impacting of the powders. First-hand experience of the problems leads to the impression that the partial success so far gained has been obtained on carefully selected matrices, and that a general, practical solution to the several problems of injecting powders into plasmas and performing quantitative analysis, has yet to be found.

Separate vaporization

Kleinmann and his fellow workers[26,27] vaporized the sample before introducing it into the plasma; solids were volatilized by ohmic heating from graphite supports held by tantalum holders. They found that the emission was very dependent upon the shape and temperature of the support. Detection limits were very much better than with the d.c. arc. Kleinmann later[78] investigated the effects of pad temperature, of the molecular nature of cadmium and lithium compounds and of the presence of sodium, acids and complexing agents, on the spectral line intensity.

Nixon *et al.*[79] described a separate vaporization method with a tantalum filament and claimed to be able to examine 20–30 samples/hr. They also reported D.L. 2–3 times better than those obtainable with nebulized samples.

Bazhov and his colleagues,[80] in a method which may be thought of as a direct volatilization system, designed a horizontal plasma torch in which they introduced powders into the plasma in small graphite crucibles. They used a 40–50-MHz generator with 1·5-kW output power to form the plasma, which was initiated by a second similar generator giving a flash discharge between two electrodes. At an argon flow-rate of 7·5 cm/sec the discharge was ring-shaped. At 5 cm/sec it was egg-shaped.

Morrison and Talmi[81] described the microanalysis of solids by atomic absorption and emission spectroscopy. They used an H.F. furnace; in this device the sample was volatilized from a graphite crucible by induction heating, and excited in a helium plasma formed by the same field.

Temperature and other physical properties

Reed[3] calculated the local field strength from the properties of the plasma and thus obtained $\Delta T/T$ where ΔT is the difference between electron and mean gas temperatures. A value of 10^{-4} was obtained and from this and other circumstantial evidence he presumed that the plasma was in LTE. He then went on to determine the temperature of the plasma spectrographically. He calculated the variation with temperature of the intensity of an argon line, and noted that the maximum intensity would be produced at a temperature of 15,000 K. He then found by an Abel inversion that the maximum emission occurred at a position off the axis. He concluded that this region was at the temperature of 15,000 K and that the temperature at the centre would exceed this. It could be estimated by the ratio of the intensity of this region to the maximum intensity.

Babat,[2] on the basis that the energy flow is directed from the central part of the discharge towards its periphery, predicted that the temperature of the gas should have its maximum value on the tube axis and its minimum value near the walls.

Gol'dfarb and Dresvin,[82] however, argued that the electron temperature T_e and the gas temperature T_g become equal in a d.c. arc at a current of 10 A and this current corresponds to an electron density (n_e) of $\approx 10^{16}\,\mathrm{cm}^{-3}$. They went on to compare an arc with an ICP and obtained an electron density of $(0{\cdot}65\text{–}1{\cdot}2) \times 10^{16}\,\mathrm{cm}^{-3}$ over the major part of the plasmoid. They inferred that T_g and T_e were equal in their plasma, so this was in local thermodynamic equilibrium. They also concluded that the maximum temperature of the plasma was 9200–9700 K, the plasmoid had sharp boundaries at the tube walls and along the vertical, the temperature gradient at the tube walls was 5×10^4 deg/cm, and in the region near the axis, the temperature and electron density decrease. The highest temperature and electron density occurred about midway between wall and axis (at 0·4–0·6 of tube radius).

The existence of a maximum temperature (about 9000 K) at an off-axis position was also argued by Johnson[83] from a variety of temperature measurements. The explanation of this is that most of the power is dissipated in the outer skin-depth and if the plasma radius exceeds this, the centre is heated largely by radiation and thermal diffusion from the outer layer. Thorpe[62] and Eckert[64] also criticised Reed's values of temperature.

Gol'dfarb, Goikhman and Dresvin,[85] and Gol'dfarb and Goikhman,[86] in two similar papers, determined temperature spectroscopically on the basis of absolute intensity of the atomic spectral lines, by the recombination continuum, by the molecular bands and by the H(β) line broadening. An ICP was used in argon, nitrogen, oxygen and air. It was found that the temperature was 6800 K in nitrogen; between 8300 and 8900 K in argon; 8650 and 9100 K in oxygen; 7200 and 7600 K in air, the electron densities being 2×10^{14}, $3{\cdot}5 \times 10^{15}$, $5{\cdot}1 \times 10^{15}$ and $1{\cdot}2 \times 10^{15}$ respectively. The lengths of the plasma were 2·6, 4, 2 and 2·7 cm respectively. There was a decrease in temperature towards the axis.

Marteney *et al.*[87] determined the temperature of an argon plasma to be approximately 8500 K by the measurement of line intensity ratios by the method of Boltzmann. They confirmed this figure by the measurement of absolute argon and argon-ion continuum intensities. Radial measurements indicated a slight rise in temperature midway between wall and axis with the lowest temperature at the walls. Kasai *et al.*[88] measured the radial temperature distribution of a plasma by Boltzmann plots using line-to-line, line-to-continuum and continuum-to-continuum ratios, and found an off-axis peak. They reported a temperature of 12,000 K on the plasma axis.

Raizer,[89] on the basis of the results of many investigations at several kW power, found that the temperature of an argon plasma reaches 9000–10,000 K and that the distribution of temperature has in general a plateau at the centre of the tube, dropping off sharply near the wall. The plateau is not quite flat, however, and in the central part there is a slight dip of several hundred degrees, thus confirming the results already mentioned.[82–88] Raizer also measured the electron densities and showed that the state of the plasma at atmospheric pressure is close to thermodynamic equilibrium. He gave calculations of the plasma temperature, ohmic resistance and inductance as functions of the current in the solenoid, based on an infinitely long solenoid and metallic cylinder model, which were in fair agreement with experimental data. He concluded that to a good approximation the plasma temperature does not depend on the frequency, or on the radius of the tube, but is determined only by the number of ampere-turns and the electric and thermal conductivities of the gas, provided that the number of ampere-turns is not large and that the temperature does not exceed 13,000–15,000 K. One important conclusion reached by Raizer was that the power necessary to reach a given temperature increases quite rapidly with increasing temperature, even ignoring losses by radiation. He suggests that W, the power input to the plasma, is proportional to T^{γ} where $\gamma = 2{\cdot}5$–3. In addition, the power required increases rapidly as a result of the increasing radiation loss. It was not clear which of the two factors plays the decisive role.

Pridmore-Brown[90] came to roughly similar conclusions on the radial distribution of temperature. However, his calculated temperatures did seem to show some dependence on frequency and on the radius of the tube as well as on the number of ampere-turns.

Spectral measurements by Trekhov *et al.*[91] also tend to confirm the work of these investigators, *i.e.*, a temperature plateau of 9000–10,000 K with a slight dip in temperature towards the centre of the plasma. Also, the coincidence, within experimental error, of the ionization temperatures from the continuum and from the broadening of the Hβ line, and of the excitation temperatures, with the calculated temperatures, led these authors to believe the source was in LTE. Much the same pattern emerges from the work of Eckert[84] and Stokes.[92] Apsit[93] attempted to establish LTE in an ICP in steady state, by a relaxation method which involved a study, with time, of the decaying plasma after switching off. He found a two-stage drop in electron temperature, first a loss of kinetic energy of the electrons rather than of the atoms and heavy ions and, in the second stage, recombination and cooling of the gas. The first stage in argon lasted $\sim 10^{-7}$ sec and material changes in the gas temperature occurred over a period of $\sim 10^{-3}$ sec in the second stage. He concluded that the electron temperature can exceed the gas temperature by as much as 2500–1500 K in discharges of 1–10-kW power, the difference decreasing slightly as the power was increased. He also found that (T_e–T_g) in each cross-section of the discharge reached a maximum at the periphery and dropped rapidly towards the axis so that the central region is nearer to LTE than the outer. He found that when a gas was forced through the tube, (T_e–T_g) along the discharge axis became asymmetrical with respect to cross-section and the largest difference in T_e appeared on the side at which the cold gas entered.

Talayrach *et al.*[94] studied the bands arising from the radical BO and used them to calculate the rotational temperature of the plasma. (It seems likely that synthesis of TiB_2 was the prime object). A temperature of 5500 K was obtained from the lines of Ti, while the temperature of the argon was 7400 K. They concluded that the sample cooled the plasma. This may be correct, but it may be that the sample was in a region which was cooler in any case.

The Abel inversion, by which a radial distribution of emission intensity is derived from the integrated values obtained experimentally, was discussed by Mermet and Robin.[95] They used a method by which the integrated values are fitted, after smoothing, to a polynomial, the coefficients of which can be used to calculate the radial distribution. They then used this distribution to calculate the temperature; this required observations and calculations for at least two (and preferably several) wavelengths. They also found a maximum temperature off the axis of the plasma.

A plasma is normally heated by collision of charged particles and as the temperature rises this process becomes less efficient owing to decreased resistivity. Dubovoi *et al.*[96] found for a very high-power (200–400 kW) plasma at low pressures a heating efficiency much higher than they would have expected for pure Coulomb conductivity. To explain this they suggested that a small-scale ion-acoustic instability can develop in the region of the skin layer and that this leads to an additional growth of the resistivity, to a corresponding increase of the H.F. energy absorbed and to a more effective heating of the plasma. (Ion-acoustic waves are longitudinal and the expression for their velocity resembles that for a sound wave in a gas composed of neutral particles with masses which are those of the ions: hence the name. They are not conventional sound waves, however, for their energy derives not from collisions, but from the electrostatic effects of the difference in the amplitudes of the electron and ion oscillations. An ion-acoustic instability is a consequence of the transfer of energy between the ion-acoustic wave and electrons having the same velocity as the wave.)

Eckert and Pridmore-Brown[97] compared the measured[98] and calculated temperatures of column and annular plasmas. In the case of annular plasmas the experimental values were about 7000 K at the inner and outer boundaries, rising to about 8000–9000 K in between. The calculated values fell to 1000–2000 K at the boundaries. Stokes (in a private communication to the authors) attributed these discrepancies to non-equilibrium conditions at the boundaries, due to electron diffusion. The annular plasma referred to here was obtained by inserting another tube in the column and may not represent the conditions pertaining to an annular plasma formed by the action of an injector flow, where one might expect temperatures closer to the measured values.

Some very interesting relationships are given in a paper by Rovinskii and Sobolev.[99] They determined discharge parameters as functions of field frequency, *via* numerical solutions, for a steady induction discharge at atmospheric pressure without gas-flow; (note that the effect on temperature of the gas-flow is said to be small).[86] They give a theoretical estimation of the optimum frequency as being equal to $35/d^2$ MHz. This is the frequency giving a specified maximum temperature ($T_{\max}$) with minimal power input (W) and the minimal number of ampere-turns per unit length of coil (I_w); d is the diameter of the tube in centimetres.

A simple relationship is also given between I_w and $T_{\max}$ which does not contain the frequency or the radius:

$$\int_0^{T_{\max}} k(T)\sigma(T)\,\mathrm{d}T = \left(\frac{I_w}{2}\right)^2$$

where $k(T)$ and $\sigma(T)$ are respectively the thermal and electrical conductivities of the plasma. The skin-layer thickness is considered to be small relative to the tube radius.

Soshnikov and his co-workers[100] point out that these relationships do not take into account plasma radiation and they give numerical results for an argon plasma at atmospheric pressure in a tube of internal radius 1·5 cm, at various frequencies and an axial temperature of 8500 K. The results show that the best frequency range is 5–10 MHz which is close to the figure previously obtained by Rovinskii and Soboley,[99] ignoring the radiation. However, they show that the importance of radiation increases rapidly with I_w and W and the simple relationship becomes inapplicable.

Medvid[101] made some observations on the effect of gas-flows on the size of a plasma produced by a 2-kW generator at 3·5 MHz. Working with a torch which could be used with tangential or axial flow, he found that increasing the gas flow, in tangential mode, decreased the diameter, length and surface area of the plasma, while in axial mode the reverse was true. Thorpe[62] observed that the size of the plasma increased with increasing power and Capitelli *et al.*[102] noted that the plasma was reduced in length when working with nitrogen. These workers gave theoretical reasons why the heat transferred to Al_2O_3 particles should be greater in a nitrogen than an argon plasma. They found experimentally a smaller increase than that predicted theoretically because of the shorter residence time in the shorter nitrogen plasma.

Thorpe[62] also noted the effect of the thermal pinch on the size of the plasma when working with hydrogen and nitrogen coolant gases, and attributed this pinch to the increased thermal conductivity of nitrogen over argon and hydrogen over nitrogen. She observed that the radiation from the plasma increased considerably when mixtures of argon and hydrogen were used as plasma gases.

The thermal properties of a plasma torch were discussed by Trekhov *et al.*[103] They assumed a central temperature and offered two different approximations to give the radial distribution of the temperature.

NOMENCLATURE

Raizer,[89] whilst clearly recognizing the difference between electrodeless discharges in a stream and com-

Table 2. Analytical applications of the H.F. inductively coupled plasma torch

Materials examined	Typical elements determined	References
Metals and alloys	B, Zn, As, Cu, Y, La, Nd, Dy, Lu, Hf, Mn, Pb, Cr, Fe, Mg, Ti, V, Ni, Mo, Si, Nb	10, 18, 23, 38, 49, 58
Minerals	Al, P, Ca, Sr, Ba, Mg, Ti, Fe, Si, Cr, Mn, Na	10, 13, 31, 33
Blood	Al, Cu, Fe, Mg, Si, Ag, Pb, P	39, 74
Oil	Al, Fe, Ni, Cr, Cu, Ti, Mg, Mn	19, 39
Refractory oxides	Be, B, Ca, Mg, Ti, Fe, Al, Li, Cu, Ni, Pb, Na	10, 34, 76
Organophosphorus compounds	Al, Mg	39
Soil	P	41
Deposits	Al, Fe, Zn, Mg, Ca	10
Effluents	Zn, Ni, Al, Cd, Fe, Cr, Pb, Cu, Sn	10
Mineral acids	Ca, Sr, Mo, Co, Ba, Zn, Ni, Cd, Cr, Pb, Cu, B, Mg, V, Na, Mn, Ce, La, Al, Fe, Ti	10
Rare earths	Yb	57
Proteins	Cd, Fe, V, Ba, Sr, Al, Mg, Si, Zn, Ni, Cu, Ca, Na	10

bustion, claims there is a deep physical and mathematical analogy between a discharge in a gas stream and the process of flame propagation in a combustible mixture. Barnes,[104] on the other hand, has criticized the use of the terms "plasma torch" and "plasma flame" for systems which are not combustion processes. It seems to us that the value of these terms as descriptions of the appearance of the particular plasmas to which they refer outweighs considerations of linguistic rigour. It is doubtful if the suggestion[105] that all plasma sources be called "plasma jets" is any improvement on the present usage, as there is a marked difference between "plasma jets" and inductively coupled "plasma torches" on the one hand and microwave plasma and capacitively coupled plasmas on the other.

ANALYTICAL APPLICATIONS

It has been recorded in the review that ICPT have a wide linear dynamic range (some five orders of magnitude), high sensitivity and precision and freedom from many, if not all, true matrix effects. This, coupled with their freedom from contamination and ability to run continuously for as long as power and gas are supplied, makes them remarkable emission sources. It is therefore surprising that so few practical analyses have been recorded. Some of these analyses are shown in Table 2 and in Table 3 are shown the best of the detection limits. These detection limits have all been obtained with ultrasonic nebulizers and desolvation and would be expected to be one or two orders of magnitude worse if pneumatic nebulizers without desolvation were used.

CONCLUSION

A study of the papers reviewed here and in Parts I and II shows the ICPT to be superior to both plasma jets and microwave torches if detection limit is the criterion. The sensitivity of the source, with few if any exceptions, is greater than that of either of the other two sources over the whole range of elements so far determined; the plasma jet in turn is rather worse than the microwave torch. The same may be said, but to a lesser degree, if precision is the basis of comparison.

Table 3. Detection limits obtained with the H.F. ICP torch

Element	ICPT detection limit, *ng/ml*	Wavelength, *nm*	Element	ICPT detection limit, *ng/ml*	Wavelength, *nm*
Aluminium[40]	0·2	396·2	Magnesium[10]	0·01	280·2
Antimony[40]	200	259·8	Magnesium[40]	0·2	285·2
Arsenic[10]	90	235·0	Manganese[10]	0·03	257·6
Arsenic[24]	100	228·8	Manganese[40]	0·6	403·1
Arsenic[40]	360	278·0	Mercury[40]	1	253·7
Barium[40,10]	0·02	455·4	Molybdenum[40]	0·2	379·8
Beryllium[40]	0·04	234·9	Neodymium[38]	10	401·2
Boron[10]	5	249·8	Niobium[24]	10	405·8
Cadmium[40]	3	326·1	Nickel[40]	0·4	352·5
Calcium[10]	0·002	396·8	Palladium[40]	2	363·5
Cerium[40]	2	418·7	Phosphorus[40]	70	253·6
Chromium[40]	0·3	357·9	Praseodymium[38]	30	390·8
Cobalt[24]	3	345·3	Samarium[38]	30	442·4
Copper[40]	0·1	324·8	Silicon[10]	30	288·2
Dysprosium[38]	9	353·2	Sodium[40]	0·3	589·0
Erbium[38]	10	400·8	Strontium[24]	0·002	407·7
Europium[38]	3	382·0	Tantalum[24]	70	301·2
Europium[38]	3	413·0	Terbium[38]	20	350·9
Gadolinium[38]	10	342·2	Thorium[24]	3	401·9
Gallium[40]	0·6	417·2	Thulium[38]	10	384·8
Germanium[40]	4	265·1	Tin[40]	30	303·4
Gold[38]	40	267·6	Titanium[40]	0·2	334·9
Hafnium[24]	10	339·9	Tungsten[40]	1	400·9
Holmium[38]	10	345·6	Uranium[24]	30	409·0
Iron[40]	0·3	372·0	Vanadium[40]	0·2	437·9
Lanthanum[40]	0·4	408·7	Ytterbium[40]	0·04	369·4
Lead[40]	2	405·8	Yttrium[40]	0·06	371·0
Lithium[40]	0·3	670·8	Zinc[24]	9	213·8
Lutetium[38]	10	347·2	Zinc[40]	16	334·5
Lutetium[38]	10	350·7	Zirconium[40]	0·4	343·8

The detection limits are 2σ for references 10, 24 and 40 and 6σ for reference 38, where σ is the standard deviation of the background.

When it comes to freedom from matrix effects, then both ICPT and plasma jets are inherently superior to microwave torches, since they both possess high gas temperatures; the ICPT is, in addition, free from contamination from electrodes. The linear range of the ICPT is greater than that of the plasma jet, which in turn is greater than that of the microwave torch. When it comes to cost the position is somewhat reversed; plasma jets and their associated equipment are cheaper than microwave torches and their supplies, which in turn are cheaper than ICPT and generators.

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MULTIPARAMETRIC CURVE FITTING—I

COMPUTER-ASSISTED EVALUATION OF CHELATOMETRIC TITRATIONS WITH METALLOCHROMIC INDICATORS

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Summary—A curve-fitting procedure has been developed for the photometric complex-formation titration of the metal–indicator complex MIn_N which is assumed to predominate in solution. By means of a least-squares procedure the following five parameters were determined: the end-point, the absorbance of the indicator complex A_{MIn_N}, the indicator concentration c_{In}, the stability constants and, if possible, K_{MY}. A modified version of Sillén's Letagrop Vrid has been used for the mathematical-statistical approach of the non-linear model based upon the non-transformed function $A = f(v)$. Additional information is obtained about the goodness of fit, indicating whether the chosen model with predominance of MIn_N is correct or not. The use of the program is demonstrated by application to chelatometric microtitrations of zinc and lead with EDTA, using Naphthylazoxine 6S and SNAZOXS as metallochromic indicators.

A number of authors[1–7] have been engaged in solving the problem of determination of the equivalence point, finding a suitable formulation of the fundamental equations or seeking optimum conditions for sharp end-point indication in photometric chelatometric titrations.

The theory of photometric titration with use of metallochromic indicators has been outlined in several basic contributions[1–3,6–17] Fortuin *et al.*[1] derived a general equation of the type $a = f(\alpha)$ where a is the titration parameter and $\alpha = [\mathrm{In'}]/c_{In}$, for the case where a single metal–indicator complex of 1:1 stoichiometry is formed. The theoretical discussion of the effect of various parameters on the shape of titration curves was illustrated by plots of families of curves calculated for different values of parameters K_{MIn}, K_{MY}, c_{In} and c_M. Ringbom and Wänninen[8] applied conclusions from the theory of photometric titrations using acid-base indicators, and pointed out the usefulness of pM for characterizing the system of a chelatometric titration. The pertinent equilibria were also solved in theoretical discussions[2,3] of visual end-point detection with metallochromic indicators in an attempt to characterize the sharpness of the indicator colour change. In both contributions the formation of a single MIn complex was considered and the plots of $\alpha = f(a)$ for various values of the parameters involved were also given. Kotrlý developed the theory of photometric titrations for a case where the indicator forms a predominating complex MIn_N (*cf.* ref. 6) or a stepwise equilibrium system of three indicator complexes[7] MIn_{N-2}, MIn_{N-1}, MIn_N. For a discussion of various effects on the shape of the titration curve he also used the transformation function $a = f(\alpha)$.

Several authors[9–17] have shown that M_2In_2 also occurs in solution and that large systematic deviations may occur when titrations are performed with very dilute solutions. For simplicity, graphical extrapolation of the linear parts of the titration curve close to the equivalence point is commonly used to locate the end-point. A computer program for this type of end-point evaluation can be conveniently based on the application of a simple linear regression (*e.g.*, see refs. 18, 19).

In some theoretical papers it is supposed that the equivalence point is known and that the parameter functions $a = f(\alpha)$ or $\alpha = f(a)$ can be studied. However, this condition is fulfilled only rarely in practical cases, and the evaluation of the end-point is sometimes complicated and accessible only by means of a graphical extrapolation.

An exception to graphical extrapolation is the approach by Sato and Momoki,[20] suggesting transformation of variables $g(1 - \alpha)/\alpha = f(v)$ and using graphical linearization without the stability constants K_{MIn} and K_{MY} being known beforehand. Corrections are made for volume change and indicator concentration and the paper appears to be, especially in practical cases, a most useful contribution.

A number of papers[4,8,21,22] use calculations of conditional stability constants, side-reaction coefficients, or their graphical interpretation, to explain the course of the chelatometric titration curve. In all the papers the indicator concentration c_{In} is supposed to be known. Chemical analyses using paper and thin-layer chromatography have revealed, however, that chelatometric indicators are substances that often contain considerable amounts of impurities from raw materials, synthesis by-products and various isomers. The removal of such impurities is difficult and sometimes impossible because of decomposition of the dye. In some cases the indicator is the only species of the mixture which reacts with the metal being titrated. A correction for indicator purity has not been taken into account in the calculations in any of these papers.

Early attempts at computation of parameters from titration curves, including chelatometry, are described in the book by Dyrssen *et al.*[23] and are based on an application of Ringbom's method.[21] Sato and Momoki[24] selected an entirely different approach to the computer evaluation of a chelatometric titration curve involving the MIn chelate. They determined three unknown parameters: the end-point, the conditional stability constant $K_{\text{MIn,cond}}$, and $K_{\text{MY,cond}}$, with a least-squares fitting method using Deming's subroutine for the minimization process. The algorithm was demonstrated for the titration of magnesium with EDTA, Calmagite being used as indicator.

The change of absorbance during a chelatometric titration involving a metallochromic indicator forming a 1:1 complex was calculated by means of a computer.[25] In addition to the absorbance, the transmittance, the free metal-ion and indicator concentrations, and the stability constants of the metal–titrant and the indicator–metal complexes were calculated.

The present paper presents a new algorithm for the evaluation of a chelatometric titration curve when the MIn_N complex predominates, and determination of the following parameters: the end-point, pIn, log K_{MIn_N} and (if possible) log K_{MY}, and the absorbance of the indicator complex A_{MIn_N}. Additional information about the goodness of fit indicates whether this model is correct or not. The least-squares method for the minimization process is based on a modified version of Sillén's Letagrop Vrid.[26] The statistical treatment is quite different from that suggested by Sato and Momoki,[24] the fundamental equation being based on Kotrlý's approach[6] but regression analysis is applied to the function $A = f(v)$. The algorithm has been applied to the titration of zinc and lead, using Naphthylazoxine 6S and SNAZOXS as metallochromic indicators.

THEORETICAL

Equation of the photometric titration curve

End-point indication in a chelatometric titration using a metallochromic indicator is based on the displacement reaction between the indicator complex MIn_N and the chelate-forming ion of a titrant Y, which can be expressed by the overall equation

$$\text{MIn}_N + \text{Y} \rightleftharpoons \text{MY} + N\,\text{In} \tag{1}$$

The equilibrium in equation (1), as written, presupposes that the metallochromic indicator forms only one complex, MIn_N. This complex has a colour different from that of the free form In, which may represent, however, a mixture of several differently protonated indicator species. The equilibrium is considerably affected by the hydrogen-ion activity, as this controls the concentration of the active forms of both competing ligands Y and In.

The chelatometric titration is usually carried out in a buffered solution. If the free indicator is predominantly in only one protonated form, *e.g.*, H_jIn, at a selected pH value, the absorbance of the titrated solution at a chosen wavelength, for a particular consumption of titrant v, is given by the equation

$$A = d\{\epsilon_{1N}[\text{MIn}_N] + \epsilon_{j1}[\text{H}_j\text{In}]\} \tag{2}$$

where d is the path-length of the cuvette, and ϵ_{1N} and ϵ_{j1} are the molar absorptivities of the species MIn_N and H_jIn, respectively. The dependence of the absorbance A on consumption of titrant v is represented by the photometric titration curve.

As the total concentration of indicator c_{In} is

$$c_{\text{In}} = [\text{H}_j\text{In}] + N[\text{MIn}_N] = c_{\text{In}}\,\alpha + N[\text{MIn}_N] \tag{3}$$

where $\alpha = [\text{H}_j\text{In}]/c_{\text{In}}$ is the fraction of indicator in the free form, equation (2) can be transcribed as a function of this relative variable:

$$\begin{aligned} A &= dc_{\text{In}}\cdot\frac{\epsilon_{1N}}{N} - dc_{\text{In}}\left\{\frac{\epsilon_{1N}}{N} - \epsilon_{j1}\right\}\alpha \\ &= A_{(\text{MIn}_N)} - \{A_{(\text{MIn}_N)} - A_{(\text{In})}\}\alpha \end{aligned} \tag{4}$$

As indicated in equation (4), the colour transition of an indicator is defined by the limiting values of the absorbance, for a point $\alpha = 0$, *i.e.*, $A_{(\text{MIn}_N)}$, where all the indicator is bound in the metal complex MIn_N, and for a point $\alpha = 1$ where the metallochromic indicator is completely converted into the free form In, *i.e.*, $A_{(\text{In})}$.

If v ml of titrant are added to the original volume V_0 ml of titrand, the measured absorbance A_{exp} should be corrected for the dilution by means of the factor $g = V/V_0$, where $V = V_0 + v$:

$$A = A_{\text{exp}}g = A_{\text{exp}}\left\{1 + \frac{v}{V_0}\right\} \tag{5}$$

To determine the theoretical value of the absorbance A from equation (4) for individual values of the titrant consumption v it is assumed that for the given set of conditional stability constants, *i.e.*,

$$K_{\text{MIn}_N\text{,cond}} = \frac{[\text{MIn}'_N]}{[\text{M}'][\text{In}']^N} \tag{6}$$

$$K_{\text{MY,cond}} = \frac{[\text{MY}']}{[\text{M}'][\text{Y}']} \tag{7}$$

where conditional concentrations are expressed by Ringbom's notation with respect to [M′], [In′], $[\mathrm{MIn}'_N]$, [Y′], [MY′], and for given total concentrations

$$c_{\mathrm{Y}} = ac_{\mathrm{M}} = [\mathrm{Y}'] + [\mathrm{MY}'] \tag{8}$$

$$c_{\mathrm{M}} = [\mathrm{M}'] + [\mathrm{MY}'] + [\mathrm{MIn}'_N] \tag{9}$$

$$c_{\mathrm{In}} = [\mathrm{In}'] + N[\mathrm{MIn}'_N] \tag{10}$$

it is then possible to calculate the values of the relative variable α for each value of v. A general explicit expression of $\alpha = f(v)$ as a function of individual parameters is not possible, as it represents a real, positive root of a polynomial in α of degree $(2N + 1)$. Many authors prefer to express the inverse functions $v = f(\alpha)$ and $a = f(\alpha)$, where a is the equivalent fraction of titrant consumed:

$$a = \frac{vf_{\mathrm{Y}}}{Vc_{\mathrm{M}}} \tag{11}$$

f_{Y} being the molarity of the titrant. For a given equilibrium system the titration-curve equation can be derived in the form of transformed variables[6] as follows

$$\begin{aligned} a = 1 &- \frac{c_{\mathrm{In}}(1-\alpha)}{Nc_{\mathrm{M}}}\left[1 + \frac{1}{K_{\mathrm{MIn}_N,\mathrm{cond}} \cdot c_{\mathrm{In}}^{N} \cdot \alpha^{N}}\right] \\ &- \frac{1}{K_{\mathrm{MY,cond}}\, c_{\mathrm{M}}} \\ &+ \frac{K_{\mathrm{MIn}_N,\mathrm{cond}} \cdot c_{\mathrm{In}}^{N-1}}{K_{\mathrm{MY,cond}}}\left[\frac{N \,.\, \alpha^{N}}{1-\alpha} - \frac{c_{\mathrm{In}} \cdot \alpha^{N}}{c_{\mathrm{M}}}\right] \end{aligned} \tag{12}$$

The values of the conditional stability constants $K_{\mathrm{MIn}_N,\,\mathrm{cond}}$ and $K_{\mathrm{MY,\,cond}}$ necessary for insertion into equation (12) can be calculated from the corresponding stability constants, provided that detailed information on all side-reactions is available. The side-reaction coefficients α_{M}, $\alpha_{\mathrm{Y(H)}}$, *etc.*, give a true picture of all competitive effects. The definitions of these coefficients,[4,21] their dependence upon experimental conditions and the method of calculation (*cf.* ref. 22) are clarified in the literature quoted.

Regression analysis

When analysing experimental photometric titration curves it should be considered that in general the values of the following parameters are known either not at all or only approximately: the titrant consumption at the end-point, v_{ep}, the indicator concentration c_{In}, the initial limiting value of the absorbance A_{MIn_N}, and the values of the stability constants K_{MIn_N} and K_{MY}. These five parameters have to be determined by numerical analysis of the titration curve.

The equation of the chelatometric titration curve is formulated as a function $a = f(\alpha)$, *i.e.*, in terms of transformed relative variables and as an inversion function with respect to the original set of variables (v; A). Considering that the reading of the volume on a microburette has a smaller error than the reading of the absorbance A, it is convenient for the application of a least-squares fitting method to take the volume v as an independent variable and absorbance A as a dependent variable. However, an explicit formulation of the absorbance from the equation of a chelatometric titration curve is not possible, as a polynomial function of degree $(2N + 1)$ would be obtained and an approximation method would be needed to find the particular real root of physical meaning. Therefore all previous authors usually worked with the inversion function $v = f(\alpha)$.

In applying the method of least-squares in order to determine the five unknown parameters of a chelatometric titration curve the assumption that the original error distribution of dependent variable A_{exp} is retained and that the original non-transformed function $A = f(v)$ can be used, should be fulfilled. An attempt was made to solve the problem by means of an indirect expression of a residuum ΔA when formulating the optimization criterion.[27] A more rigorous method is to use an approximation method, *e.g.*, the Newton iterative method.

In formulating the non-linear model it seemed convenient to make a formal rearrangement of equation (12) to give (13) for the *i*th point on the titration curve:

$$v_i = R\frac{\alpha_i^N}{1-\alpha_i} - S \,.\, \alpha_i^N - T\frac{1-\alpha_i}{\alpha_i^N} + Q \,.\, \alpha_i + W \tag{13}$$

where

$$R = \frac{K_{\mathrm{MIn}_N,\mathrm{cond}} \cdot c_{\mathrm{In}}^{N-1} \,.\, N \,.\, v_{\mathrm{eq}}}{KG_{\mathrm{MY,cond}}} \tag{14}$$

$$S = \frac{K_{\mathrm{MIn}_N,\mathrm{cond}} \cdot V \,.\, c_{\mathrm{In}}^{N}}{K_{\mathrm{MY,cond}} \cdot f_{\mathrm{Y}}} \tag{15}$$

$$T = \frac{1}{K_{\mathrm{MIn}_N,\mathrm{cond}} \,.\, N \,.\, c_{\mathrm{In}}^{N-1} \,.\, f_{\mathrm{Y}}} \tag{16}$$

$$Q = \frac{c_{\mathrm{In}} \,.\, V}{N \,.\, f_{\mathrm{Y}}} \tag{17}$$

$$W = v_{\mathrm{eq}} - \frac{V}{f_{\mathrm{Y}}}\left[\frac{c_{\mathrm{In}}}{N} + \frac{1}{K_{\mathrm{MY,cond}}}\right] \tag{18}$$

The chelatometric titration curve involves all the parameters to be determined in the expressions R, S, T, Q and W and so it is advantageous to investigate the contributions of these particular expressions to the shape of a titration curve. The members R, S, T, Q and W are useful for illustration how a change in the individual parameters can cause a change in the function U.

According to the optimization criterion the function U is given by

$$U = \sum_i w_i(A_i - A_{i,\mathrm{cal}})^2 = \sum_i w_i(\Delta A_i)^2 \tag{19}$$

where w_i is the statistical weight, usually taken as unity. Absorbance A_{cal} is calculated from the equation

$$f(v, A) - v = \phi(A) \tag{20}$$

and the modified Newton iterative method

$$A^{(k+1)} = A^{(k)} - \eta \cdot \frac{\phi(A^{(k)})}{\phi'(A^{(k)})} \tag{21}$$

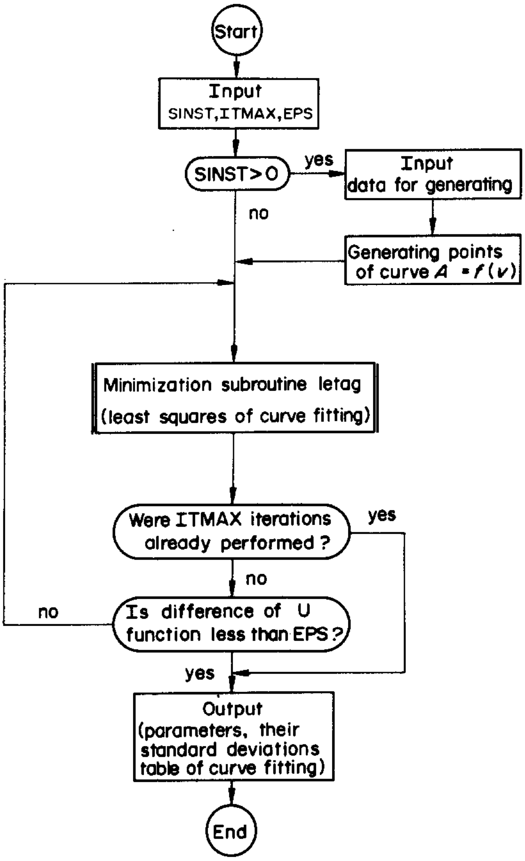

Fig. 1. Schematic flow chart of the program NCHEL-LETAG.

where η is a convergence coefficient, and ϕ' is the first derivative of ϕ. For the initial approximation the experimental value A_{exp} is used for $A^{(0)}$ in the iterative process.

COMPUTER PROGRAM

The schematic flow-chart of the program NCHEL-LETAG is given in Fig. 1. The program is written in Fortran and has been run on a Hewlett-Packard 2116 C computer, and is available on request.

NCHEL-LETAG consists of a main program which reads in a title and the part of the input needed for a simulation of titration curve points, if requested. It then calls subroutines as follows and organizes outputs of determined parameters, a table of curve fittings and a graph of curve fitting.

LETAG—this routine, which is Sillén's Letagrop Vrid adapted for a smaller computer and modified to the subroutine form,[28] performs the main minimization. The functional diagram of LETAG is given in Fig. 2. The subroutine contains "blocks" which are logical units; one of them, KNUT, is a switchboard to which the computer returns after fulfilling each task. Depending on which value for the control number Rurik it then reads, the computer jumps from KNUT to another block for a new task. The block DATA reads input data being called by Rurik 6. PUTS, a special block, follows the block DATA automatically (marked by a letter A) and may use these data to calculate some quantities which will be needed for further calculations. UBBE, called by subroutine LETAG or by the main program, calculates the error-square sum-function U defined by relationship (19). Block LASK, called by Rurik 7, reads in preliminary values for the parameters to be determined. STEG, called by Rurik 3 or 4, reads the general orders for systematic variation of parameters. (IK) means which parameter is to be varied, and by how much (W). LETA, called by Rurik 5, governs the systematic variation of the unknown parameters. Other blocks such as SKRIK or MIKO, PROVA, VRID, *etc.* are contained in the REST OF SUBROUTINE LETAG and their function is explained in another contribution[28] of this series.

RNDNR—a standard routine for the generation of errors having a normal Gaussian distribution—was adapted from Communications of the Association for Computing Machinery, Algorithm 314 (1968).

DATA—data input; some experimental constants describing titration condition are read in, then the calculation of side-reaction coefficients α_{MIn_N} and α_{MY}, follows and finally the matrix of titration data (v, A) or (v, T) is read in. The absorbance values are corrected for dilution and with regard to the reference solution. Titration curve points which are not contained in the interval $(\alpha_{min}, \alpha_{max})$ are then eliminated.

UBBE—this routine calculates A_{cal} for each volume v and a given set of parameters by the Newton iterative method. Then follows calculation of the error-square sum-function U.

Data input instructions

Simulated or experimental input data can be evaluated by the NCHEL-LETAG program. For a given set of parameters the absorbance ASIM, loaded by a calculated ERROR, is calculated for each volume v. Then a least-squares fit is applied to a set of (v; ASIM) and parameters XK(1), . . ., XK(5) are evaluated. Such input data are illustrated in Table 1a. (*a*) 1 card: SINST is optional and is the instrumental error of the measured absorbance; when experimental data are to be evaluated then SINST < 0 and the other data on this card are not read; EPS1 is the absolute criterion of convergence of A_{cal} in the Newton iterative process; if $(A_{cal}^{(n)} - A_{cal}^{(n-1)}) <$ EPS1 then the iteration process terminates; EP2 is the η coefficient of convergence in the Newton iterative method; NX is the

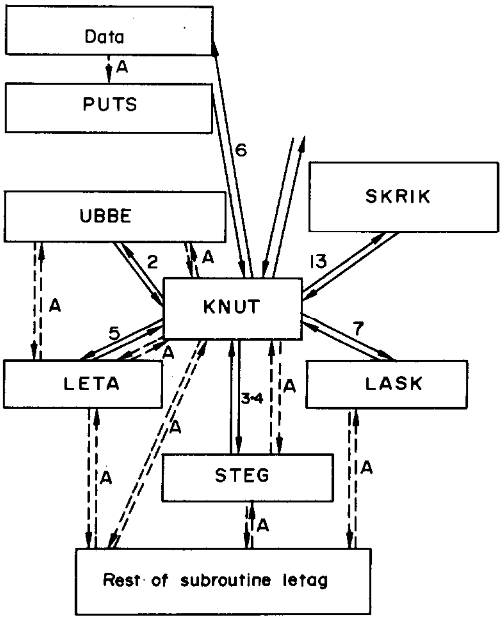

Fig. 2. Function diagram of minimization subroutine Letag.

Table 1*a*. Input data in case of previous simulation of titration curve are contained in principal parts A, B, C, and D

Data			Explanation	
Part A				
0·001 0·008 0·9 5 0·31388			SINST EPS1 EP2 NX XK(1)	
12·209 18·2 4·9314 0·17 2368			XK(2) XK(3) XK(4) XK(5) IR	
Part B				
2 20 0·001 207·19 0·05 0·95 0			N VO FY VM ALMIN ALMAX ASB	
0·53 5·75 27 0·171			AI PH NB X5	
7·0 2·868 −3·0 −3·0			A(1) A(2) A(3) A(4) for ind.	
10·26 6·16 2·67 2·0			A(1) A(2) A(3) A(4) for t.a.	
0·1050 0·2575 0·1200 0·2621 0·1350 0·2675			VA(1) VA(2)...	
0·1500 0·2730 0·1650 0·2805 0·1800 0·2896				
0·1900 0·2967 0·2000 0·3048 0·2100 0·3137				
0·2200 0·3249 0·2300 0·3378 0·2400 0·3527				
0·2500 0·3698 0·2550 0·3791 0·2600 0·3890				
0·2650 0·3989 0·2700 0·4099 0·2750 0·4214				
0·2800 0·4332 0·2850 0·4454 0·2900 0·4580				
0·2950 0·4709 0·3000 0·4840 0·3050 0·4974				
0·3100 0·5051 0·3150 0·5120 0·3500 0·5200			...VA(NB-1) VA(NB)	
Part C				
0·00000001 30 1 6 6 0·9			EPS ITMAX NGR XL YL UF	
("V in millilitres")			NAZX	
("Absorbance")			NAZY	
PB-SNAZOXS-EDTA system, 12. 11. 1973			Name of system	
Part D				
7			RURIK CALL LASK	
5 5			NK NBYK	
0·31 12·0 18·2 5·0 0·165			XK(1) XK(2) XK(3) XK(4) XK(5)	
1 1 1 1			ISKIN I J S(I, J)	
3			RURIK CALL STEG	
2			N	
1 0·003			IK W	
2 0·2			IK W	
5			RURIK CALL LETA	
3			RURIK CALL STEG	
4			N	
1 0·001			IK W	one iteration
2 0·06			IK W	
4 0·03			IK W	
5 0·001			IK W	
5			RURIK CALL LETA	
3				
4				
1 0·003				
2 0·008				
4 0·006				
5 0·0008	continued			
5	3	3		*etc.*
3	4	4		
4	1 0·0001	1 0·00003		
1 0·0002	2 0·0015	2 0·00075		
2 0·004	4 0·002	4 0·001		
4 0·0035	5 0·00025	5 0·0001		
5 0·0005	5	5		
5	3	3		
3	4	4		
3	1 0·00006	1 0·00001		
1 0·00015	2 0·001	2 0·0005		
2 0·002	4 0·0015	4 0·0005		
4 0·00035	5 0·0002	5 0·00005		
5	5	5		

Table 1*b*. Output of program NCHEL-LETAG for simulated data from Table 1*a*

```
PB-SNAZOXS-EDTA system, 12.11.1973
Simulation for parameters
     SINST          VEQ          LKMIN          LKMY          PCIN          AMIN
    0·00100       0·31388        12·209        18·200         4·931         0·1700
Condition of titration
 N      VO        FY            AW           ALMIN          ALMAX          PH            AI
 2     20·0     0·00100       207·190        0·050          0·950         5·750         0·5300
INDICATOR:       PK11         PK21       PK31        PK41            ALPH(IN)(IN(H))(H)
                 7·000        2·868     −3·000      −3·000           0·188E + 02
TIT. AGENT:      PK11         PK21       PK31        PH41            ALPH(Y)(Y(H))(H)
                10·260        6·160      2·670       2·000           0·1156E + 06

Titration curve
             Experimental                      Simulated
  V(ML)      AEXP          ALPHA       ASIM         ERROR
  0·1050     0·2575        0·2494      0·2569       −0·0006
  0·1200     0·2621        0·2630      0·2629        0·0008
  0·1350     0·2675        0·2784      0·2682        0·0007
  0·1500     0·2730        0·2944      0·2721       −0·0009
  0·1650     0·2805        0·3157      0·2809        0·0004
  0·1800     0·2896        0·3418      0·2915        0·0019
  0·1900     0·2967        0·3620      0·2971        0·0004
  0·2000     0·3048        0·3852      0·3060        0·0012
  0·2100     0·3137        0·4105      0·3160        0·0023
  0·2200     0·3249        0·4422      0·3245       −0·0004
  0·2300     0·3378        0·4788      0·3386        0·0008
  0·2400     0·3527        0·5210      0·3528        0·0001
  0·2500     0·3698        0·5693      0·3684       −0·0014
  0·2550     0·3791        0·5957      0·3797        0·0006
  0·2600     0·3890        0·6237      0·3892        0·0002
  0·2650     0·3989        0·6518      0·3970       −0·0019
  0·2700     0·4099        0·6828      0·4087       −0·0012
  0·2750     0·4214        0·7153      0·4216        0·0002
  0·2800     0·4332        0·7488      0·4340        0·0008
  0·2850     0·4454        0·7834      0·4449       −0·0005
  0·2900     0·4580        0·8192      0·4605        0·0025
  0·2950     0·4709        0·8556      0·4705       −0·0004
  0·3000     0·4840        0·8928      0·4836       −0·0004
  0·3050     0·4974        0·9308      0·4992        0·0018
  0·3100     0·5051        0·9522
  0·3150     0·5120        0·9727
  0·3500     0·5200        0·9975
Total number of points: 27   Number of points used: 24
Minimization process LETAG
I = 0
                               0·31000     12·0000     18·2000     5·0000     0·1650
I = 1   MINUSGROP
U = 0·13454E − 03              0·31125     12·1523     18·2000     5·0000     0·1650
I = 2   MINUSGROP
U = 0·68026E − 04              0·31225     12·1523     18·2000     4·9700     0·1650
I = 3   SIGY = 0·8783E − 02
U = 0·47436E − 04              0·31231     12·1603     18·2000     4·9640     0·1650
I = 4   SIGY = 0·1138E − 02
U = 0·23582E − 04              0·31308     12·1743     18·2000     4·9470     0·1649
I = 5   SIGY = 0·1054E − 02
U = 0·23305E − 04              0·31308     12·1726     18·2000     4·9470     0·1649
I = 6   SIGY = 0·1076E − 02
U = 0·22890E − 04              0·31314     12·1710     18·2000     4·9444     0·1644
I = 7   SIGY = 0·1033E − 02
U = 0·22591E − 04              0·31320     12·1683     18·2000     4·9436     0·1642
I = 8   SIGY = 0·1028E − 02
U = 0·22533E − 04              0·31323     12·1668     18·2000     4·9432     0·1641
 ..    ..    ..                              ..          ..          ..         ..
 ..    ..    ..                              ..          ..          ..         ..
I = 30  SIGY = 0·1045E − 02
U = 0·21869E − 04              0·31306     12·1327     18·2000     4·9469     0·1593
After 30 declared iterations at U value = 0·21869E − 04 and parameters:
                                     VEQ = 0·31306 ± 0·00032
                                   LKMIN = 12·1327 ± 0·0285
                                    LKMY = 18·2000
                                    PCIN = 4·9469 ± 0·0065
                                    AMIN = 0·1593 ± 0·0041
```

Table 1*b*—*continued*

Calculated auxiliary values:
Milligrams of metal: 0·64862E − 01
Molar concentration of metal: 0·157E − 04
Molar concentration of indicator: 0·113E − 04

Table of curve fitting

V(ML)	A	ACAL	DEL A	DEL A KV	ALPHA
0·1050	0·2569	0·2571	−0·0002	0·6157E − 07	0·2669
0·1200	0·2629	0·2619	0·0010	0·9594E − 06	0·2838
0·1350	0·2670	0·2672	−0·0002	0·3688E − 07	0·2954
0·1500	0·2721	0·2734	−0·0013	0·1584E − 05	0·3098
0·1650	0·2809	0·2810	−0·0001	0·1775E − 07	0·3342
0·1800	0·2915	0·2901	0·0014	0·1875E − 05	0·3637
0·1900	0·2958	0·2969	−0·0012	0·1332E − 05	0·3757
0·2000	0·3050	0·3051	−0·0001	0·1962E − 07	0·4013
0·2100	0·3160	0·3146	0·0014	0·1877E − 05	0·4317
0·2200	0·3245	0·3252	−0·0008	0·5951E − 06	0·4552
0·2300	0·3386	0·3380	0·0006	0·4144E − 06	0·4942
0·2400	0·3528	0·3525	0·0003	0·1061E − 06	0·5334
0·2500	0·3676	0·3690	−0·0014	0·2034E − 05	0·5742
0·2550	0·3790	0·3784	0·0006	0·3051E − 06	0·6057
0·2600	0·3886	0·3882	0·0004	0·1603E − 06	0·6322
0·2650	0·3970	0·3984	−0·0013	0·1791E − 05	0·6555
0·2700	0·4087	0·4094	−0·0007	0·4793E − 06	0·6876
0·2750	0·4216	0·4210	0·0006	0·3924E − 06	0·7232
0·2800	0·4340	0·4330	0·0010	0·9845E − 06	0·7573
0·2850	0·4449	0·4452	−0·0003	0·8974E − 07	0·7877
0·2900	0·4605	0·4584	0·0021	0·4556E − 05	0·8305
0·2950	0·4705	0·4713	−0·0008	0·5790E − 06	0·8583
0·3000	0·4836	0·4848	−0·0012	0·1510E − 05	0·8944
0·3050	0·4992	0·4989	0·0003	0·1092E − 06	0·9376

number of parameters to be read in for generation of simulated error; XK(1) is the value of the first parameter, *i.e.*, equivalence point v_{eq}, in ml; XK(2) is the value of the second parameter, *i.e.*, the concentration stability constant of the indicator complex, log K_{MIn_N}; XK(3) is the value of the third parameter, *i.e.*, the concentration stability constant of complex with the titration agent, log K_{MY}; XK(4) is the value of the fourth parameter, *i.e.*, the total indicator concentration ($-\log c_{In}$); IR is the initial value for subroutine RNDNR and is the optional value from an interval (5; 6000), this interval is given by the word-length of the computer used and the algorithm RNDNR.

(*b*) 1 card: N is the stoichiometric coefficient in the indicator complex MIn_N; VO is the initial volume of solution to be titrated, in ml; FY is the molar concentration of the titrant; VM is the atomic weight of the metal to be titrated; ALMIN is the lower limit α_{min}; ALMAX is the upper limit α_{max}; ASB is the correction to be made to the sample absorbance for the absorbance of the reference solution.

(*c*) 1 card: AI is the absorbance of the free indicator measured after the titration is completed; PH is the pH value of the solution to be titrated; NB is the total number of points on the titration curve; X5 is the absorbance of the indicator complex measured before the titration A_{MIn_N}.

(*d*) 1 card: A(1), . . ., A(4) are the four dissociation constants of the indicator acid; "−3" is written in place of any dissociation constant not available.

(*e*) 1 card: A(1), . . ., A(4) are the four dissociation constants of the titrant; "−3" is written in place of any dissociation constant not available.

(*f*) A number of NB/5 cards: these contain the co-ordinates of experimental points on the titration curve: VA(I) is the volume v of titrant added; VA(I + 1) is the absorbance or transmittance value, depending on the switch 6.

(*g*) 1 card: EPS is the absolute criterion of convergence of function U; when $U^{(n)} < \text{EPS}$ then the minimization process is terminated; ITMAX is the number of iterations in the minimization process; NGR is the number which controls the plotter output; when it is not equal to zero then a graph is printed; data for the plotter are given by XL for the length of the abscissa and YL for the length of the ordinate (in inches); UF is a fraction specifying the change in the iterative steps for all parameters after each iteration.

(*h*) 1 card: NAZX, the description of the abscissa.

(*i*) 1 card: NAZY, the description of the ordinate.

(*j*) 1 card: descriptive title.

(*k*) 1 card: 7, Rurik, which calls block LASK to read the initial estimation of the parameters to be determined.

(*l*) 1 card: NK is the total number of parameters to be determined in the course of the LETAG minimization process; NBYK is the number of non-negative parameters to be determined.

(*m*) 1 card: XK(1), . . ., XK(5), the initial guesses for the parameters to be determined.

(*n*) 1 card: ISKIN is the number of matrix elements to be read in; I or J denotes the co-ordinates of a matrix element; S(I, J) is the value of a matrix element.

(*o*) 1 card: 3, Rurik, which calls the block STEG where the minimization steps for each parameter are read in.

(*p*) 1 card: N is the number of parameters to be varied in an actual shot.

(*q*) 1 card: IK is the number of parameters for which the steps are read in; W is the value of a step; the pair (IK, W) is written for each varied parameter.

(*r*) 1 card: 5, Rurik, which calls the block LETA where a systematic variation of parameters is performed.

When the experimental titration curve is to be analysed, in part A, SINST is written equal to −1 and the values of parameters XK(1), . . ., XK(5) are not written. Then follows part C, which calls block DATA, part B and part D.

Interpretation of output

At the top of the table, the name of the titration system, the parameters for a simulation process and the titration conditions are printed together with the values of SINST, the five parameters, N, VO, FY, AW, ALMIN, ALMAX, PH, AI, and the pK_a values for the successive deprotonation of the indicator and the titrant, respectively, which are denoted as PK11, PK21, PK31, PK41. The proton side-reaction coefficients of the indicator and titrant are also printed as ALPHA IN(H) and ALPHA Y(H).

Experimental and simulated values are given in the following sequence: the volume of titration agent V(ML), the absorbance AEXP, the corresponding value of α, ALPHA, and last the simulated values of absorbance ASIM and calculated error ERROR if the simulation process is requested. Under the table the total number of experimental points is printed and the number of points within the interval α_{min}, α_{max} which are selected for regression analysis.

The outputs of the successive minimization processes can be controlled by switches and some parts of them can be omitted. The particular iterations are printed next and for each of them the standard deviation SIGY, the U-function, and the approximations of all parameters are given.

When the absolute criterion of the convergence of the U-function is fulfilled or when a declared number of iterations is reached, the minimization process terminates. In order to test the fit of the experimental points to the regression curve, the final table of curve fitting is printed.

EXPERIMENTAL

Spectrophotometer

A Spekol single-beam spectrophotometer (Zeiss, Jena) was equipped for photometric microtitrations with the multipurpose attachment TAL (*cf.* refs. 27, 29–31) with a thermostated cell and equipment for simultaneous measurement of pH. The design and function of TAL has been described previously.[31,32] The accuracy of the spectrophotometric measurements was checked with standard solutions of potassium chromate and copper(II) sulphate.[33] The pH of the titrand was recorded at the beginning and checked during the titration, with a Radiometer PHM 4d pH-meter (G202B glass electrode and saturated calomel electrode, calibrated with standard buffers[34]).

The titration cell was a 50-mm path-length cuvette, total volume 23 ml (type C, Zeiss, Jena). All the measurements were made at 25 ± 0·1°.

Burettes

A Metrohm E457 500-μl microburette was used, its polyethylene capillary tip being immersed in the titrand. Metal and indicator solutions were measured out with home-made microburettes[31] of 500 μl or 250 μl capacity, calibrated by weighing water delivered under medicinal paraffin (standard deviations for 25 deliveries of 200 and 100 μl were 0·3 and 0·2 μl, respectively).

Reagents and solutions

EDTA solution, 0·001M. Prepared in doubly distilled water. Standardized against twice recrystallized lead(II) chloride by photometric titration, using Naphthylazoxine 6S as indicator.

Naphthylazoxine 6S and SNAZOXS solutions, 0·001M. Both indicators were purified[35] and the effective concentration of indicator was determined by the molar-ratio method with copper.[35] The disodium salts of the indicators were fully protonated on a cation-exchanger column in H$^+$-form.

Zinc(II) solution, 0·001M. Prepared by dissolving 0·074 g of $Zn(NO_3)_2 \cdot 6H_2O$ in water and diluting to 250 ml. Standardized by chelatometric titrations using Xylenol Orange as indicator.

Hexamine buffer, 0·04M. Adjusted to pH 6·0 with 0·05M nitric acid and to ionic strength 0·02 with 0·1M potassium nitrate. Purified by extraction with dithizone solution in carbon tetrachloride.

The solutions titrated with 0·001M EDTA always contained the same amount of individual components and the same sample volume was used. The solution titrated had a constant ionic strength of 0·01 and pH 5·80 adjusted with hexamine buffer and potassium nitrate, and temperature 25°. The solutions titrated had the same metal-ion concentration $c_M = 1{\cdot}0 \times 10^{-5}M$ (except for investigation of effect of c_M) and the same indicator concentration $c_{In} = 1{\cdot}0 \times 10^{-5}M$ (except for investigation of effect of c_{In}).

Procedure

Take an aliquot of metal-ion solution and a suitable portion of indicator stock solution in a calibrated 50-ml flask, add a few ml of buffer solution and make up the volume to 50 ml with doubly distilled water. Transfer 20·00 ml of this mixture into the titration cell, place this in the apparatus and adjust the equipment. Fill the reference cell with a solution containing no indicator but the same amounts of all other components. Place the reference cell in the light-beam and adjust the meter scale (0 and 100% T). Put the measuring cell into position and take readings of absorbance (or transmittance) at the beginning of the titration and at every 10 μl (ever 5 μl in the vicinity of the end-point) of titrant added, until constant absorbance is reached. About 35 points are usually read.

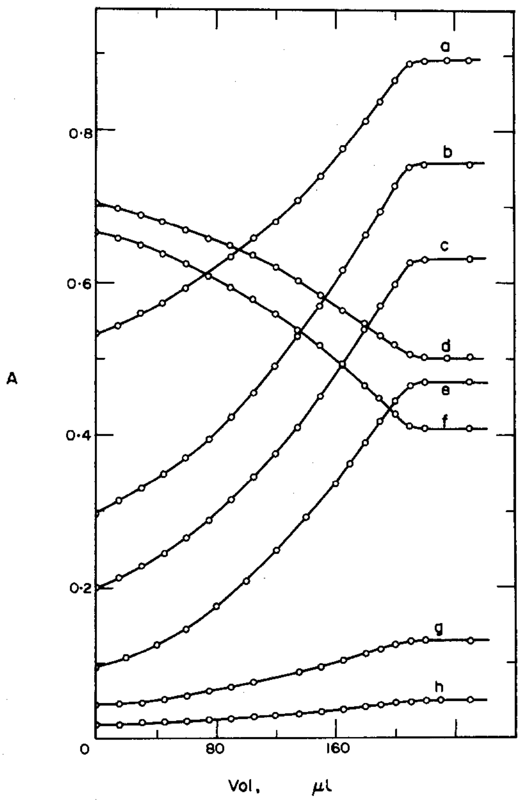

Fig. 3. Photometric titrations of zinc(II) with 0·001M EDTA, using Naphthylazoxine 6S as indicator, at various wavelengths. $c_{In} \approx 10^{-5}M$, $c_{Zn} = 1{\cdot}045 \times 10^{-5}M$, pH 5·80 (hexamine), $I = 0{\cdot}01$ (KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Theoretical equivalence point: 0·209 ml. Wavelengths, *nm*: (*a*) 500, (*b*) 525, (*c*) 540, (*d*) 450, (*e*) 550, (*f*) 425, (*g*) 565, (*h*) 575. Evaluations of the curves are listed in Table 2.

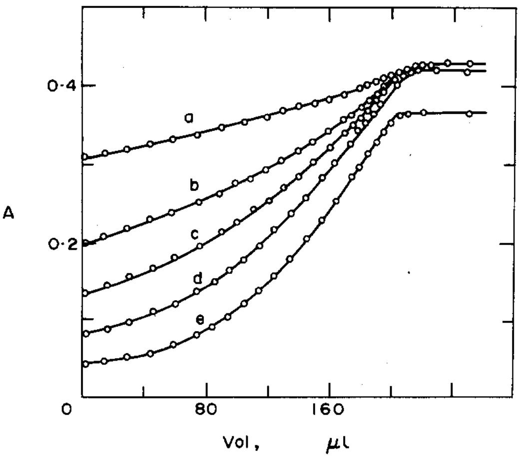

Fig. 4. Photometric titrations of zinc(II) with 0·001*M* EDTA, using SNAZOXS as indicator, at various pH values. $\lambda = 550$ nm, $c_{\mathrm{Zn}} = 1{\cdot}060 \times 10^{-5}M$, $c_{\mathrm{In}} \approx 10^{-5}M$, $I = 0{\cdot}01$ (hexamine + KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Theoretical equivalence point: 0·212 ml, value of pH (adjusted with 1*M* HNO_3): (*a*) 4·72, (*b*) 5·34, (*c*) 5·80, (*d*) 6·23, (*e*) 6·84. Evaluations of the curves are listed in Table 3.

RESULTS AND DISCUSSION

Photometric titrations of zinc(II) and lead(II) with 0·001*M* EDTA, using Naphthylazoxine 6S and SNAZOXS as indicators, were chosen as models because formation of MIn_2 complexes is expected. Both indicators form predominantly simple MIn_2 type complexes[27] and have been studied in our laboratory for several years. End-points were located by graphical extrapolation and also by numerical analysis of the curves. During the minimization process log K_{MY} was kept constant at a value taken from tables because MY was too stable for determination of K_{MY} to be considered certain.

The effect of choice of wavelength is demonstrated in Fig. 3. Only one component should absorb significantly so the difference between the molar absorptivities of the free indicator ϵ_{In} and its complex $\epsilon_{\mathrm{MIn}_N}$ should be as great as possible. The graphical and numerical evaluations of the curves are shown in Table 2. The end-points evaluated numerically are slightly but negligibly earlier than those obtained graphically. The evaluation of the indicator concentration and stability constant of the indicator complex was not substantially influenced by the choice of wavelength. The standard deviations of both parameters had low values. In some cases subroutine Letag was not able to determine a standard deviation.[26]

The effect of pH is shown in Fig. 4 and Table 3. At low pH the difference between the absorbance of the free form of the indicator and its complex is reduced and the sharpness of the titration curve is also decreased. However, at pH higher than 6·4, acid–base reactions interfere with the complexation equilibria. The end-points of the five curves evaluated were not substantially influenced except for those at the two extreme pH values 4.42 and 6·85 and were in good agreement with the equivalence point.

The evaluation of the indicator concentration was also not influenced by pH. Corrections for $\alpha_{\mathrm{In(H)}}$ at various pH values led to the same value of K_{MIn_2}.

The influence of indicator concentration is demonstrated in Fig. 5. The use of more indicator markedly

Table 2. Calculated results for the titration data in Fig. 3 [log$\alpha_{\mathrm{In}(H)} = 1{\cdot}47$; log $K_{\mathrm{MY}} = 16{\cdot}15$ (*cf.* Ref. 27); log $\alpha_{Y(H)} = 4{\cdot}97$]

λ, *nm*	End-point volume, *ml* Graphical	Numerical	Rel. dev. %	$-\log c_{\mathrm{In}}$	log K_{MIn_2}
425	0·211	0·2091 ± 0·0021	0·05	4·91 ± 0·03	13·04 ± 0·09
450	0·212	0·2086 ± 0·0011	−0·19	4·91	12·82
500	0·210	0·2095 ± 0·0017	0·24	4·85	13·06 ± 0·14
525	0·209	0·2091 ± 0·0012	0·05	4·98	13·91 ± 0·19
540	0·210	0·2087 ± 0·0018	−0·14	4·89 ± 0·04	13·03 ± 0·12
550	0·210	0·2081 ± 0·0012	−0·43	4·90 ± 0·05	13·01 ± 0·13
565	0·208	0·2083 ± 0·0018	−0·33	4·91	13·07 ± 0·14
575*	0·220	0·2173 ± 0·0019	−0·81	4·91 ± 0·05	13·29 ± 0·14
Average	0·210	0·2086 ± 0·0005	−0·19	4·91 ± 0·04	13·13 ± 0·18

* Results at this wavelength were not taken into account for the average value.

Table 3. Calculated results for the titration data in Fig. 4 [log $K_{\mathrm{MY}} = 16{\cdot}15$ (*cf.* ref. 27)]

pH	log α_{MIn_2}	log α_{MY}	End-point volume, *ml* Graphical	Numerical	Rel. dev. %	$-\log c_{\mathrm{In}}$	log K_{MIn_2}
4·72	2·29	7·01	0·210	0·2052 ± 0·0015	−2·74	4·87 ± 0·05	12·15
5·34	1·68	5·81	0·210	0·2168 ± 0·0023	2·26	5·00	12·55
5·80	1·23	4·99	0·210	0·2107 ± 0·0015	−0·61	5·00	12·27
6·23	0·84	4·30	0·210	0·2126 ± 0·0012	0·28	4·91	12·55
6·84	0·39	3·51	0·208	0·2140 ± 0·0032	0·96	4·80	12·09
Average			0·210	0·2119 ± 0·0031	−0·05	4·92 ± 0·09	12·31 ± 0·24

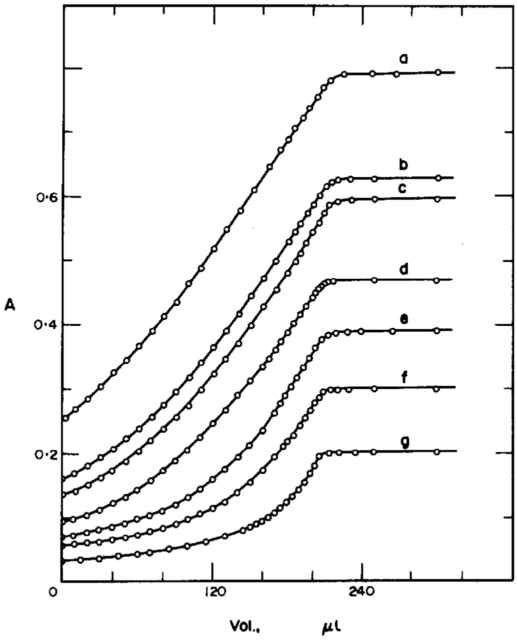

Fig. 5. Photometric titrations of zinc(II) with 0·001*M* EDTA, using Naphthylazoxine 6S, with various concentrations of the indicator. $\lambda = 555$ nm, $c_{Zn} = 1{\cdot}065 \times 10^{-5}M$, pH 5·75 (hexamine), $I = 0{\cdot}01$ (KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Theoretical equivalence point: 0·213 ml; indicator concentration, *M*: (*a*) $1{\cdot}78 \times 10^{-5}$, (*b*) $1{\cdot}41 \times 10^{-5}$, (*c*) $1{\cdot}20 \times 10^{-5}$, (*d*) $1{\cdot}0 \times 10^{-5}$, (*e*) $0{\cdot}79 \times 10^{-5}$, (*f*) $0{\cdot}60 \times 10^{-5}$, (g) $0{\cdot}40 \times 10^{-5}$.

improves the shape of the titration curve, mainly in the linearity before the end-point. The optimum amount to use is related to the accuracy in reading the absorbance. The indicator concentrations evaluated correspond to the actual analytical concentrations of the indicator in the solutions titrated. The indicator concentration does not influence the position of the end-point or the value of the stability constant of the indicator complex.

The effect of the metal-ion concentration is demonstrated in Fig. 6. The evaluated end-points were in agreement with the theoretical values. No marked difference was found between the graphical and numerical approach. The SIGY value[26] of the best curve fitting for a set of titrations of zinc(II) with SNAZOXS as indicator had the same value as the standard deviation of the absorbance, *i.e.*, 0·0035. The worst curve fitting was found for a family of lead(II) titrations, with the same indicator. Higher SIGY values indicate that the experimental points are subject to greater errors or that the curve does not correspond to the suggested mathematical model, *e.g.*, there may be consecutive complex-forming equilibria.

CONCLUSIONS

The application of the program is limited. When the shape of the titration curve contains a long linear part before the equivalence point the estimation of the parameter $\log K_{MY,cond}$ is not reliable. This parameter and $\log K_{MIn_N,cond}$ are ill-conditioned in the model. In such cases the $\log K_{MY,cond}$ value is kept constant during the minimization process.

The value of $c_{In}^2 K_{MY}$ determines the curvature of the titration curve before the equivalence point and $c_M K_{MY}$ can only be determined from the titration

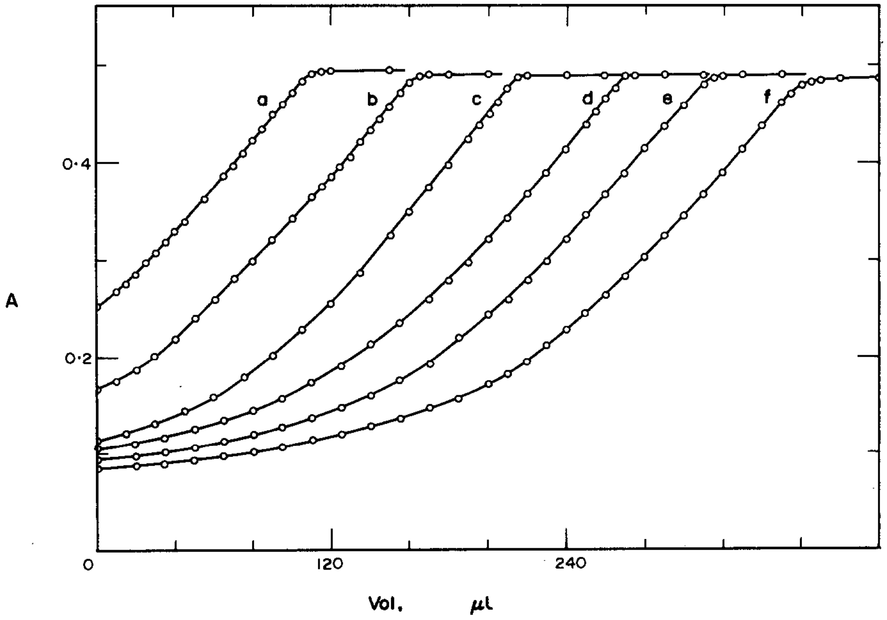

Fig. 6. Photometric titration of lead(II) with 0·001*M* EDTA, using Naphthylazoxine 6S as indicator, for various metal concentrations. $\lambda = 555$ nm, $c_{In} \approx 10^{-5}M$, pH 5·75 (hexamine) $I = 0{\cdot}01$ (KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Metal concentration c_{Pb}, *M*: (*a*) $0{\cdot}56 \times 10^{-5}$, (*b*) $0{\cdot}83 \times 10^{-5}$, (*c*) $1{\cdot}07 \times 10^{-5}$, (*d*) $1{\cdot}35 \times 10^{-5}$, (*e*) $1{\cdot}55 \times 10^{-5}$, (*f*) $1{\cdot}78 \times 10^{-5}$.

curve with an acceptable accuracy when the curvatures are large. In that case, however, the titration itself is inaccurate and no longer of analytical interest. When, as commonly in practice, we deal with "good" curves, it will hardly be possible to determine K_{MY}, and only K_{MIn_N} can be determined in particular cases (no impurities giving interactions, MIn_N the only indicator complex formed in solution, $c_{In}^2 . K_{MIn_N} < 10^4$).

A preliminary analysis of the metal-indicator and the metal-titration reagent system is necessary in order to obtain preliminary information on the stoichiometric coefficient N, the absence of consecutive equilibria, and all the competing equilibria occurring in the solution. For the NCHEL-LETAG program to be usable for evaluation of the titration curve it is necessary that the indicator complex predominantly formed is of the type MIn_N.

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COMPARATIVE KINETIC STUDY FOR RATE CONSTANT DETERMINATION OF THE REACTION OF ASCORBIC ACID WITH 2,6-DICHLOROPHENOLINDOPHENOL

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Summary—The rate constant k of the reaction of ascorbic acid with 2,6-dichlorophenolindophenol (DCPI) in oxalic acid solutions is determined, by stopped-flow techniques. Four different methods are used to evaluate the results. The values and errors are compared statistically. The average of the rate constant is $56{\cdot}5 \times 10^3$ l. mole^{-1}. sec^{-1} and the overall standard deviation is $0{\cdot}6 \times 10^3$ l. mole^{-1}. sec^{-1} or 1·0% relative. The pH-dependence of the rate constant suggests that DCPI reacts with undissociated ascorbic acid.

The reaction of ascorbic acid and 2,6-dichlorophenolindophenol has been widely applied for the assay of ascorbic acid in various biological and food samples. The stoichiometry of the reaction was first proposed by Tilmans,[1] the products being dehydroascorbic acid and the leuco-compound of the indophenol. The reaction is very fast and first-order in respect to each of the participants. To our knowledge no kinetic study of the reaction has been undertaken in order to determine the second-order rate constant.

In the present investigation we have applied stopped-flow techniques to determine the rate constant and to study the effect of pH on the reaction. Oxalic acid solutions were used as reaction media, these being solvents commonly used for the extraction and isolation of ascorbic acid from natural or biological samples.

EXPERIMENTAL

Apparatus

A Durrum stopped-flow spectrophotometer, model D-131, was used. The course of the reaction was displayed on the screen of a storage oscilloscope (Tektronix R 564 B) and photographed with a "Polaroid" camera (Tektronix C-12).

Reagents

The solutions of ascorbic acid and 2,6-dichlorophenolindophenol (DCPI) were standardized volumetrically, with a 5-ml burette and class-A glassware. All runs were performed at 27°, the temperature being thermostatically controlled.

All solutions were prepared in distilled water from *p.a.* grade reagents. Ascorbic acid solutions were prepared from a 0·1000 *M* stock solution in 0·05 *M* oxalic acid. The buffers used were hydrochloric acid–potassium chloride for pH 1·3–2·0, 0·1 *M* potassium hydrogen phthalate–0·1 *M* hydrochloric acid (or 0·1 *M* sodium hydroxide) for pH 2·2–6·0, 0·1 *M* potassium dihydrogen phosphate–0·1 *M* sodium hydroxide for pH 6·0–7·5. Solutions of DCPI were prepared from a $1{\cdot}0 \times 10^{-3}$ *M* stock solution in a 210 mg/l. sodium bicarbonate solution. The DCPI solutions were standardized titrimetrically against prestandardized solutions of ascorbic acid, or photometrically on a Beckman DK double-beam spectrophotometer with a 1-cm cuvette. The molar absorptivity was taken to be $8{\cdot}60 \times 10^3$ l. mole^{-1}. cm^{-1} at 522 nm[2].

Procedure

The stopped-flow spectrophotometer was calibrated for zero and 100% transmittance with water in the observation cell. All measurements were performed at 522 nm which is the isosbestic point for DCPI at various pH values.[2] In all experiments the light-path was adjusted to give a signal of 800 mV with water in the observation cell (T = 1). The course of reaction was followed with the storage oscilloscope and the trace on the screen was photographed with a "Polaroid" camera.

Evaluation of the experimental data

All concentrations of ascorbic acid and DCPI given in the tables and diagrams are the actual values in the reacting mixtures at zero time after mixing.

In order to avoid systematic errors which may have been introduced during the experimental work, or appear during the evaluation of the data, four different techniques were applied for the calculation of the second-order rate constant k. The analytical conditions in each case were adjusted in such a way as to ensure the applicability of the treatment used.

Method A. For the bimolecular reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \text{Products}$$

the rate law is given by the equation

$$\frac{-\mathrm{d}A_t}{\mathrm{d}t} = \frac{-\mathrm{d}B_t}{\mathrm{d}t} = kA_tB_t \tag{1}$$

where k, the rate constant, applies to a particular set of reaction conditions such as temperature, ionic strength and pH. If a spectrophotometric method is used and the transmittance T of the reacting mixture is monitored as the reaction progresses, the following mathematical expressions are valid, provided that the reactant B is the only absorbing species at the wavelength used:

$$\log\frac{V}{V_0} = -\epsilon_\mathrm{B}\,.\,b\,.\,B_t \tag{2}$$

where ϵ_B = molar absorptivity of B (l. mole^{-1}. cm^{-1}), b = light-path (cm), V_0 = output signal of the photomultiplier at transmittance $T = 1$ (800mV in the present work), V = output signal of the photomultiplier at transmittance T, and B_t = the instantaneous concentration of reactant B.

Differentiation of equation (2) with respect to time, and substitution of dB_t/dt from equation (1) gives

$$\frac{dV}{dt} = k\frac{(\mathrm{Abs})_t \cdot V}{0{\cdot}4343} \cdot A_t \tag{3}$$

where $(\mathrm{Abs})_t$ is the instantaneous absorbance of the reacting mixture, which is equal to $\epsilon_B . b . B_t$. At V = 294·3 mV the value of $(\mathrm{Abs})_t$ is 0·4343, the product $(\mathrm{Abs})_t . V$ has its maximum value and the value of the quantity $Q = (\mathrm{Abs})_t . V/0{\cdot}4343$ remains independent of V for the range 250–350 mV.[3] If the analytical concentration of B is adjusted to achieve the conditions above and $A_0 \gg B_0$ the simpler equation

$$\frac{dV}{dt} = k . Q . A_0 \tag{4}$$

can be used to determine k. This can be done by measuring the slope dV/dt of the reaction curve at signal level around 300 mV where the change of V with t is linear. The slope of the line $dV/dt = f(A_0)$ is the product kQ. Since values of Q can be calculated at each value of V, the rate constant k can be evaluated from the slopes in the diagrams.

Figure 1 is a typical oscilloscope picture of the reaction curves. A plot of dV/dt for the curves of Fig. 1, as a function of concentration of ascorbic acid, is a straight line, the slope of which is a measure of the rate constant and equal to Qk according to the theory above.

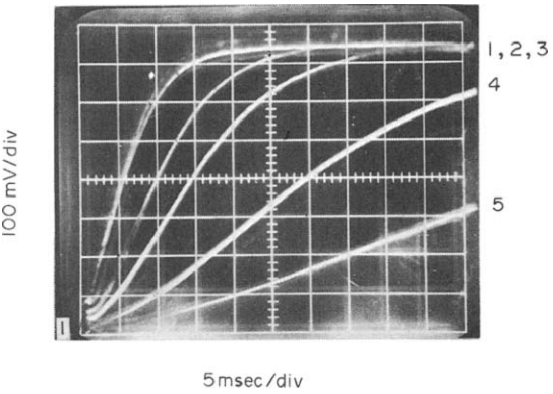

Fig. 1. Oscilloscope picture of the reaction of ascorbic acid and DCPI. DCPI, 1·0 × 10^{-4}M in NaHCO$_3$ solution; ascorbic acid, (1), 5 × 10^{-3}M; (2), 3 × 10^{-3}M; (3), 2 × 10^{-3}M; (4), 1 × 10^{-3}M; (5), 5 × 10^{-4}M.

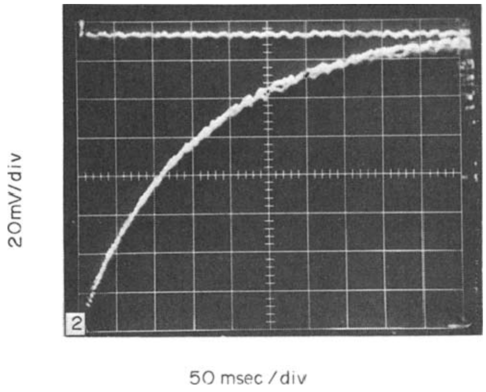

Fig. 2. Typical oscilloscope picture fot the application of methods B and D. DCPI, 5·0 × 10^{-6}M in NaHCO$_3$ solution; ascrobic acid, 12·5 × 10^{-5}M in 0·025M oxalic acid.

Table 1 lists the results of a series of eight such experiments evaluated by this method. The mean value of k is 55·9 × 10^3 l. mole^{-1}.sec^{-1}.

Method B. Starting from equation (3) and substituting ϵ_B = 8·60 × 10^3 l. mole^{-1}.cm^{-1} and b = 2 cm, we obtain:

$$\frac{2{\cdot}525 \times 10^{-5}}{V} \cdot \frac{dV}{dt} = kA_tB_t \tag{5}$$

A plot of the left-hand side of this equation against A_tB_t can be used to evaluate k, as follows. The slope dV/dt is measured at several values of V, then B_t is calculated at each V by calculating first the absorbance and then applying Beer's law. Finally A_t is calculated from

$$A_t = A_0 - B_0 + B_t \tag{6}$$

The starting concentrations A_0 and B_0 must be of the same order.

Three oscilloscope pictures, similar to the one shown in Fig. 2, were evaluated according to this method. When normalized, the results gave a linear plot for equation (5). Table 2 lists the results of 10 experiments which were evaluated by this method. The mean value of k is 56·8 × 10^3 l. mole^{-1}.sec^{-1}. The difference in the shape of the oscilloscope curves in Figs. 1 and 2 is due to the fact that the first shows the course of a pseudo first-order reaction, and the second that of a pure second-order reaction.

Method C. The oscilloscope pictures used in connection with method A were evaluated differently in this method. Since concentrations A_0 and B_0 are adjusted so as to create pseudo first-order conditions, with respect to B ($A_0 \gg B_0$), equation (1) can be written

$$\frac{dB}{dt} = -k_{ob} . B_t \tag{7}$$

Table 1. Values of k determined according to method A

DCPI, 10^{-6} M	k, 10^3 *l. mole*$^{-1}$.*sec*$^{-1}$ (corrected for Y)	k, 10^3 *l. mole*$^{-1}$.*sec*$^{-1}$ (corrected for Y and ϵ_{DAA})
5	—	56·7
10	51·0	54·9
30	51·8	55·0
38	54·4	57·3
39	54·4	56·8
67	52·7	55·0
69	51·2	54·8
100	51·7	56·6
		Mean k = 55·9
		s_k = 1·0
		$s_{\bar{k}}$ = 0·4

Table 2. Values of k determined according to Method B

DCPI, $10^{-6}\,M$	Ascorbic acid, $10^{-6}\,M$	k, 10^3 $l.\ mole^{-1}.\ sec^{-1}$
5	10	56·5
5	25	54·3
5	50	55·3
5	125	56·3
5	250	57·2
9	50	59·1
48	50	56·5
90	50	56·5
9	500	58·8
68	87	57·5
		Mean k = 56·8
		s_k = 2·1
		$s_{\bar{k}}$ = 0·7

where $k_{ob} = kA_t \simeq kA_0$ is the observed rate constant. By the infinite time method,[4] k_{ob} can be determined from the oscilloscope pictures taken at different values of A_0 and at constant concentration B_0 (in all cases $A_0 \gg B_0$). On plotting k_{ob} against A_0 we can calculate k from the slope. A plot of ln $(A_\infty - A_t)$ *vs.* t, for the reaction curves of Fig. 1, gives a set of straight lines. From the slopes, k_{ob} values are calculated for each concentration of ascorbic acid. A plot of k_{ob} *vs.* A_0 gives k, since $k_{ob} = kA_0$. The results of 6 such experiments are shown in Table 3. The mean value is $k = 56·8 \times 10^3$ l. mole^{-1}.sec^{-1}.

Method D. The course of a second-order reaction of A and B, which is first-order with respect to each reactant and obeys the stoichiometric equation A + B = products, can be described mathematically by

$$\frac{1}{B_0 - A_0} \ln \frac{A_0 . B_t}{B_0 . A_t} = kt \qquad (8)$$

Experimental data may be presented linearly either by plotting the left-hand side of equation (8) against t, or with less calculation by plotting log B_t/A_t against t. The experimental data can also be evaluated without plotting, but just by solving equation (8) for k, after substitution of successive observed values of A_t, B_t and t.[5] This is also a test for second-order reaction kinetics, which was justified in our case.

A typical plot according to method D is linear. The final result of treating five such curves is shown in Table 4. The mean value of k obtained by this method is $56·2 \times 10^3$ l. mole^{-1}.sec^{-1}.

Effect of pH on the reaction rate constant k

The effect of pH was studied in four different experiments which were performed with various concentrations of the reagents DCPI and ascorbic acid. The pH range 1·1–6·0 was covered by mixing buffered solutions of ascorbic acid with solutions of DCPI in sodium bicarbonate ($NaHCO_3$ 210 mg/l.). The pH range 6·0–7·5 was covered by mixing aqueous unbuffered solutions of ascorbic acid with buffered solutions of DCPI. This procedure was followed to avoid prolonged exposure of the ascorbic acid to an alkaline environment, where it auto-oxidizes.

Table 3. Values of k determined according to Method C

DCPI, $10^{-6}\,M$	k, 10^3 $l.\ mole^{-1}.sec^{-1}$
5	57·5
29	55·8
38	57·0
39	57·1
68	57·3
100	55·8
	Mean k = 56·8
	s_k = 0·8
	$s_{\bar{k}}$ = 0·3

Table 4. Values of k determined according to Method D

DCPI, $10^{-6}\,M$	Ascorbic acid, $10^{-6}\,M$	k, 10^3 $l.\ mole^{-1}.\ sec^{-1}$
5	10	57·2
5	25	57·2
5	125	56·1
5	250	54·6
5	500	56·2
		Mean k = 56·2
		s_k = 1·3
		$s_{\bar{k}}$ = 0·6

The results of these experiments are shown in Fig. 3.

RESULTS AND DISCUSSION

Tables 1–4 list the results of the evaluation of the experimental data according to methods A, B, C, and D as described above. In most of the cases shown in Table 1 the values of k were calculated by measuring dV/dt at $V = 300$ mV on the reaction curve, where Q has its maximum value. In some cases where the starting concentration of DCPI was lower than $2·0 \times 10^{-5}\,M$, the slope dV/dt was measured at $V > 360$ mV where $Q < 294·3$ mV and the linear part of the reaction curve is shorter. Both experimental conditions have their advantages and disadvantages, which are discussed elsewhere.[3] Column 2 of Table 1 lists the values of k corrected for a parameter Y.

$$Y = 1 - \frac{B_0}{A_0} + \frac{B_t}{A_0} \qquad (9)$$

appearing as a result of the substitution of A_0 for A_t in equation (3). These are the "apparent" values of the rate constant k. A second correction was applied to the "apparent" values for the contribution of species other than DCPI, in the absorbance of the

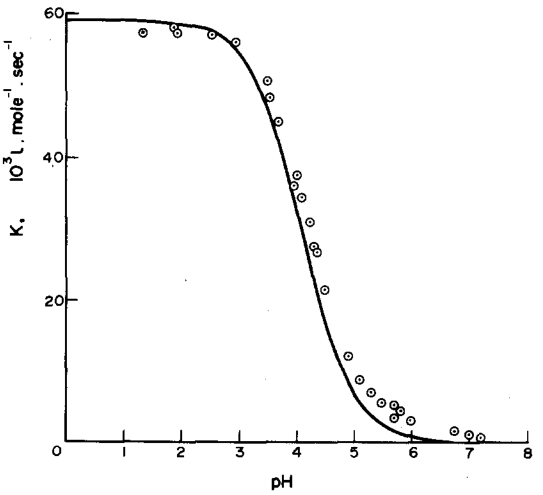

Fig. 3. Dependence of the rate constant k on the pH of the reaction mixture.

reacting mixture. This has a negative effect on the slope dV/dt which entails negative error in the final value of the slope kQ. The correction is based on the following considerations. In equation (3) magnitude (Abs) refers to the absorbance due to DCPI. We found that at 522 nm dehydroascorbic acid abbreviated DAA) also absorbs, having a molar absorptivity $\epsilon_{DAA} = 526$ l. mole^{-1}.cm^{-1}. This value is about 6% of ϵ_{DCPI}. If the contribution of DAA to the absorbance calculated from the oscilloscope pictures is considered, equation (3) must be replaced by

$$\frac{dV}{dt} = k.\frac{(\text{Abs})_t^m . V}{0{\cdot}4343}\left(1 - \frac{\epsilon_{DAA}}{\epsilon_{DCPI}}\right)A_0 Y \tag{10}$$

where $(\text{Abs})_t^m$ is the instantaneous absorbance of the reacting mixture. Equation (10) contains all corrections applied for the calculation of the k values given in column 3 of Table 1. Equation (10) shows that the Q values for each V must be corrected for the factor $1 - \epsilon_{DAA}/\epsilon_{DCPI}$, which has the value 0·939 for this particular case. The standard deviations of the means are calculated according to the equation

$$s_{\bar{k}} = \sqrt{\frac{\Sigma(k - k_i)^2}{N(N-1)}} \tag{11}$$

and the standard deviations for the method by using the equation

$$s_k = \sqrt{\frac{\Sigma(k - k_i)^2}{N - 1}} \tag{12}$$

Methods A and C give better reproducibility than methods B and D. This is obvious, since the measurement of the slope dV/dt in method A is accurate, because of the relatively long part of the reaction curves that is used. Method B requires the measurement of dV/dt at different points of a curved trace such as that shown in Fig. 2, which is less accurate.

The method of determining k_{ob} by the infinite-time method involves many points on the reaction curves and consequently the values obtained are accurate. This enhances the accuracy of method C. Methods B and D require the computation of the product A_tB_t of two small numbers, one of which is read from the trace and the other is computed by using equation (6). The probable error in B_t affects the accuracy of A_t as well as that of the product A_tB_t, thus introducing larger errors.

We have calculated the weighted average of the mean k values by using the relation[6]

$$k = \frac{\Sigma k_i w_i}{\Sigma w_i} \tag{13}$$

where w_i is the number of degrees of freedom for the ith method. The value of this average is $k =$ 56·5 × 10^3 l. mole^{-1}. sec^{-1}. The error associated with this average value was calculated by conventional methods of analysis of variance. The variance of the average k was calculated according to the equation[6]

$$s_k^2 = \frac{\Sigma s_i^2 w_i}{\Sigma w_i} \tag{14}$$

The result of this calculation is $s_k = 0{\cdot}6 \times 10^3$ l. mole^{-1}. sec^{-1} which is taken as the overall error for the average k.

Referring to Fig. 3, the S-shaped curve is reminiscent of titration curves and can be explained by the hypothesis that the main species participating is the product of a protolytic reaction. This suggests that the effect of $[H^+]$ on the reaction rate is indirect. Hydrogen ions do not participate directly in the reaction, but control the concentration of the reacting species in the mixture. Ascorbic acid acts as a weak diprotic acid with dissociation constants $K_{a_1} = 6{\cdot}17 \times 10^{-5}$ and $K_{a_2} = 1{\cdot}62 \times 10^{-12}$ ($pK_{a_1} = 4{\cdot}21$, $pK_{a_2} = 11{\cdot}79$) at 20°.[7] If we consider only the first dissociation, the experimental data can be explained by the hypothesis that the active species is undissociated ascorbic acid. The solid line in Fig. 3 is a theoretical curve which was derived by multiplying the value $k = 59{\cdot}0 \times 10^3$ l. mole^{-1}. sec^{-1} (extrapolated value of the experimental curve), by the ratio of the concentration of the acid form to the analytical concentration of ascorbic acid, at each pH. The two lines of Fig. 3 do not overlap fully at higher pH. Two explanations can be given for this disagreement. First, the experimental value $pK_{a_1} = 4{\cdot}25$ deviates from the theoretical (4·21) at higher pH values because of the effect of ionic strength. As stated above the measurements were carried out in buffers of relatively high ionic strength. Alternatively, the ascorbate ion may react with DCPI in a similar manner to ascorbic acid, but with a different rate constant, thus altering the overall value of the rate constant k. Both explanations can be justified by the experimental results.

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CHROMATOGRAPHY OF ALKALOIDS ON TITANIUM ARSENATE PAPERS AND QUANTITATIVE SEPARATION OF SOME ALKALOIDS FROM NICOTINE ON TITANIUM ARSENATE COLUMNS

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Summary—Columns and papers of titanium arsenate have been utilized for chromatographic studies of several alkaloids in aqueous and mixed solvent systems. The results have been compared with those obtained with plain papers. A number of separations have been achieved on papers impregnated with titanium arsenate. Distribution coefficients of these alkaloids have been determined. A number of alkaloids have been separated quantitatively from nicotine on titanium arsenate columns.

Analytical applications of inorganic ion-exchange papers have considerably increased in number during the last few years,[1–4] but very few investigations of organic compounds have been made. Inorganic ion-exchange papers were first introduced in this field by Catelli,[5] who performed chromatography of amino-acids on zirconium phosphate papers. Chromatographic studies of alkaloids[6] on zirconium phosphate papers in a limited number of solvent systems have been reported. As far as we are aware no further attempt has been made to utilize inorganic ion-exchangers for the separation of organic compounds.

It has been found that titanium arsenate offers excellent ion-exchange properties and has a great separation potential for metal ions.[7] We decided to use titanium arsenate papers and columns for the separation of alkaloids and this paper summarizes the results of our studies.

EXPERIMENTAL

All chemicals used were of analytical grade.

Preparation of ion-exchange papers

Whatman No. 1 paper strips (15 × 3 cm) were first dipped in 0·5*M* titanium(IV) chloride for 10 sec and then dried on a sheet of paper for 15–20 min. The papers were then treated with 0·5*M* sodium arsenate solution for 20–30 sec to precipitate the ion-exchanger. The strips were again dried, washed with demineralized water to remove excess of reagents and finally dried at room temp. To check the reproducibility of the paper three sets were prepared and chromatography was performed on each. The results were found to be reproducible.

Preparation of solutions

Alkaloids. Solutions (1%) of all the alkaloids were prepared in ethanol, except for nicotine, which was dissolved in demineralized water.

Detection reagent. Dragendorff's reagent[8] was used for the detection of alkaloids, which give a red–orange spot with this reagent.

Chromatographic procedure

Ascending chromatography[1] was performed in ordinary glass jars (25 × 5 cm). The solvent was allowed to travel 11 cm from the point of application in all cases. The R_f values of the front and rear limits of the spot (R_L and R_T respectively) were recorded to determine the actual position of the spot. The developed chromatogram was air-dried and the spots detected by spraying with the reagent. Results are given in Tables 1–3.

Determination of distribution coefficients

Ion-exchanger in the H^+ form (0·5 g) was equilibrated at room temp (20 ± 5°) with solutions of the alkaloids,

Table 1. R_L and R_T values of alkaloids on plain papers and titanium arsenate papers (TiAs)

Solvent	5% NH_4Cl				1 *N* HCl				5% Acetic acid				10% Acetic acid			
	Plain paper		TiAs paper		Plain paper		TiAs paper		Plain paper		TiAs paper		Plain paper		TiAs paper	
Compound	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Quinine	0·65	0·90	0·80	0·92	0·90	1·00	0·75	0·95	0·85	1·00	0·25	0·90	0·90	1·00	0·10	0·60
Cinchonine	0·70	1·00	0·75	0·95	0·90	1·00	0·75	0·95	0·90	1·00	0·15	0·70	0·70	0·90	0·20	0·70
Brucine	0·60	0·70	0·40	0·60	—	—	0·55	0·75	0·65	0·90	0·40	0·70	0·80	0·95	0·48	0·75
Atropine	0·90	1·00	0·75	0·85	0·90	1·00	0·85	0·95	0·90	1·00	0·80	0·90	0·90	1·00	0·80	0·98
Nicotine	0·90	1·00	0·75	0·90	0·90	1·00	0·00	0·65	0·90	1·00	0·00	0·20	0·90	1·00	0·00	0·26
Strychnine	0·70	0·85	0·70	0·80	0·65	0·85	0·60	0·75	0·70	0·90	0·38	0·62	0·80	0·95	0·55	0·80
Codeine	0·85	0·95	0·80	0·90	0·90	1·00	0·80	0·95	0·86	1·00	0·75	0·95	0·90	1·00	0·80	0·98

Table 2. R_L and R_T values of alkaloids in mixed-solvent systems on plain papers and titanium arsenate papers

Solvent	Ethyl alcohol:acetic acid 1:2				Ethyl formate:acetone:water 1:1·4:0·4				Ethyl acetate: acetic acid:water 7·5:0·9:0·9				n-Butanol:acetic acid:water 2:1:2				Ethyl acetate:water:pyridine 2:2:0·9			
	Plain paper		TiAs paper		Plain paper		TiAs paper		Plain paper		TiAs paper		Plain paper		TiAs paper		Plain paper		TiAs paper	
Alkaloids	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
Quinine	0·90	1·00	0·00	1·00	0·85	1·00	0·40	0·70	0·65	1·00	0·75	0·95	0·75	0·85	0·85	1·00	0·65	1·00	0·80	1·00
Cinchonine	0·85	1·00	0·20	0·90	0·80	1·00	0·20	0·40	0·70	1·00	0·10	0·20	0·75	0·90	0·80	0·90	0·70	0·90	0·80	0·90
Brucine	0·90	1·00	0·65	0·95	0·40	0·80	0·60	0·80	0·40	0·80	0·10	0·50	0·75	0·85	0·80	0·90	0·20	0·30	0·50	0·70
Atropine	0·90	1·00	0·80	1·00	0·60	0·70	0·70	0·85	0·20	0·30	0·10	0·35	0·75	0·85	0·90	1·00	0·30	0·40	0·40	0·60
Nicotine	0·40	1·00	0·00	0·30	0·20	0·60	0·00	0·10	0·00	0·25	0·00	0·10	0·60	0·70	0·00	0·45	0·15	0·20	0·00	0·75
Strychnine	0·90	1·00	0·00	0·80	0·70	0·85	0·80	0·95	0·50	0·80	0·10	0·40	0·70	0·80	0·90	1·00	0·30	0·50	0·65	0·85
Codeine	0·90	1·00	0·65	1·00	0·70	0·80	0·40	0·50	0·10	0·25	0·15	0·30	0·75	0·85	0·70	0·80	0·20	0·35	0·75	0·85

Table 3. Some binary separations of alkaloids achieved on titanium arsenate papers

Solvent systems	Separation achieved
0·01 *M* HNO_3	Brucine(0·23–0·51)–Nicotine(0·00–0·20) Codeine(0·74–0·95)–Nicotine(0·00–0·20) Atropine(0·77–0·88)–Nicotine(0·00–0·19) Strychnine(0·47–0·64)–Nicotine(0·00–0·10) Atropine(0·75–0·91)–Strychnine(0·48–0·60)
0·1 *M* HNO_3	Quinine(0·45–0·76)–Nicotine(0·00–0·22) Atropine(0·80–0·93)–Brucine (0·50–0·65) Codeine(0·76–0·89)–Brucine(0·50–0·56)
n-Butanol:acetic acid:water (2:1:2)	Codeine(0·80–0·99)–Nicotine(0·00–0·19) Cinchonine(0·73–0·88)–Nicotine(0·00–0·19) Atropine(0·86–0·99)–Nicotine(0·00–0·15) Brucine(0·81–0·93)–Nicotine(0·00–0·15) Quinine(0·78–0·94)–Nicotine(0·00–0·16) Strychnine(0·86–0·96)–Nicotine(0·00–0·14)
10% Acetic acid	Codeine(0·69–0·92)–Nicotine(0·00–0·13) Strychnine(0·44–0·66)–Nicotine(0·00–0·10) Codeine(0·84–0·97)–Quinine(0·27–0·65)
5% Acetic acid	Strychnine(0·44–0·66)–Nicotine(0·00–0·10) Atropine(0·77–0·91)–Nicotine(0·00–0·12)
Ethyl acetate: water:pyridine (2:2:9)	Cinchonine(0·82–0·90)–Brucine(0·31–0·45) Cinchonine(0·85–1·00)–Strychnine(0·52–0·65)
Ethanol:acetic acid (1:2)	Codeine(0·64–0·94)–Nicotine(0·00–0·24) Atropine(0·73–1·00)–Nicotine(0·00–0·29) Brucine(0·83–0·95)–Nicotine(0·00–0·28)
Ethyl acetate: acetic acid: water (7·5:0·9:0·9)	Cinchonine(0·22–0·64)–Nicotine(0·00–0·13) Atropine(0·41–0·65)–Nicotine(0·00–0·12)
n-Butanol:HNO_3(100:1)	Brucine(0·80–0·88)–Strychnine(0·90–0·95)
n-Butanol:HCl(100:1)	Brucine(0·54–0·60)–Strychnine(0·63–0·74)
n-Butanol:HCl(100:15)	Brucine(0·46–0·56)–Strychnine(0·59–0·66)
n-Butanol:HCl(100:5)	Brucine(0·43–0·50)–Strychnine(0·56–0·66)
Cyclohexane saturated with water	Brucine(0·00–0·20)–Strychnine(0·22–0·30)

in conical flasks. The total volume was adjusted to 50 ml with the desired solvents. The amount of alkaloid remaining in solution was determined spectrophotometrically.[9] The distribution coefficients were calculated according to the formula.

$$K_d = \frac{I - F}{F} \times \frac{50}{0{\cdot}5}$$

Where I = amount of alkaloid applied and F = amount of alkaloid found in solution after equilibration. The results are summarized in Table 4.

Separation of other alkaloids from nicotine on titanium arsenate columns

Exchanger in the H^+ form (1·5 g, 50–100 mesh) was placed in a glass tube (bore 0·69 cm). Binary mixtures of

Table 4. Distribution coefficients (10^3 ml/g) of alkaloids on titanium arsenate

Solvent system / Alkaloids	0·05*M* HNO_3	0·1*M* HCl	5% CH_3COOH	5% NH_4NO_3	0·5 *M* HNO_3: 0·5 *M* NH_4NO_3 (9:1)	0·5 *M* HNO_3: 0·5 *M* NH_4NO_3 (1:1)	0·5 *M* HNO_3: 0·5 *M* NH_4NO_3 (1:9)	$CH_3COOC_2H_5$: CH_3COOH:H_2O (75:9:9)
Quinine	1·80	0·100	1·50	0·70	0·007	0·180	0·200	3·90
Cinchonine	0·80	0·100	TA	3·90	0·220	0·120	0·263	TA
Strychnine	1·50	TA	TA	TA	0·181	TA	TA	TA
Brucine	2·00	1·50	TA	TA	TA	TA	TA	TA
Nicotine	TA	TA	TA	TA	TA	TA	TA	TA
Ephederine	0·51	0·49	7·90	7·90	0·51	1·50	1·50	TA
Codeine	0·186	0·43	0·186	0·100	0·038	0·47	0·70	TA

TA = total adsorption.

Table 5. Quantitative separations of some alkaloids from nicotine on titanium arsenate columns

Alkaloid*	Amount taken, μg	Amount recovered, μg
Quinine	1000	998
Quinine	1500	1490
Cinchonine	1000	1000
Cinchonine	1500	1495
Strychnine	2000	1998
Strychnine	2000	2002
Brucine	2000	1990
Brucine	1500	1505
Ephedrine	2000	1990
Ephedrine	1500	1496
Codeine	1000	1000
Codeine	2000	2004

* Mixed with 2000 μg of nicotine.

solutions of nicotine (2000 μg) with other alkaloids (1000–2000 μg) were passed through the exchanger. Alkaloids other than nicotine were eluted with 0·1 M nitric acid, 40–50 ml (flow-rate 0·5 ml/min) being required. Nicotine interacts strongly with the exchanger and cannot be eluted. For each new separation, a fresh column was used. Results of the separations are given in Table 5.

RESULTS AND DISCUSSION

A comparison of the R_f values of the alkaloids on plain and ion-exchange papers reveals that in almost all the solvent systems the R_f values are lower on the ion-exchange papers. The R_f values generally increase with increasing hydrogen-ion concentration. On the basis of the R_f values, several separations are possible. Table 3 summarizes a number of binary separations.

The effect of reagent concentration on R_f was studied by using papers of different composition; the R_f values in general decrease with increase in the concentration of reagent. It was found that papers impregnated with 0·5 M titanium chloride and sodium arsenate solutions gave the best results. The affinity of various alkaloids for titanium arsenate in 10% acetic acid is in the order atropine > strychnine > brucine > cinchonine > quinine, which is the same as in the case of zirconium arsenate. However, the affinity trend observed in 1M hydrochloric acid on titanium arsenate is atropine > cinchonine > quinine > strychnine > brucine, which is different from the trend obtained on zirconium phosphate with the same solvent. It may be concluded that it is the anion of the exchanger which is responsible for the adsorption of the alkaloids.

Distribution coefficients of the alkaloids on titanium arsenate in various solvent systems were also determined and compared with the R_f values obtained on titanium arsenate papers. It is interesting to note that the sequence of K_d values is the reverse of the R_f values in almost all systems.

Codeine, atropine, strychnine, quinine and cinchonine have been recovered quantitatively from synthetic mixtures with nicotine, on titanium arsenate columns. Therefore titanium arsenate is specifically useful for the removal of nicotine impurities from a mixture containing a number of alkaloids.

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QUELQUES APPLICATIONS DE LA COLORIMETRIE DE PRECISION A LA MICROANALYSE ELEMENTAIRE

DOSAGES DU TITANE, DU PLATINE, DU PALLADIUM, DU MOLYBDENE ET DU PHOSPHORE

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Résumé—Le prélèvement analytique (organique et dans certains cas inorganique), de masse inférieure à 5 mg, est attaqué par voie humide, dans un micromatras, en vue de la mise en solution des éléments à doser. Le titane, le platine, le palladium, le molybdène et le phosphore sont dosés par colorimétrie spectrophotométrique en mettant respectivement en oeuvre les réactions suivantes: formation du complexe Ti(IV)–Tiron; formation de l'ion $[PtCl_4]^{2-}$ par réduction de l'ion $[PtCl_6]^{2-}$ par le chlorure stanneux; formation de l'ion $[PdI_4]^{2-}$; réduction ménagée de Mo(VI) en présence d'ions thiocyaniques; formation du complexe phosphovanadomolybdique.

La colorimétrie de précision déjà mise en oeuvre dans notre Service depuis plusieurs années pour le microdosage du fluor,[1–2] du phosphore[1] et du silicium[3] y est également appliquée à nombre d'autres microdosages dont, notamment, ceux du titane, du platine, du palladium et du molybdène, dans les composés organiques et certains composés inorganiques, après attaque par voie humide. Par ailleurs, le domaine de son application au microdosage du phosphore dans de semblables composés y est sensiblement élargi.

Les réactifs utilisés sont des produits classiques, commerciaux, qui présentent l'inconvénient d'un manque de spécifité; néanmoins, lorsque les produits soumis à l'analyse contiennent simultanément l'élément à doser et des éléments gênants, la quantité de ces derniers que peut contenir un prélèvement microanalytique est si petite qu'en général leur interférence sur le résultat du dosage est négligeable ou faible et peut alors être éliminée grâce à une correction appropriée ou à une légère modification du mode opératoire.

En vue d'appliquer à la microanalyse des méthodes colorimétriques jusqu'ici réservées à l'analyse de traces et dont, de ce fait, la sensibilité est trop élevée, nous avons été conduits à prélever 2 ou 3 parties aliquotes sur les solutions obtenues après attaque par voie humide; ces parties aliquotes fournissent le même nombre de résultats de dosage dont on effectue la moyenne qui est adoptée comme résultat définitif. Cette façon d'opérer permet d'éviter que l'analyse sur des parties aliquotes entraîne une réduction de la précision des résultats; elle permet, en outre, en jouant sur la diminution du volume des fioles jaugées définissant le volume initial de la solution obtenue après attaque par voie humide ou sur l'augmentation du volume de chacune des parties aliquotes, soit de diviser par 10 la masse des prélèvements milligrammiques du domaine microanalytique classique, soit d'effectuer les déterminations de très faibles teneurs.

Un autre intérêt de cette méthode est de permettre le dosage de nombreux éléments, hors séries, avec un même appareillage qui, à l'exception du spectrophotomètre, est peu coûteux; cet appareil doit permettre la détermination des absorbances à un ou deux millièmes d'unité près.

Les complexes ou ions colorés auxquels il est fait appel pour les dosages colorimétriques sont indiqués ci-après ainsi que les réactions qui permettent de les obtenir. Les références bibliographiques sont citées dans le tableau II.

Titane. Le Tiron (dihydroxybenzène-1,2 disulfonate de sodium-3,5), forme un complexe jaune avec le titane(IV) à pH 4,7; par ailleurs, l'addition d'acide oxalique permet d'éviter l'hydrolyse des sels de titane.

Platine. Le chlorure stanneux réduit l'ion $[PtCl_6]^{2-}$ en ion $[PtCl_4]^{2-}$ jaune.

Palladium. L'iodure de potassium forme un ion complexe $[PdI_4]^{2-}$, rose brunâtre, avec le palladium(II); l'iode produit est éliminé par réduction par le sulfite de sodium.

Molybdène. La réduction ménagée de Mo(VI) par l'iodure de potassium en présence d'ions thiocyaniques donne lieu à la formation de Mo(V) coloré en jaune; l'iode produit est éliminé par réduction par le sulfite de sodium.

Phosphore. La méthode déjà mise en oeuvre,[1] qui fait appel au complexe phosphovanadomolybdique, est adaptée en vue de son application élargie au domaine de la décimilligrammanalyse.

PARTIE EXPERIMENTALE

L'attaque, du type micro-Lorenz[4–5] ou micro-Lorenz modifié, est effectuée en micromatras, du type "Kjeldahl" (capacité du bulbe: 16 ml), sur une rampe de minéralisation à gaz[6] avec collecteur de fumées. Le chauffage au gaz peut être avantageusement remplacé par un chauffage électrique à faible inertie thermique (les dispositifs du type "grille électrique" trouvés sur le marché ne permettent pas, en effet, un refroidissement rapide des matras). A cette fin, conviennent des fours électriques tubulaires de 18 mm de diamètre intérieur, disposés comme l'a décrit Bigois.[7] L'ébullition est régularisée par l'introduction d'un petit morceau de plaque de verre fritté (porosité n° 1). La substance est pesée en tube pèse-substance de Lieb,[8a] en microampoule à un capillaire[8b] (à briser sous la surface du liquide) ou éventuellement en sachet de terphane.[9] Afin de pouvoir utiliser une microbalance électronique ou une ultramicrobalance permettant des pesées très précises (extension à la décimilligrammanalyse), le pèse-substance peut être remplacé par une micronacelle de platine. L'ensemble nacelle–prélèvement analytique est taré puis la nacelle est introduite horizontalement à l'intérieur du matras à l'aide de longues pinces droites à extrémités plates. Elle est alors renversée de telle sorte qu'une quantité maximale de produit tombe dans le bulbe du matras. Elle est ensuite retournée dans la position initiale et extraite du matras toujours horizontalement en évitant qu'à aucun moment elle ne touche les parois de ce dernier. Sa nouvelle pesée fournit, par différence avec la première, la masse de substance tombée dans le matras.

Après attaque par voie humide (*cf.* tableau 1) le contenu limpide de chaque matras est dilué avec de l'eau* et transvasé

—soit dans une fiole jaugée de capacité F (25, 50 ou 100 ml), dont le volume est ajusté avec de l'eau et de laquelle seront prélevées des parties aliquotes pour la colorimétrie,

—soit directement dans des fioles de colorimétrie† de capacité f dans lesquelles on peut d'ailleurs avoir préalablement introduit un réactif (acide oxalique dans le cas du dosage du titane).

Le terme "solution d'attaque" désigne la solution obtenue après attaque de l'échantillon par voie humide, et dans le cas de prélèvement de parties aliquotes, après dilution et ajustement du volume dans la fiole jaugée de capacité F.

L'option pour l'emploi ou non d'aliquotes est fonction de plusieurs facteurs dont le principal est la sensibilité de la méthode colorimétrique utilisée; en général, pour le phosphore et le molybdène, l'emploi d'aliquotes n'est pas recommandé.

En même temps que sont effectuées les attaques par voie humide, sont préparés des "blancs de solution d'attaque" en utilisant les mêmes réactifs, ainsi que le sachet de terphane si celui-ci doit être employé, et en suivant le même mode opératoire (avec dilution éventuelle lorsque la méthode comporte des prélèvements de parties aliquotes) que pour les attaques proprement dites; la seule différence est qu'il n'est pas procédé à l'introduction dans le matras, de substance à analyser. En effet, si l'influence desdits réactifs est négligeable dans les cas des dosages du titane, du platine et du phosphore à l'échelle milligrammique, elle ne l'est plus dans ceux des dosages du palladium et du molybdène; il faut alors en tenir compte.

A cette fin, il suffit alors d'introduire éventuellement dans chacune des fioles de colorimétrie les réactifs employés pour une attaque proprement dite après leur avoir fait subir un traitement identique à celui des conditions d'attaque§. Les quantités de réactifs à introduire doivent être telles que leurs concentrations finales soient égales entre elles dans toutes les fioles de colorimétrie (*cf.* remarque ci-après).

La colorimétrie est effectuée sans recours à une courbe d'étalonnage;[1] son usage est remplacé par celui de solutions étalons *cf.* tableau 2), contenant chacune une quantité connue (p mg) de l'élément à doser, introduite dans la fiole de colorimétrie sous la forme de v ml d'une solution titrée appropriée, préparées en même temps que les solutions inconnues contenant P mg de l'élément à doser. La solution inconnue est introduite dans une fiole de colorimétrie f sous forme de solution d'attaque soit en totalité (son volume est alors s), soit sous forme d'aliquotes (de volumes $a_1, a_2 \ldots a_i \ldots a_n$ ml) prélevées par pipettage dans la fiole F où la solution totale (de volume s) a été préalablement diluée.

La solution étalon étant toujours préparée en triple, en vue d'améliorer la précision, soit d', d'' et d''' les absorbances correspondantes et soit D celle de la solution inconnue, toutes mesurées par rapport à l'absorbance de la solution d'essai à blanc de réactifs (cette dernière est préparée comme une solution étalon, à l'exclusion de l'addition de solution titrée). La quantité inconnue P est calculée à partir de p par une simple règle de proportionnalité, d'après la formule:

$$P = \frac{pD}{(d' + d'' + d''')/3}$$

Il est recommandable que p et P aient des valeurs voisines; cependant, en ce qui concerne les éléments considérés dans le présent travail, la loi de Lambert–Beer étant assez bien suivie, la précision reste acceptable s'il arrive que l'écart croisse entre les valeurs de p et P, sous réserve que p demeure à l'intérieur des limites indiquées pour P dans le tableau 2.

Remarque. Lorsque les parties aliquotes prélevées ont des volumes $a_1, a_i \ldots a_n$ différents ($a_1 > a_i \ldots > a_n$), elles contiennent des quantités de réactifs d'attaque différentes, proportionnelles à leurs volumes respectifs. Lorsqu'il s'est avéré, au cours de l'étude préliminaire, que l'influence des réactifs d'attaque n'est pas négligeable, on s'arrange pour que la quantité totale de réactifs d'attaque soit égale, dans chacune des fioles de colorimétrie, à celle que contient l'aliquote a_1 dont le volume est le plus élevé.

A cette fin, on introduit:

—$w = a_1$ ml de "blanc de solution d'attaque" dans les "solutions d'essai à blanc de réactif" et les solutions étalons,

—$w = a_1 - a_1 = 0$, $w = a_1 - a_i$ ou $w = a_1 - a_n$ ml de "blanc de solution d'attaque" dans les solutions inconnues, lesquelles contiennent déjà respectivement a_1, a_i ou a_n ml de solution aliquote.

Pendant le temps (t) qui doit s'écouler entre la fin de la préparation des solutions (étalons, inconnues, d'essai à blanc) de colorimétrie et les lectures au spectrophotomètre (*cf.* tableau 2), les fioles sont laissées en attente à la température ambiante et à l'abri de la lumière (bien que cette dernière précaution puisse être superflue dans le cas de certains dosages).

Réactifs

Les réactifs sans mention spéciale sont des réactifs Prolabo "pour analyses", les réactifs employés tant pour l'attaque par voie humide que pour la colorimétrie sont uniquement cités sous la rubrique "attaque". L'eau utilisée est distillée au laboratoire dans un appareil en acier inoxydable.

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* De l'eau bouillante doit être employée lors des dosages du phosphore et du titane.

† Le terme "fiole de colorimétrie" désigne la fiole jaugée dans laquelle est préparée la solution du complexe coloré, objet des mesures colorimétriques.

§ C'est cette possibilité de travailler dans des conditions identiques qui permet d'élargir le domaine d'application de la colorimétrie.

Titane

Attaque. Acide sulfurique (p.s. = 1,83); acide nitrique (p.s. = 1,38); eau oxygénée (110 vol).

Colorimétrie. Acide oxalique: solution aqueuse à 25%.

—Ammoniaque (p.s. = 0,90).

—Solution tampon à pH 4,7: solution aqueuse contenant 68 g d'acétate de sodium $NaCH_3COO.3H_2O$ (ou à défaut 50 g d'acétate de potassium KCH_3COO) et 30 ml d'acide acétique (p.s. = 1,05) par litre de solution.

—Tiron: solution aqueuse à 4% préparée au moins 4 à 5 h avant emploi. La solution doit être incolore; elle ne se conserve que quelques jours à l'abri de la lumière. La qualité du Tiron est très importante; le Tiron "Prolabo" a toujours donné satisfaction.

—Papier pH permettant de déterminer le pH à 0,5 unité près.

—Solution titrée de titane[10a] à 1 mg/ml: chauffer, à 200° au bain de sable jusqu'à dissolution complète (durée: environ 90 mn), 1,668 g de dioxyde de titane pur Prolabo (le lot utilisé s'est avéré de pureté suffisante), 10 g de sulfate d'ammonium et 55 ml d'acide sulfurique (p.s. = 1,83). Ajuster à 1 litre avec de l'eau. La solution est stable pendant plusieurs mois.

—Solution titrée de titane à 0,020 mg/ml: diluer avec de l'eau une partie de la solution précédente. Il n'est pas recommandé de préparer et de conserver une solution à 0,010 mg/ml par simple dilution de la solution à 1 mg/ml; en effet, la solution ainsi obtenue ne serait stable que pendant une quinzaine de jours (probablement parce que son pH est légèrement plus élevé: 2 au lieu de 1,5).

Platine

Attaque. Acide sulfurique (p.s. = 1,83); acide nitrique (p.s. = 1,38); acide chlorhydrique (p.s. = 1,19).

Colorimétrie. Chlorure stanneux: solution à 10% préparée tous les 8 jours. Peser 50 g de chlorure stanneux cristallisé, $SnCl_2.2H_2O$, ajouter 80 ml d'acide chlorhydrique (p.s. = 1,19) et compléter à 500 ml avec de l'eau; faire chauffer éventuellement jusqu'à température voisine de l'ébullition si la solution est hydrolysée; elle devient alors limpide. Arrêter aussitôt le chauffage et laisser refroidir.

—Fil de platine pur (à 99,95%) d'environ 0,05 mm de diamètre. Ce diamètre doit rester faible: la durée de dissolution d'un fil de 0,5 mm de diamètre, par exemple, serait, en effet, beaucoup trop longue dans les conditions décrites.

—Solution titrée de platine à 0,100 mg/ml: introduire dans un micromatras 100 mg de fil de platine préalablement grillé au rouge, dans la flamme d'un bec Bunsen, 1 ml d'acide nitrique (p.s. = 1,38) et 1 ml d'acide chlorhydrique (p.s. = 1,19). Faire bouillir sur la rampe de minéralisation jusqu'à évaporation presque à sec. Laisser refroidir et recommencer l'opération jusqu'à dissolution complète du platine; 3 ou 4 additions d'acides nitrique et chlorhydrique sont nécessaires. Faire ensuite bouillir 3 ou 4 fois avec 1,5 ml d'acide chlorhydrique jusqu'à disparition des vapeurs nitreuses. Evaporer chaque fois presque à sec sauf la dernière pour laquelle le volume résiduel doit être de 1 ml environ. Transvaser quantitativement le contenu du matras dans une fiole jaugée de 1 litre et ajuster avec de l'eau.

—Solution titrée de platine à 0,010 mg/ml: diluer avec de l'eau une partie de la solution précédente.

Palladium

Attaque. Mêmes réactifs que ceux utilisés pour le platine.

Colorimétrie. Ammoniaque (p.s. = 0,90).

—Iodure de potassium: solution à 50% préparée tous les 15 jours. Verser dans une fiole 2,5 ml d'ammoniaque (p.s. = 0,90), 250 g d'iodure de potassium et de l'eau en quantité suffisante pour dissoudre l'iodure. Compléter à 500 ml avec de l'eau. Conserver la solution à l'abri de la lumière.

—Sulfite de sodium anhydre Merck p.a.: solution aqueuse à 0,8% renouvelée par préparation tous les 2 jours.

—Mousse de palladium à 99,9%.

—Solution titrée de palladium à 0,100 mg/ml: introduire dans un micromatras 100 mg de mousse de palladium, 1 ml d'acide chlorhydrique (p.s. = 1,19) et 1 ml d'acide nitrique

Tableau 1. Attaques par voie humide

*E**	*m**	Type de substances analysées	Opérations successives effectuées en micromatras
Ti	0,5 à 5	Substances organiques	0,8 ml H_2SO_4 + 3 à 4 gouttes HNO_3; Eb* = 15; 2 fois 2 à 3 gouttes HNO_3; Eb = 15 + 15; 3 fois 3 à 4 gouttes H_2O_2; Eb = 15 + 15 + 30; 1,5 ml H_2O bouillante; Eb = 0.
	1 à 3	Substances inorganiques (nitrures, borures et boronitrures de titane...)	0,8 ml HNO_3 + 3 à 4 gouttes H_2O_2; Eb = 10; 0,8 ml H_2SO_4 + 3 à 4 gouttes H_2O_2; Eb = 15; 3 fois 3 à 4 gouttes H_2O_2; Eb = 15 + 15 + 15; 1,5 ml H_2O; Eb = 20.
Pt et Pd	1 à 5	Substances organiques	0,8 ml H_2SO_4 + 3 à 4 gouttes HNO_3; Eb = 15; 2 fois 2 à 3 gouttes HNO_3; Eb = 15 + 15; 2 fois 0,7 ml HCl; Eb = 8 + 10 1 ml HCl; Eb = 0.
Mo	1 à 3	Substances organiques et quelques substances inorganiques (produits de recherche)	*cf.* Titane "organique".
P	0,4 à 5	Substances organiques	*cf.* Titane "organique"

* Signification des symboles.

E: Elément dosé.

m: Masse du prélèvement analytique en mg.

Eb: Durées d'ébullition exprimées en minutes; ces durées sont données à titre indicatif; les vapeurs nitreuses doivent être totalement chassées lors de la dernière addition d'acide chlorhydrique ou d'eau oxygénée; laisser refroidir après chaque ébullition (d'où l'intérêt d'un système de chauffage à faible inertie thermique). Eviter toute évaporation à sec.

(p.s. = 1,38). Porter à l'ébullition sur la rampe de minéralisation jusqu'à évaporation presque à sec. Laisser refroidir, introduire 1 ml d'acide chlorhydrique et faire bouillir jusqu'à ce que l'évaporation réduise le volume au 1/3 de sa valeur initiale. Recommencer l'opération 2 ou 3 fois jusqu'à disparition complète des vapeurs nitreuses. Transvaser le contenu du matras dans une fiole jaugée de 1 litre et ajuster avec de l'eau.

—Solution titrée de palladium à 0,010 mg/ml: diluer avec de l'eau une partie de la solution précédente.

Molybdène

Attaque. Mêmes réactifs que ceux utilisés pour le titane. *Colorimétrie.* Acide chlorhydrique (p.s. = 1,19).

—Iodure de potassium: solution aqueuse à 4% renouvelée par préparation quotidienne.

—Thiocyanate de potassium: solution aqueuse à 12%.

—Sulfite de sodium anhydre Merck p.a.: solution aqueuse à 1% renouvelée par préparation tous les 2 jours.

—Solution titrée de molybdène à 0,100 mg/ml: peser 0,1840 g de molybdate d'ammonium $(NH_4)_6Mo_7O_{24}.4H_2O$ et ajuster à un litre avec de l'eau.

Phosphore

Attaque et colorimétrie. Mêmes réactifs pour les prélèvements décimilligrammiques que ceux antérieurement décrits pour le niveau milligrammique[1] et pesages sans problèmes sur une ultramicrobalance grâce au transvase-

Tableau 2. Colorimetrie

*E**	*F, ml*	*f, ml*	*P, mg*	*DO**	e,* *cm*	λ,* *nm*	*t**	*R**
Ti[10a à 13]	25, 50 ou 100	50	0,01 à 0,09	0,1 à 0,9	2	410	≥12 h	Acide oxalique:[13] 1 ml
			0,09 à 0,18	0,45 à 0,9	1			*A* ml Ajuster à pH 4–5 (NH_3 13*M* et 7*M*, H_2SO_4 3,5*M*) *V* = 35 ml Tampon: 5 ml Tiron: 5 ml H_2O
Pt[14 à 16]	25, 50 ou 100	50	0,02 à 0,40	0,03 à 0,7	2	406	≥45 mn	*A* ml HCl 6*M*: 15 ml *V* = 40 ml Chlorure stanneux: 5 ml H_2O
Pd[17,18]	25, 50 ou 100	50	0,015 à 0,15	0,06 à 0,6	2	408	≥45 mn	*A* ml
			0,15 à 0,25	0,3 à 0,5	1			*w* ml HCl 6*M*: 2 ml *V* = 40 ml Iodure de potassium: 5 ml Sulfite de sodium: 2 ml H_2O
Mo[10b]		100	0,03 à 0,4	0,06 à 0,8	2	475	2 h 30 mn	*A* ml
			0,4 à 0,8	0,4 à 0,8	1			*w* ml Iodure de potassium: 5 ml Thiocyanate de potassium: 10 ml HCl 6*M*: 50 ml Sulfite de sodium: 1 ml H_2O
P[1,19]		200	0,1 à 1	0,07 à 0,7	2	410	≥30 mn	*A* ml H_2SO_4 18*M*: 2,8 ml (2 ml seulement pour les solutions inconnues) *V* = 170 ml Laisser refroidir Molybdate d'ammonium: 10 ml Métavanadate d'ammonium: 10 ml H_2O
P		50	0,02 à 0,3	0,06 à 0,9	2	410	≥30 mn	*A* ml *w* ml Molybdate d'ammonium: 2 ml Métavanadate d'ammonium: 2 ml H_2O

* Significations des symboles non définis dans le texte:

E: élément dosé.

F: capacité de la fiole dans laquelle est dilué le contenu du matras dans le cas de prélèvements aliquotes.

f: capacité de la fiole jaugée utilisée pour la colorimétrie.

P: masse d'élément à doser.

DO: absorbance.

e: épaisseur de la cuve de colorimétrie.

λ: longueur d'onde à laquelle est effectuée la mesure.

t: temps d'attente avant la lecture de l'absorbance sur le spectrophotomètre.

R: réactifs.

V: volume approximatif de solution à obtenir après addition d'eau.

Tableau 3. Exemples de résultats

			Teneur en élément, %*		
E	Composé	m, mg	x_i	x	T
Ti	Dichlorure de titanocène	2,863	19,2		19,24
		3,415	19,3		—
		2,239	19,1	19,3	—
		5,204	19,5		—
		2,023	19,2		—
	Diborure de titane	1,280	69,5		68,99
		1,170	69,1		—
		1,650	69,3	69,2	—
		2.940	68,4		—
		1,750	69,7		—
Pt	Acétylacétonate de platine	4,525	50,0		49,60
		3,969	49,3		—
		3,447	49,1	49,5	—
		3,106	49,6		—
		2,138	49,6		—
	Produit de recherche A	2,520	23,8		23,55
		1,470	23,4		—
		1,446	23,3	23,4	—
		0,914	23,1		—
		0,859	23,3		—
Pd	Acétylacétonate de palladium	4,015	34,7		34,93
		2,583	35,2		—
		4,623	35,4	35,0	—
		3,498	35,1		—
		3,024	34,7		—
	Produit de recherche B	3,453	17,4		17,44
		3,896	17,3		—
		2,500	17,3	17,4	—
		2,468	17,6		—
		2,727	17,5		—
Mo	Acétylacétonate de molybdényle	2,139	29,4		29,41
		1,455	29,8		—
		1,035	29,2	29,5	—
		2,097	29,3		—
		2,325	29,7		—
	Composé de recherche C	2,704	26,0		25,78
		2,831	25,9		—
		3,196	25,5		—
		2,329	25,9	25,8	—
		2,668	25,8		—
P	Triphénylphosphine	4,133	11,9		11,81
		4,822	11,9		—
		0,398	11,8		—
		0,436	11,8		—
		0,970	11,6	11,8	—
		0,870	12,0		—
		0,830	11,8		—

x_i: Résultats trouvés.
x: Moyenne des résultats trouvés.
T: Teneur calculée.

ment dans le matras à l'aide d'une micronacelle de platine (*cf.* au dessus) ou à l'emploi de sachets de terphane.

Attaques par voie humide

Diverses méthodes sont mises en oeuvre selon l'élément à doser, elles sont réparties dans le tableau 1.

Colorimetrie

Les conditions de la colorimétrie sont indiquées dans le tableau 2, mais il reste toujours possible de modifier la capacité de la fiole utilisée pour la colorimétrie sous réserve de modifier également les volumes des réactifs qui y sont introduits. Les réactifs sont introduits dans la fiole jaugée de capacité f dans l'ordre indiqué dans la colonne R de ce tableau. Trois sortes de solutions sont ainsi préparées de façon similaire: solutions inconnues, solutions étalons, solutions d'essai à blanc.

Toutefois, introduire dans la fiole de colorimétrie

—*dans les cas des solutions inconnues*

(1) soit le volume total $A = s$ de la solution d'attaque, soit lors de prélèvements de parties aliquotes des volumes $A = a_1 \ldots A = a_i \ldots A = a_n$ de solution d'attaque avec $a_1 > \ldots > a_i \ldots > a_n$

(2) si nécessaire des volumes $w = s - s = 0$, $w = a_1 - a_1 = 0$, $w = a_1 - a_2 \ldots$, $w = a_1 - a_i \ldots w = a_1 - a_n$, de "blanc de solution d'attaque" selon que $A = s$, $A = a_1 \ldots$, $A = a_i \ldots$, $A = a_n$; lorsqu'il s'est avéré que l'influence des réactifs d'attaque est negligeable, on n'ajoute pas de "blancs de solution" dans les fioles de colorimétrie ($w = 0$ dans tous les cas), qu'il s'agisse de solutions inconnues,

de solutions étalons ou d'essai à blanc,

—*dans les solutions étalons*

(1) un volume $A = v$ de solution titrée

(2) éventuellement un volume $w = a_1$ ou $w = s$ de "blanc de solution d'attaque" selon que l'on procède, ou non, au prélèvement de parties aliquotes,

—*dans les solutions d'essai à blanc*

si nécessaire, un volume $w = a_1$ ou $w = s$ de "blanc de solution d'attaque".

Calculs

Teneur centésimale en élément E:

$$x\% = \frac{P \times F \times 100}{m \times a_i}$$

avec

$$P = \frac{p \times D}{(d' + d'' + d''')/3}$$

Lorsqu'il n'est pas procédé au prélèvement de parties aliquotes, la formule s'écrit plus simplement

$$x\% = \frac{P \times 100}{m}$$

RESULTATS ET DISCUSSION

Quelques résultats représentatifs de la méthode sont reportés dans le tableau 3.

Nous avons étudié l'influence de la présence simultanée d'éléments gênant le dosage de l'élément considéré, dans les produits soumis à l'analyse, au fur et à mesure que les problèmes se sont présentés; leurs listes reportées, ci-après, ne sont donc pas exhaustives. Les teneurs en éléments gênants sont de l'ordre de grandeur de quelques dixièmes de milligrammes pour 1 ou 2 mg de prélèvement analytique.

Dosage du titane

As, B, Br, Cl, Co, Cu, F, Hg, K, N, Na, P, Pt, S, Sb, Se, Sn ne gênent pa (*cf.* également Yoe[11] et Clark[13]). Ba ne gêne plus après filtration préalable de la solution d'attaque. Fe, I, Mo, Pd gênent.

Dosage du platine

Al, Br, Cl, Fe, K, N, Na, Ni, P, S, Ti ne gênent pas. Cs, Pd et Rb gênent.

Dosage du palladium

As, B, Br, Cl, I, Mo, N, P, S, Sn, Ti ne gênent pas. Se gêne.

Dosage du molybdène

As, B, Br, Cl, Cs, F, Hg, I, K, N, Na, P, S, Sb, Sn ne gênent pas. Ag, Pd, Pt, Se gênent. Si ne gêne plus après filtration en vue d'éliminer le précipité qui apparait lors de la dilution du contenu du matras.

Dosage du phosphore

Ag, B, Br, Ca, Cd, Ce, Cl, Co, Cu, F, Fe, Ga, Hg, I, K, La, Li, Mg, Mo, N, Na, Nd, Ni, Pb, Re, S, Sb, Se, Sn, Te, Th, Ti, V, Zn ne gênent pas. Ba, Ru ne gênent plus après filtration préalable de la solution d'attaque.

Ir gêne mais Ge et W ne gênent pas dans tous les cas; l'influence de leur présence dépend vraisemblablement de la forme moléculaire sous laquelle ils passent en solution qui dépend elle-même des compositions et structures des composés soumis à l'analyse.

En présence de Pd, Pt, Rh, la solution d'attaque est colorée en jaune ce qui conduit à l'obtention de résultats légèrement erronés par excès. Il est cependant possible de leur apporter une correction, fonction de la teneur en Pd, Pt, Rh; c'est ainsi que la présence de 0,6 mg de Pd, Pt ou Rh donne lieu à des corrections négatives respectives correspondant à 0,014, 0,004 et 0,007 mg de phosphore. Ces corrections étant faibles, il suffit de connaître approximativement la teneur en Pd, Pt ou Rh pour les calculer.

L'effet gênant de Si est éliminé (après filtration éventuelle de la solution d'attaque) comme l'indique Charlot[10c] en effectuant la colorimétrie en milieu acide nitrique (remplacer 2 ml de H_2SO_4 18M par 12 ml de HNO_3 13M lors de l'emploi de fioles de 200 ml) et en effectuant la lecture d'absorbance à une longueur d'onde de 420 nm au lieu de 410 nm; la loi de Lambert–Beer est alors un peu moins suivie.

L'effet gênant de As est éliminé en ajoutant au contenu du matras après attaque 2 ml d'eau, environ 100 mg de bromure de potassium[20] p.a. et en portant à l'ébullition pour bien concentrer le liquide. Ce liquide doit être incolore et le col du matras clair (le chauffer légèrement, à cette fin, si nécessaire, avec un bec Bunsen*).

CONCLUSION

Les méthodes spectrophotométriques, associées à une attaque par voie humide des composés à analyser sont faciles à mettre en oeuvre et susceptibles de s'appliquer aux microdosages d'un grand nombre d'éléments, dans les substances organiques et certaines substances inorganiques, non seulement sur des prélèvement milligrammiques mais souvent, également, décimilligrammiques. Elles rendent donc de précieux services, dans les laboratoires de microanalyse, du fait de la tendance actuelle à la diversification croissante des dosages élémentaires qui leur sont demandés.

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SHORT COMMUNICATIONS

COMPUTER CALCULATION OF DISTRIBUTION DIAGRAMS

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To study equilibria in solutions containing several metals and ligands, we must know the concentrations of the various species. Generally, as the formation of the complexes is a function of acidity, a convenient way of representing the distribution of species is to plot the function $\alpha_j = f(\mathrm{pH})$, where α_j indicates the degree of formation of the *j*th species. If the formation constants of all the species and the analytical concentrations of the various components (metals and ligands) are known, they can be used to calculate distribution diagrams, which will (*a*) facilitate choice of experimental conditions for obtaining better values for the formation constants, (*b*) give the pH for maximum formation of certain species, (*c*) indicate which complexes are formed to a negligible extent.

In the last ten years various programs have been published for dealing with equilibrium systems; the most important are HALTAFALL[1], COMICS[2] and EQUIL.[3] HALTAFALL and COMICS use simple iterative methods, and EQUIL uses the Newton–Raphson method. As a rule the Newton–Raphson method is preferable as it requires fewer iterations; on the other hand, each of its iterations requires a longer calculation time, the program is more complicated and therefore requires more computer memory space, and finally, the program sometimes diverges more easily than other iterative methods.

We have developed a practical and simple program (DISDI) for obtaining quickly the distribution diagrams of systems containing up to one metal and two ligands, producing various species in equilibrium.

METHOD

The mass balance equations for the most complex case are

$$\mathrm{M} = \mathrm{m} + \textstyle\sum p\, \beta_{pqrs}\, \mathrm{m}^p\, \mathrm{a}^q\, \mathrm{b}^r\, \mathrm{h}^s$$

$$\mathrm{A} = \mathrm{a} + \textstyle\sum q\, \beta_{pqrs}\, \mathrm{m}^p\, \mathrm{a}^q\, \mathrm{b}^r\, \mathrm{h}^s$$

$$\mathrm{B} = \mathrm{b} + \textstyle\sum r\, \beta_{pqrs}\, \mathrm{m}^p\, \mathrm{a}^q\, \mathrm{b}^r\, \mathrm{h}^s$$

$$\mathrm{H} = \mathrm{h} + \textstyle\sum s\, \beta_{pqrs}\, \mathrm{m}^p\, \mathrm{a}^q\, \mathrm{b}^r\, \mathrm{h}^s$$

where M, A, B and H are the analytical concentrations of the metal, the two ligands and the hydrogen ions respectively, and the small letters indicate the free concentrations of these species.

All iterative methods require an initial guess. Starting at low pH, where we can assume that there is little formation of complexes, we have

$$\mathrm{m}^0 = \mathrm{M}$$

$$\mathrm{a}^0 = \mathrm{A}/(1 + \textstyle\sum \beta_s^{\mathrm{H}}\, \mathrm{h}^s)$$

$$\mathrm{b}^0 = \mathrm{B}/(1 + \textstyle\sum \beta_s^{\mathrm{H}}\, \mathrm{h}^s)$$

where the β_s^{H} terms represent the protonation oconstants of the two ligands. Successive approximations are obtained by means of these equations:

$$\mathrm{m}_i = \mathrm{m}_{i-1}\, (\mathrm{M}/\mathrm{M}_{\mathrm{calc}} + 1)/2$$

$$\mathrm{a}_i = \mathrm{a}_{i-1}\, (\mathrm{A}/\mathrm{A}_{\mathrm{calc}} + 1)/2$$

$$\mathrm{b}_i = \mathrm{b}_{i-1}\, (\mathrm{B}/\mathrm{B}_{\mathrm{calc}} + 1)/2$$

This iterative method is similar to the one used by Perrin and Sayce for the program COMICS $[\mathrm{m}_i = \mathrm{m}_{i-1}\, (\mathrm{M}/\mathrm{M}_{\mathrm{calc}})^{1/2};\ x \sim (x+1)/2 \text{ if } x \sim 1]$. For successive points, we generally use the preceding value of the free concentration as the initial value:

$$\mathrm{m}_k^0 = \mathrm{m}_{k-1};\ \mathrm{a}_k^0 = \mathrm{a}_{k-1};\ \mathrm{b}_k^0 = \mathrm{b}_{k-1}$$

If we consider, on the other hand, that $\mathrm{m} = g_{\mathrm{m}}(\mathrm{pH})$, $\mathrm{a} = g_{\mathrm{a}}(\mathrm{pH})$ and $\mathrm{b} = g_{\mathrm{b}}(\mathrm{pH})$ are monotonic continuous functions†, we can apply a simple method of interpolation to obtain an approximate value of m_k^0 (and analogously for a_k^0 and b_k^0):

$$\mathrm{m}_k^0 = \mathrm{m}_{k-1} - (\mathrm{m}_{k-2} = \mathrm{m}_{k-1})RW$$

$$R = (\mathrm{pH}_{k-1} - \mathrm{pH}_k)/(\mathrm{pH}_{k-2} - \mathrm{pH}_{k-1})$$

If the pH intervals are kept constant ($R = 1$), we can simplify the equation to:

$$\mathrm{m}_k^0 = \mathrm{m}_{k-1} - (\mathrm{m}_{k-2} - \mathrm{m}_{k-1})W$$

where W is a correction factor for non-linear functions. We should take a different W for every point, but in practice we obtain a good approximation by giving W a value of 0·85.

RESULTS

The program has been written in FORTRAN IV in two versions. In the first, DISDI, it calculates the concentrations of all the species present over a given pH range, starting from the analytical concentrations of the components, the formation constants, the initial pH, the pH increments and the pH range, and prints them in tabular form together with the degree of formation $\alpha_j = C_j/\mathrm{M}$ (for the species containing the metal) and $\alpha_j = C_j/\mathrm{A}$ or $\alpha_j = C_j/\mathrm{B}$ (for the species that do not contain the metal). The second, DISDI*, besides doing the same as DISDI, prints out the distribution diagram. To show species

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† A function $y = f(x)$ is said to be monotonic in a certain range if, as x increases within this range, the change of y is always of the same sign, or zero, but not positive in one part of the range and negative in another.

Table 1. Some characteristics of the programs COMICS, EQUIL, DISDI and DISDI* used on a CDC 6600 computer

Program	S	Tco	Tca	M	D	M-D
COMICS	176	1·2	170	19·2	9·6	9·6
EQUIL	429	2·6	80–190	14·8	4·1	9·6
DISDI	154	1·2	100	9·3	0·3	9·0
DISDI*	237	1·6	135	17·0	7·6	9·4

S: number of cards. For the program COMICS and EQUIL there is a little difference from the original number, but only in the data input.

Tco: compilation time, *sec.*

Tca: calculation time referred to the program DISDI (= 100).

M: total number of memories (K storage locations) required for the programs in the version used.

D: total number of memories required by dimensions assigned to the variables.

M − D: difference between the total memories and those required by dimensions assigned to the variables. This parameter is more significant than either D or M because the dimensions can be easily varied according to the requirements of the program user.

formed in a minor or negligible quantity, a graph of log $\alpha = f(\mathrm{pH})$ can also be printed.

These two programs have been applied to more than 30 different systems and have never shown any convergence problem. They have also been compared with COMICS and EQUIL. DISDI used many fewer iterations than COMICS for most of the points, and although EQUIL converged faster, the calculation time was not lower. Table 1 gives some data for DISDI, DISDI*, COMICS and EQUIL.

In testing the program DISDI*, the dimensions used for the distribution diagrams were 32 × 23 cm, but were later reduced to 25 × 17 cm, which is sufficient in most cases. If the iterative process is stopped when the differences $M - M_{\mathrm{calc}}$, $A - A_{\mathrm{calc}}$ and $B - B_{\mathrm{calc}}$ are less than 0·01% (and not 0·001% as for the data reported in Table 1) the number of iterations and hence the calculation time is reduced by 20–60%, with a difference of 0·001, at most, in $-\log C_j$.

DISDI is simple to use, does not greatly encumber the computer memory and is rapid. The more complex version, DISDI*, has the advantage of giving immediate representation of the species distribution in the system considered.

The complete listing of the program DISDI* is available from the authors on request.

Acknowledgements—We thank Dr. C. Rigano for the valuable advice he has given us in developing the programs, and the C.N.R. for financial support.

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DETERMINATION OF IRON IN SILICATE ROCKS BY SUBSTOICHIOMETRIC RADIOISOTOPE DILUTION ANALYSIS

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(*Received* 5 *February* 1975. *Accepted* 16 *April* 1975)

Although substoichiometric isotope dilution analysis is considered most useful at trace element levels, it can also be advantageously used for the precise determination of major components.[1] This is so because the two most important factors for the overall precision of such a method, *i.e.*, the reproducibility of the substoichiometric separation and the counting statistics, may both be kept at a very low variablity where relatively large amounts of an element are to be determined. In a previous work by the authors[2] it was shown that the determination of iron in biological reference materials could be carried out with high precision at the concentration levels concerned. It was decided to see whether a similar method could be used for the determination of the total concentration of iron in rocks with satisfactory precision and accuracy.

The method for biological material is based on wet-ashing of the sample with nitric acid and sulphuric acid and subsequent extraction of iron from $3M$ sodium chloride medium and back-extraction with dilute nitric acid. A procedure similar to that of Starý and Růžička[3] is then followed. A substoichiometric amount of EDTA is added, and the solution is applied to a cation-exchange column, where the excess of iron is retained, while the Fe(III)–EDTA complex passes through quantitatively.

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The method for biological material is based on wet-ashing of the sample with nitric acid and sulphuric acid and subsequent extraction of iron from 3*M* sodium chloride medium and back-extraction with dilute nitric acid. A procedure similar to that of Starý and Růžička[3] is then followed. A substoichiometric amount of EDTA is added, and the solution is applied to a cation-exchange column, where the excess of iron is retained, while the Fe(III)–EDTA complex passes through quantitatively.

Table 1. Concentration of iron in five U.S. Geological Survey standard rocks, determined by substoichiometric radioisotope dilution (% Fe)

	Andesite AGV-1	Basalt BCR-1	Granite G-2	Granodiorite GSP-1	Diabase W-1
	4·71	9·30	1·89	3·00	7·78
	4·71	9·39	1·90	2·95	7·80
	4·72	9·28	1·91	3·01	7·83
	4·71	9·43	1·88	3·00	7·87
	4·79	9·31	1·95	3·00	7·80
	4·81	9·32	1·92	3·01	7·85
Mean value	4·74	9·34	1·91	3·00	7·82
Relative standard deviation, %	0·97	0·62	1·26	0·78	0·45
Expressed as % Fe_2O_3	6·78	13·35	2·73	4·29	11·18
Johansen and Steinnes,[4] neutron activation	6·75	13·40	2·65	4·31	11·12
Fleischer,[5] recommended value					11·09
Flanagan,[6] average value	6·80	13·51	2·77	4·33	

After some preliminary experiments it appeared that the method, with some small modifications, could be applied to the determination of total iron in rocks after hydrofluoric acid dissolution of the sample.

EXPERIMENTAL

Apparatus

Counting equipment. A scintillation counter with a 75 × 75 mm NaI(Tl) crystal.

Cation-exchange columns. Tubes of 12 mm internal diameter filled with Dowex 50W-X8, 100–200 mesh, Na^+-form, to give a 50-mm height of resin bed. The column is prepared by treating the resin in the H^+-form with an excess of 1*M* sodium hydroxide and washing with water until the eluate is neutral.

Reagents

The reagents used were *pro analysi* grade.

EDTA solution. Prepared by dissolving the disodium salt of EDTA in water. The solution was standardized against Fe(III) solutions of known concentration, according to the substoichiometric procedure given below.

^{59}Fe tracer. A solution of specific activity 3000 mCi/g was diluted with 0·1 M hydrochloric acid to a concentration of about 1μCi/ml.

Boric acid solution, 30 *mg/ml.*

Procedure

Weigh accurately about 50 mg of finely divided rock powder into a 100-ml Teflon beaker. Add 10 ml of concentrated hydrofluoric acid, 2 ml of concentrated nitric acid and 1·00 ml of ^{59}Fe tracer solution. Evaporate the mixture to complete dryness on a hot-plate. Then add 5 ml of 6*M* hydrochloric acid and 1 ml of boric acid solution and evaporate to dryness again. Dissolve the residue in 5 drops of concentrated nitric acid and 15 ml of 4*M* sodium chloride, then extract with 15 ml of isopropyl methyl ketone. Back-extract the iron with 15 ml of 0·01*M* nitric acid. To the resulting solution add a known volume of EDTA solution corresponding stoichiometrically to an amount of iron (y) which is about 60% of the estimated amount of iron in the sample (1 molecule of EDTA corresponds to 1 atom of Fe).

Allow the solution to stand for 10–15 min at 30–40°, and then pass it through the cation-exchange column (flow-rate about 0·5 ml/min), taking care to transfer the solution quantitatively to the column. Wash the column with two 5-ml portions of water. Measure the activity of the combined eluates (A_s) with the scintillation counter, and the activity of 1·00 ml of ^{59}Fe tracer solution diluted to the same volume (activity A_r). Calculate the amount of iron (x) present in the sample from the relationship $x = y\,A_r/A_s$.

The reagent blank, determined in the same way as described above, was found to be insignificant when working in the concentration range in question.

RESULTS AND DISCUSSION

The method was tested on five U.S. Geological Survey standard rocks with composition ranging from basaltic to granitic and with iron contents in the range 1·9–9·3%. These standard rocks have been analysed in many laboratories by a variety of analytical techniques, and their iron contents can be assumed to be well known. Before this work the same rocks were analysed in the authors' laboratory by a radiochemical neutron-activation method[4] assumed to yield results of high accuracy. A comparison of the results obtained by substoichiometric isotope dilution with the literature values is given in Table 1. The agreement with the recommended values is within 1·5% relative in all cases. A similarly good agreement is evident with the work of Johansen and Steinnes,[4] except in the case of G-2 where the neutron-activation values seem to be about 3–4% low.

The good agreement with the literature values seems to indicate that no significant systematic errors were present in the analyses. The relative standard deviation is about 0·5–1% for iron contents exceeding 3%. This implies that the quality of data obtained by the substoichiometric isotope dilution method described in this work would be as good as that of most data produced by the conventional methods of rock analysis. The present method may not be well suited for routine analyses, but could be a useful supplement in cases where the results obtained by other methods are to be checked.

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Summary—Iron is determined in rocks by an isotope dilution method involving dissolution with hydrofluoric acid, extraction of iron(III) chloride into isopropyl methyl ketone, stripping with dilute nitric acid, and substoichiometric separation of the Fe–EDTA complex on a cation-exchange column. The precision and accuracy are 1·5% relative or better, as indicated by analyses of some U.S. Geological Survey standard rocks.

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SEQUENTIAL DETERMINATION OF THORIUM AND RARE EARTHS WITH EDTA AND KOJIC ACID

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The significant differences in the stabilities of the EDTA complexes of thorium and the rare earth metals can, in principle, be exploited for sequential determination of these ions. Thorium can be conveniently titrated at pH 2·0 followed by the rare earths at pH 5·5. Such a procedure, however, meets with difficulty in practice. The indicator suitable for this pH range is Xylenol Orange (XO). The free indicator is lemon-yellow and its complexes red-violet. After the initial titration of thorium, however, the Th-EDTA complex produces a pink colour when the pH is raised to 5·5, thus making titration of the rare earths impossible. Přibil and Veselý[1] ascribed this colour to the formation of a ternary complex Th–EDTA–XO and suggested the use of excess of acetylacetone to prevent its formation so that the rare earths could be titrated. We have found kojic acid to be a similar masking agent for this purpose and its use is described in this note. Though the use of ligands such as DTPA or TTHA obviates the need for such a masking agent, the ready availability of EDTA makes its use still attractive.

EXPERIMENTAL

Reagents

Rare earth solutions. Rare earth metal oxides (purity $\geqslant$ 99·9%) were dissolved in nitric acid and the solutions standardized by EDTA titration with hexamine as buffer and XO as indicator.

Thorium solution. Thorium nitrate ($\geqslant$99·9%) was dissolved and the solution standardized with EDTA.

Xylenol Orange. A freshly prepared 0·5% solution of sodium salt in water.

Kojic acid. The BDH (biochemical grade) product was recrystallized from alcohol (with animal charcoal added) to give buff needles.

All other reagents were analytical grade.

Procedure

Dilute the sample solution containing about 10 mg of thorium and 50–60 mg of rare earth metals to about 200 ml and adjust the pH to 1·9–2·0 with ammonia or nitric acid, using a pH-meter. Add a few drops of XO and titrate slowly with 0·05*M* EDTA till the colour changes from pink to lemon-yellow. Add kojic acid (solid) equivalent to about ten times the thorium content and stir well to dissolve it. Raise the pH to 5·5 (pH paper) with a saturated solution of hexamine. Titrate further with 0·05*M* EDTA till the pink colour again completely changes to yellow.

Analysis of monazite. Isolate thorium and rare earth metals from the sample as oxalates by the method of Schoeller and Powell.[2] Carefully ignite to the oxides at 650–700°, dissolve these in hydrochloric acid (to keep cerium in the 3+ state) and make up to standard volume. Titrate a suitable aliquot as above.

RESULTS AND DISCUSSION

Our potentiometric studies on mixed-ligand chelates of thorium have revealed that kojic acid forms a colourless ternary complex with Th–EDTA at a pH as low as 4·5, and can be used to suppress the formation of the pink Th–EDTA–XO chelate. If kojic acid is added after the first end-point, sequential titrations of mixtures containing different amount of Th^{4+} and Ln^{3+} can be successfully accomplished (Table 1).

The advantage of kojic acid over acetylacetone is its higher solubility in water and thus it can be used for higher concentrations of thorium. The colour change is quite sharp and no heating is necessary as in the case of acetylacetone. However, the heavier rare earths, if present in amounts higher than that of thorium, have been found to interfere in the thorium determination. The method has been found to work successfully for monazite, which mainly contains lanthanum, cerium, neodymium and praseodymium, the validity being established by titration of a second aliquot of solution with DTPA for comparison.

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The advantage of kojic acid over acetylacetone is its higher solubility in water and thus it can be used for higher concentrations of thorium. The colour change is quite sharp and no heating is necessary as in the case of acetylacetone. However, the heavier rare earths, if present in amounts higher than that of thorium, have been found to interfere in the thorium determination. The method has been found to work successfully for monazite, which mainly contains lanthanum, cerium, neodymium and praseodymium, the validity being established by titration of a second aliquot of solution with DTPA for comparison.

Acknowledgement—Our thanks are due to Dr M. Sankar Das, Head, Analytical Chemistry Division, for his help and keen interest in the work.

Table 1. Determination of thorium and rare earths in synthetic mixtures and monazite

Taken		Found		Difference	
Th	R.E.	Th	R.E.	Th	R.E.
12·91	22·7$_9$(La)	12·91	22·7$_5$	—	−0·0$_4$
51·6$_4$	45·5$_8$(La)	51·7$_6$	45·7$_2$	+0·1$_2$	+0·1$_4$
123·5	—	123·5*	—	—	—
12·91	36·1$_4$(Ce)	12·91	36·14	—	—
12·91	31·5$_0$(Pr)	12·91	31·5$_0$	—	—
12·91	47·2$_5$(Pr)	13·06	47·5$_5$	+0·1$_5$	+0·3$_0$
12·91	30·4$_7$(Nd)	13·06	30·4$_8$	+0·1$_5$	+0·0$_1$
78·4$_2$	15·60(Nd)	78·4$_2$	15·67	—	+0·0$_7$
13·07	35·4$_0$(Sm)	13·07	35·4$_0$	—	—
7·82	74·1$_8$(La)	7·95	74·0$_5$	+0·13	−0·1$_3$
Monazite		6·86%	43·5$_5$%†	(DTPA method)	
		6·86%	43·6$_5$%	(Present method)	

* After titration, kojic acid was added and pH raised to 5·50. No pink colour appeared.

† Rare earth mixture as in monazite (La–22·7$_6$ mg Ce–36·4$_0$ mg, Pr–3·68 Nd–11·06 mg) expressed as La.

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2. W. R. Schoeller and A. R. Powell, Analysis of Minerals and Ores of the Rarer Elements, p. 110. Griffin, London, 1955.

Summary—Kojic acid can be used instead of acetylacetone to form a ternary complex with Th–EDTA that is more stable than the corresponding Xylenol Orange ternary complex, thus making it possible to titrate lanthanides with EDTA at pH 5·5 after titration of thorium at pH 2.

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THE CHALCOCITE COPPER MEMBRANE ELECTRODE

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(*Received* 18 *December* 1974. *Accepted* 30 *April* 1975)

Copper-sensitive membrane electrodes have been used several times recently as potentiometric sensors in complexometric titrations,[1–12] both of copper ions, and of other metals with copper as the indicator ion. Several electrodes are at present commercially available. In our studies a new type of electrode has been used, in which a single crystal of chalcocite—a copper(I) sulphide—has been employed as the membrane.

EXPERIMENTAL

Reagents and apparatus

A Radiometer PHM 26 pH meter was used for potential measurements, and a Radelkis OP-206 pH meter for pH measurements. A Metrohm Multidosimat E 415-10 G was used for the titrations. A Radiometer K 401 saturated calomel electrode was used as the reference electrode. The indicator electrode was made by mounting a 1-mm thick crystalline plate, 5 mm in diameter, at the end of a glass tube, by means of silicone rubber. An Ag/AgCl electrode was immersed in the internal solution containing copper(II) chloride.

All reagents were of analytical grade, except tetraethylenepentamine (TETREN) (Koch–Light) which was further purified.[13] Solutions were prepared with twice-distilled water. The copper(I) solutions were prepared from CuCl and the Cu(I)/Cu(II) ratio was determined by redox potential measurement.

The numerical calculations were carried out on the GIER computer of the Dept. of Numerical Calculations of this University.

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Table 1. Determination of thorium and rare earths in synthetic mixtures and monazite

Taken		Found		Difference	
Th	R.E.	Th	R.E.	Th	R.E.
12·91	$22{\cdot}7_9$(La)	12·91	$22{\cdot}7_5$	—	$-0{\cdot}0_4$
$51{\cdot}6_4$	$45{\cdot}5_8$(La)	$51{\cdot}7_6$	$45{\cdot}7_2$	$+0{\cdot}1_2$	$+0{\cdot}1_4$
123·5	—	123·5*	—	—	—
12·91	$36{\cdot}1_4$(Ce)	12·91	36·14	—	—
12·91	$31{\cdot}5_0$(Pr)	12·91	$31{\cdot}5_0$	—	—
12·91	$47{\cdot}2_5$(Pr)	13·06	$47{\cdot}5_5$	$+0{\cdot}1_5$	$+0{\cdot}3_0$
12·91	$30{\cdot}4_7$(Nd)	13·06	$30{\cdot}4_8$	$+0{\cdot}1_5$	$+0{\cdot}0_1$
$78{\cdot}4_2$	15·60(Nd)	$78{\cdot}4_2$	15·67	—	$+0{\cdot}0_7$
13·07	$35{\cdot}4_0$(Sm)	13·07	$35{\cdot}4_0$	—	—
7·82	$74{\cdot}1_8$(La)	7·95	$74{\cdot}0_5$	+0·13	$-0{\cdot}1_3$
Monazite		6·86%	$43{\cdot}5_5$%†	(DTPA method)	
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* After titration, kojic acid was added and pH raised to 5·50. No pink colour appeared.

† Rare earth mixture as in monazite (La–$22{\cdot}7_6$ mg Ce–$36{\cdot}4_0$ mg, Pr–3·68 Nd–11·06 mg) expressed as La.

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EXPERIMENTAL

Reagents and apparatus

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All reagents were of analytical grade, except tetraethylenepentamine (TETREN) (Koch–Light) which was further purified.[13] Solutions were prepared with twice-distilled water. The copper(I) solutions were prepared from CuCl and the Cu(I)/Cu(II) ratio was determined by redox potential measurement.

The numerical calculations were carried out on the GIER computer of the Dept. of Numerical Calculations of this University.

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* Institute of Mathematical Machines, University of Warsaw.

RESULTS AND DISCUSSION

When calibrated in copper(II) solution prepared by successive dilution, a strictly Nernstian relationship with 29-mV slope was obtained down to pCu = 5. With the copper(II) ion buffers—the so called pCu buffers[14]—a linear plot was obtained over a much broader range, namely to below 10^{-20} M (Fig. 1). Buffers perfectly suitable for such purposes were obtained by varying the pH of a 10^{-3} M Cu^{2+} solution containing a fivefold amount of TETREN. The shape of the curve calculated by using the HALTAFALL program,[15] is in good overall agreement with the experimental results, but the position of the curve along the pCu axis depends significantly on the numerical values of the constants, which differ when taken from various references. This is especially severe at low pH values, where formation of protonated complexes makes the data less reliable.

Beside the dependence on the copper(II) ion activity, with a slope of about 29 mV per decade, a dependence on the activity of copper(I) ions has also been found, with a slope equal to 53 mV per decade. These results suggest that the following relationship holds for the copper electrode:

$$E = E^0 + \frac{RT}{F}\ln[a_{\mathrm{Cu}^+} + K_{\mathrm{Cu}^{2+},\mathrm{Cu}^+}(a_{\mathrm{Cu}^{2+}})^{1/2}] \qquad (1)$$

When

$$a_{\mathrm{Cu}^+} \ll K_{\mathrm{Cu}^{2+},\mathrm{Cu}^+}(a_{\mathrm{Cu}^{2+}})^{1/2} \qquad (2)$$

and

$$E^{0'} = E^0 + \frac{RT}{F}\ln K_{\mathrm{Cu}^{2+},\mathrm{Cu}^+} \qquad (3)$$

then an equation for the potential as a function of the activity of copper(II) ions can be obtained, having the form:

$$E = E^{0'} + \frac{RT}{2F}\ln a_{\mathrm{Cu}^{2+}} \qquad (4)$$

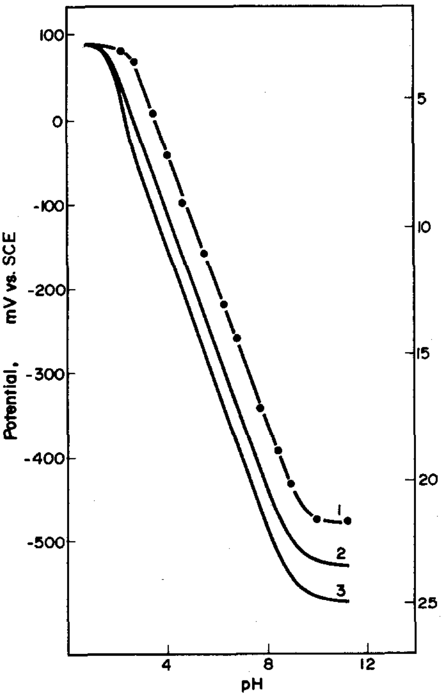

Fig. 1. Calibration curve for copper electrode in $10^{-3}M$ Cu, $5 \times 10^{-3}M$ TETREN, 0·1M $\mathrm{KNO_3}$. Curve 1—experimental, 2—theoretical acc. to Paoletti *et al.*,[20] 3—theoretical acc. to Ringbom.[21]

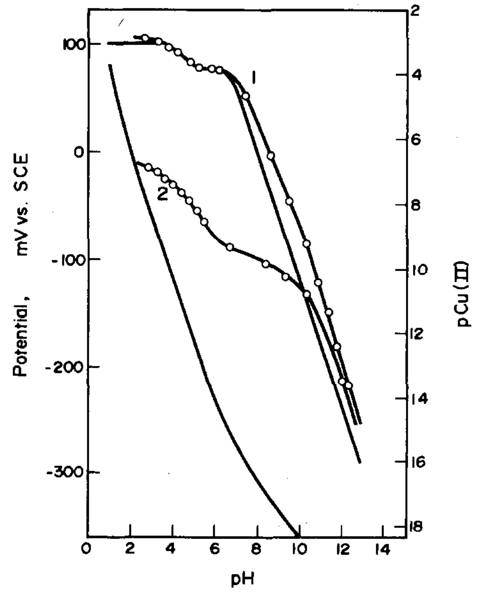

Fig. 2. Potential–pH diagram for copper electrode in 0·1M acetate buffer—curve 1 and for $10^{-3}M$ Cu–EDTA, $10^{-3}M$ EDTA solution—curve 2. The unprimed curves are experimental, the primed are calculated with the HALTAFALL program.

When the activity of copper(I) ions is relatively high, *i.e.*, of the order of 10^{-7}–10^{-8} M calculated on the basis of stability constants of the chloride complexes,[16] and the activity of copper(II) ions is as low as possible, the second term in the brackets in equation (1) may be neglected and the value of E^0 estimated. On the other hand from equation (4), in conditions when the copper(I) activity can be neglected, the value of $E^{0'}$ can be determined. Substituting these values into equation (3) gives the selectivity coefficient $K_{\mathrm{Cu}^{2+},\mathrm{Cu}^+}$ as $10^{-5.9}$. Using the Schmidt–Pungor procedure[17] and literature data[18,19] on the solubility products of $\mathrm{Cu_2S}$ and CuS one obtains a selectivity coefficient value of

$$K_{\mathrm{Cu}^{2+},\mathrm{Cu}^+} = \left(\frac{K_{\mathrm{so\,Cu_2S}}}{K_{\mathrm{so\,CuS}}}\right)^{1/2} = 10^{-6.6} \qquad (5)$$

which is in good agreement with our experimental findings.

In these experiments the effect of chloride ions on the response of the chalcocite electrode[21] is significantly low, most probably because the membrane does not contain $\mathrm{Ag_2S}$.

To establish the best conditions for the titration of copper with EDTA and TETREN in various buffers the potential *vs.* pH relationships were determined, by using different copper to titrant ratios. Such diagrams are shown in Fig. 2 for the acetate buffer. The experimental points are indicated by small circles, and the solid lines are calculated by the HALTAFALL program from published values for stability constants of Cu-EDTA complexes. Satisfactory agreement was obtained only in the absence of EDTA as a ligand. A similar discrepancy was found by Veselý[10] for the copper(I) selenide electrode, while Ross and Frant[1] and Hansen *et al.*,[4] who used the copper(II) sulphide membrane, did not mention such electrode response. Thus we can assume that the presence of copper(I) ions originating from the membrane is responsible for this behaviour. The experimental titration curve for copper(II) ions with EDTA in an acetate buffer (Fig. 3, curve 1), with the theoretical curve (curve 2) indicates that after the end-point an ion at constant activity must control the measured potential.

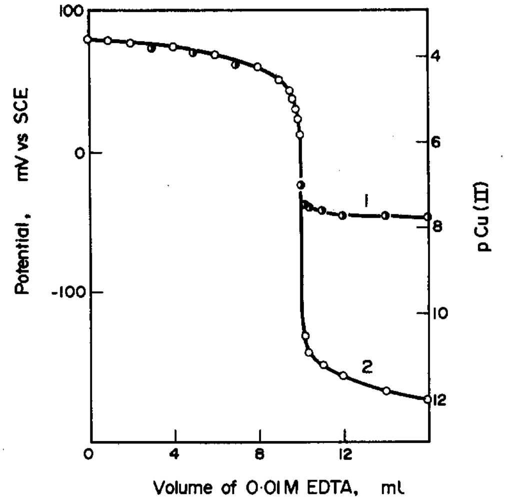

Fig. 3. Titration curves of $10^{-3}M$ Cu(II) with EDTA in 0·1M acetate buffer, pH 5. Curve 1—experimental, curve 2—theoretical.

Table 1. Complexometric titration of copper with the copper-sensitive electrode

Titrant	Buffer	pH	Copper, *mmole* Taken	Copper, *mmole* Found	Error, %
EDTA	Borate	9·2	0·1000	0·0999	−0·1
			0·1000	0·1003	+0·3
	Ammonia	9·0	0·1000	0·0999	−0·1
			0·1000	0·0999	−0·1
	Acetate	4·5	0·1000	0·1001	+0·1
			0·1000	0·1000	0
TETREN	Borate	9·2	0·0987	0·0987	0
			0·0987	0·0991	+0·4
			0·0973	0·0977	+0·4
	Ammonia	9·0	0·0987	0·0986	−0·1
			0·1104	0·1109	+0·5
	Acetate*	4·5	0·0973	0·0968	−0·5

*In presence of equimolar Al^{3+} and Fe^{3+}.

At the beginning of the titration ($f = 0$) the electrode potential (neglecting activity coefficients) is given by the equation:

$$E_{f=0} = E^0 + \frac{RT}{F}\ln[Cu^{2+}]^{1/2} K_{Cu^{2+},Cu^+} \qquad (6)$$

while after the end-point ($f = 2$), the copper(II) concentration is so strongly depressed that the potential should be described by the equation:

$$E_{f=2} = E^0 + \frac{RT}{F}\ln[Cu^+] \qquad (7)$$

Thus the total potential change in the titration is equal to:

$$\Delta E_{0,2} = E_{f=2} - E_{f=0} = 0{\cdot}059\log\frac{[Cu^+]}{[Cu^{2+}]^{1/2} K_{Cu^{2+},Cu^+}} \qquad (8)$$

When the potential change $\Delta E_{0,2}$ in a titration was measured, and the selectivity coefficient was assumed to be equal to $10^{-6{\cdot}6}$, the concentration of copper(I) ions was calculated to be $10^{-10{\cdot}6}M$, which corresponds to a potential of −35 mV *vs.* SCE. This is in good agreement with the potential found from the titration curve after the end-point ($f = 2$).

Such differences between experimental and calculated values were not observed when TETREN was used as titrant. In spite of the fact that none of the stability constants of the copper(I) complexes is known, it seems reasonable to assume that TETREN binds univalent copper much more strongly than does EDTA. When EDTA is used as titrant, however, an ammoniacal buffer is desirable, because of the strong tendency of ammonia to complex copper(I).

The experimental results from titrations with both titrants are presented in Table 1. They are relatively accurate and TETREN can also be used in the presence of other cations, such as iron or aluminium.

A similar decrease in the potential break at the end-point was also observed in EDTA titrations of other ions (Pb^{2+}, Zn^{2+}, Ca^{2+}) when copper was used only as the indicator ion. However in those cases the accuracy was

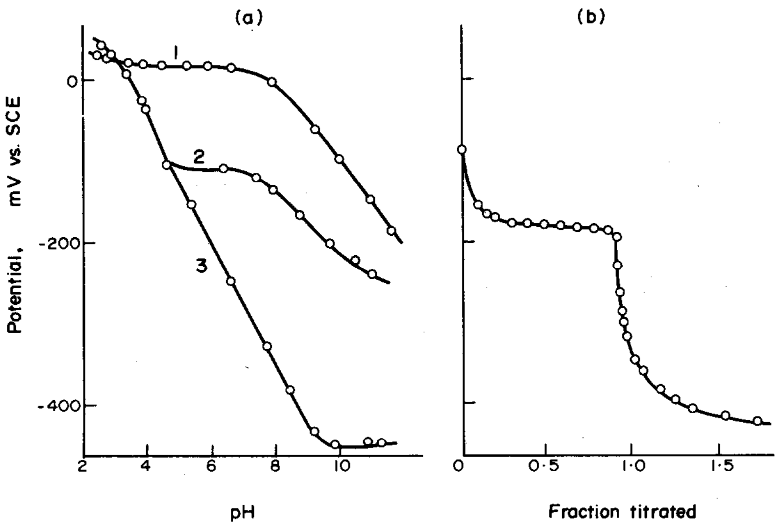

Fig. 4. (*a*) Potential–pH diagram for the copper electrode. Curve 1—$10^{-6}M$ $Cu(NO_3)_2$, curve 2—$10^{-6}M$ $Cu(NO_3)_2$. 5 × $10^{-4}M$ Zn–TETREN, 5 × $10^{-4}M$ TETREN, curve 3—$10^{-6}M$ $Cu(NO_3)_2$, $10^{-3}M$ Zn–TETREN, $10^{-3}M$ TETREN. (*b*) Titration curve of $10^{-3}M$ $Zn(NO_3)_2$ in presence of $10^{-6}M$ $Cu(NO_3)_2$ with $10^{-2}M$ TETREN in borate buffer, with a copper membrane electrode.

Table 2. Complexometric titration of various metals with the copper-sensitive electrode

Titrant	Ion determined	Buffer	pH	Metal, *mmole* Taken	Metal, *mmole* Found	Error, %
EDTA	Ca^{2+}	Borate	9·2	0·1011	0·1017	+0·6
				0·1011	0·1017	+0·6
		Hexamine	6·7	0·1011	0·1019	+0·8
	Pb^{2+}	Hexamine	7·0	0·1027	0·1031	+0·4
TETREN	Zn^{2+}	Borate	9·2	0·1025	0·1024	−0·1
		Ammonia	9·0	0·1040	0·1046	+0·6
	Cu^{2+} + Pb^{2+}	Borate	9·2	0·1038 (Cu + Pb)	0·1037	−0·1
	Cu^{2+} + Zn^{2+}	Borate	9·2	0·1025 (Cu + Zn)	0·1026	+0·1
				0·1025 (Cu + Zn)	0·1031	+0·6
		Ammonia	9·0	0·05194 (Cu)	0·05031	−3·1
				0·1040 (Zn)	0·1050	+1·0

also quite satisfactory (Table 2) when the titration conditions (buffer and pH) were selected on the basis of the potential–pH diagrams; such a diagram for the zinc-TETREN system is given in Fig. 4, together with the experimental titration curve, which in spite of its asymmetry may be advantageously used in practical analytical titrations.

Mixtures of ions may also be titrated in the same way. Satisfactory results were obtained using an ammoniacal buffer for the copper–zinc system. However when the borate buffer was used, advantageous because it complexes metal ions only weakly, the precipitate formed at the beginning and persisting nearly up to the end of the titration prevents determination of individual ions (*e.g.*, Cu^{2+} and Pb^{2+}).

Acknowledgements—The authors are greatly indebted to Prof. Andrzej Pomianowski (Polish Academy of Science, Kraków) for samples of chalcocite crystals.

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Summary—The membrane electrode based on a synthetic chalcocite (Cu$_2$S) single crystal responds primarily to the activity of copper(I) ions in solution. The experimental selectivity coefficient with respect to copper(II) ions is in good agreement with the value calculated on the basis of solubility products of both sulphides. The electrode has been calibrated with metal-ion buffers containing a strongly complexing ligand, TETREN, and can be used as an indicator in titrations of copper with EDTA and TETREN. Comparison of an experimental titration curve with one calculated with the aid of the program HALTAFALL showed good agreement in the case of TETREN, but there were discrepancies for the EDTA titration, which are attributed to the presence and complexation of copper(I) ions. The electrode has also been applied in metal titrations with Cu^{2+} as indicator ion, though the potential changes observed were smaller than predicted. All titrations showed errors less than 1%.

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SOLVENT EXTRACTION OF GALLIUM(III) WITH 2-THENOYLTRIFLUOROACETONE

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Acetylacetone has been used for the extraction of gallium[1,2] but the extraction was not quantitative. Gallium and indium have been separated with acetylacetone[3] but the process was time-consuming as it involved several steps. The complexes of gallium, indium and aluminium with trifluoroacetylacetone[4] have been separated by gas chromatography. Benzoylacetone and dibenzoylmethane[5] have also been used for the extraction of gallium. The synergistic extraction[6] of gallium with thenoyltrifluroacetone (TTA) and tetraphenylarsonium chloride is also reported, but the pH range for extraction was rather narrow. TTA has been used for extraction and determination of many elements,[7] and it is now shown that it affords clean-cut separation of gallium at microgram levels. The gallium can be determined by a Rhodamine B method.

EXPERIMENTAL

Reagents

Gallium nitrate solution. The octahydrate (0·563 g) was dissolved in 100 ml of distilled water containing 1% of nitric acid. The solution was standardized gravimetrically.[8] The stock solution was diluted tenfold (gallium concentration 98 μg/ml).

2-Thenoyltrifluoroacetone solution in xylene, 0·03*M*.

Rhodamine B solution, 0·5% *in* 6*M hydrochloric acid.*

General procedure

An aliquot (2 ml) of gallium nitrate solution was diluted and its pH adjusted to 4·5–6 with 0·01*M* nitric acid and 0·01*M* ammonia solution in a total volume of 25 ml. It was then shaken in a separatory funnel for about 10 min (wrist-action shaker) with 10 ml of 0·03*M* TTA in xylene. The two layers were allowed to settle and separate. The aqueous phase was carefully withdrawn. The colourless organic layer was then shaken with 10 ml of 6*M* hydrochloric acid containing 0·5% of Rhodamine B, for about 10 min.[9] The two layers were allowed to separate. The reddish violet complex of gallium was measured photometrically at 565 nm against a reagent blank.

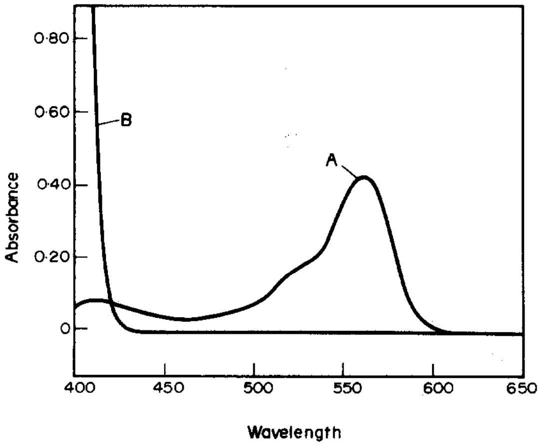

Fig. 1. Absorption spectra of Ga–Rhodamine B in TTA–xylene. A. Ga–Rhodamine B in TTA–xylene *vs.* reagent blank. B. Reagent blank *vs.* xylene Ga = $2{\cdot}81 \times 10^{-4}M$, TTA = $3 \times 10^{-2}M$.

RESULTS AND DISCUSSION

Spectral properties

The absorption spectrum of a solution of Ga(III)–TTA complex [Ga(III) = $2{\cdot}812 \times 10^{-4}M$] shows strong absorbance at 565 nm (Fig. 1). The reagent blank shows no absorbance at this wavelength. The molar absorptivity is $1{\cdot}07 \times 10^{3}$ l. mole^{-1}.cm^{-1} at 565 nm.

Extraction of various amounts of gallium at pH 4·5–6·0 and measurement of the absorbance at 565 nm showed that the system conforms to Beer's law over the gallium concentration range 2–60 μg/ml. The colour is stable for at least 24 hr.

Effect of pH and other parameters

The extraction was studied over the pH range 1–9 (Fig. 2). The results show that the optimum pH is 4·5–6·0.

All other factors being kept constant, the concentration and volume of the reagent were varied (Table 1). It was observed that the extraction of 196 μg of gallium was complete with 10 ml of 0·03*M* TTA in xylene, but incomplete

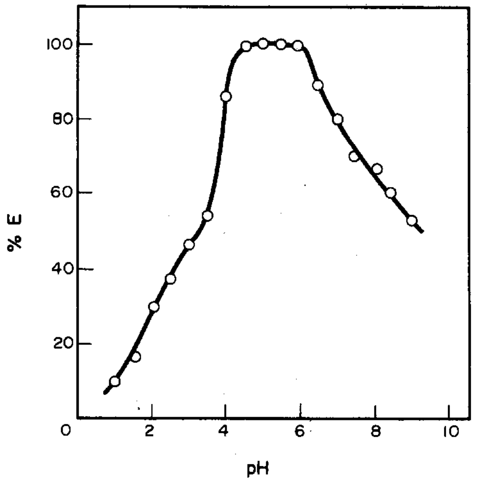

Fig. 2. Extraction as a function of pH.

Table 1. Effect of reagent concentration [Ga(III) = 196 μg; pH 5·0]

[TTA], *M*	TTA added, *ml*	Absorbance at 565 nm	Extraction, %
0·010	10	0·260	86·7
0·015	10	0·260	86·7
0·03	10	0·300	100
0·045	10	0·305	100
0·060	10	0·305	100
0·030	2·5	0·100	33·3
0·030	5·0	0·170	56·7
0·030	7·5	0·230	76·7
0·030	10	0·300	100
0·030	15	0·200	—
0·030	20	0·150	—

at lower concentrations of reagent. There was no significant increase in the absorbance when the concentration of reagent was increased from 0·01 to 0·06*M*. The use of varying volumes of 0·03*M* reagent showed that the extraction was quantitative with 10 ml of reagent.

The period of equilibration was varied from 2 to 20 min. The extraction was quantitative after 8 min of equilibration (Fig. 3). It is therefore recommended that the mixture be shaken for at least 10 min.

Ammonium, sodium, potassium, calcium and magnesium nitrates were tested as salting-out agents in the concentration range 1–3*M*, but none enhanced the extraction.

Effect of other ions

Several ions were examined for their effect on the extraction of gallium. The tolerance limit was taken as the amount required to cause a ±2% error in the gallium recovery (Table 2). The ions showing strong interference were EDTA, citrate and ascorbate. Several masking agents were used to eliminate the interference of some ions, *e.g.*, copper and osmium were masked with potassium cyanide, bismuth, chromium, aluminium, uranium, and zirconium were masked with sodium fluoride, iron was masked with alkali metal phosphate, cerium was masked with tartrate and indium was masked with thiocyanate.

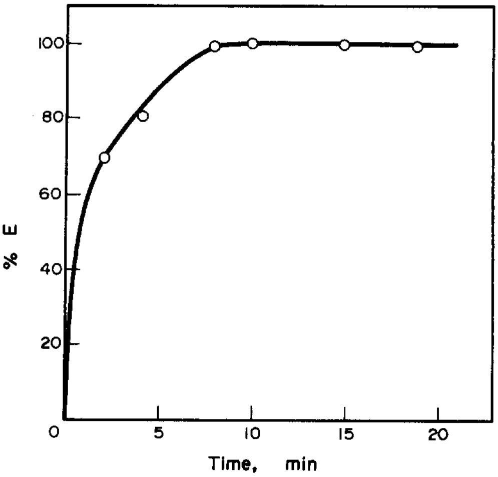

Fig. 3. Extraction as a function of period of equilibration.

The proposed method possesses several advantages, as it is possible to separate gallium from indium, thallium and aluminium, with which it is usually associated. The method is selective, as it is possible to separate gallium

Table 2. Effect of diverse ions on determination of gallium [Ga(III) = 98 μg; 0·03*M* TTA; pH = 4·5]

Foreign ion	Added as	Tolerance limit, μg	Foreign ion	Added as	Tolerance limit, μg
Ag^+	$AgNO_3$	500	Ba^{2+}	$BaCl_2.2H_2O$	10000
Pb^{2+}	$Pb(NO_3)_2$	2000	Li^+	LiCl	10000
Hg^{2+}	$HgCl_2$	3000	Rb^+	RbCl	5000
Tl^+	TNO_3	2000	Cs^+	CsCl	5000
Cu^{2+}	$CuSO_4.5H_2O$	500[a]	Ge^{4+}	$GeCl_4$	4000
Cd^{2+}	$3CdSO_4.8H_2O$	2000	Sn^{2+}	$SnCl_2.2H_2O$	500[b]
Sb^{3+}	$SbCl_3$	1000	In^{3+}	$InCl_3$	500[d]
Au^{3+}	$HAuCl_4.xH_2O$	1000	Ti^{4+}	$Ti(SO_4)_2$	500
Bi^{3+}	$Bi(NO_3)_3$	500[b]	Re^{7+}	$KReO_4$	2000
Pd^{2+}	$PdCl_2$	1000	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}.4H_2O$	1000
Pt^{4+}	$H_2PtCl_6.xH_2O$	2000	WO_4^{2-}	Na_2WO_4	2000
Ir^{3+}	$IrCl_3$	800	VO_3^-	NH_4VO_3	1000
Rh^{3+}	$RhCl_3$	2000	SeO_3^{2-}	Na_2SeO_3	500
Os^{8+}	OsO_4	500[a]	TeO_3^{2-}	Na_2TeO_3	1000
Ru^{3+}	$RuCl_3$	500	F^-	NaF	5000
Fe^{3+}	$FeCl_3.6H_2O$	500[c]	I^-	KI	2000
Cr^{3+}	$CrCl_3$	500[b]	Br^-	KBr	2000
Al^{3+}	$Al(NO_3)_3.9H_2O$	100[b]	CN^-	KCN	5000
Zn^{2+}	$ZnSO_4.7H_2O$	2000	SCN^-	KSCN	5000
Mn^{2+}	$MnCl_2.4H_2O$	2500	$S_2O_3^{2-}$	$Na_2S_2O_3.2H_2O$	2000
Co^{2+}	$Co(NO_3)_2.6H_2O$	2000	SO_3^{2-}	Na_2SO_3	5000
Ni^{2+}	$NiSO_4.6H_2O$	5000	SO_4^{2-}	Na_2SO_4	10000
UO_2^{2+}	$UO_2(NO_3)_2.6H_2O$	200[b]	$EDTA^{4-}$	EDTA(disodium salt)	None
Th^{4+}	$Th(NO_3)_4.4H_2O$	500	Cit^{3-}	Citric acid	None
Zr^{4+}	$Zr(NO_3)_4$	500[b]	$Tart^{3-}$	Tartaric acid	500
Ce^{4+}	$Ce(SO_4)_2$	500[e]	Mal^{-2}	Malonic acid	5000
Be^{2+}	$Be(NO_3)_2.4H_2O$	2000	$Ascorb^-$	Ascorbic acid	None
Sr^{2+}	$SrCl_2.2H_2O$	10000	CH_3COO^-	CH_3COOH	10000

Interference eliminated by masking with alkali metal (*a*) cyanide, (*b*) fluoride, (*c*) phosphate, (*d*) thiocyanate and (*e*) tartaric acid.

from a large number of elements at trace concentrations. The method is rapid as the extraction and determination require only 30 min. Concentrations as low as 1·96 μg/ml can be determined. The results are reproducible. The average recovery of gallium is 99·9 ± 0·1% (relative standard deviation 1·0%).

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2-AMINO-3-HYDROXYPYRIDINE AS A CHROMOGENIC REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

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Several reagents have been suggested for the spectrophotometric determination of osmium.[1–6] Practically all the methods deal with the problem of interfering constituents. The methods available are dependent upon various factors such as temperature, acidity, concentration of the reagent and certain other anions and cations. However, none provides a method for the selective determination of osmium in the presence of the other platinum metals. In most, a prior separation of osmium as volatile osmium tetroxide is required. The present paper deals with the use of 2-amino-3-hydroxypyridine (AHP) as a chromogenic reagent for the spectrophotometric determination of osmium. This reagent has already been successfully used for the determination of iron[7] and ruthenium(III).[8] AHP reacts immediately with osmium(IV), (VI) and (VIII) solutions in the cold, forming different coloured species according to the acidity. The characteristics of the complexation have been studied spectrophotometrically and AHP has been used for selective and sensitive determination of osmium.

EXPERIMENTAL

Reagents

Standard osmium(*VIII*) *solution.* A 1-g ampoule of osmium tetroxide (Johnson Matthey) was broken beneath the surface of about 100 ml of 4*M* sodium hydroxide in a glass-stoppered flask, as described by Ayres and Wells.[9] The red-orange solution was washed into a 1-litre volumetric flask, made up to volume with doubly distilled water, and standardized by the modified method of Klobbie.[10]

Osmium(*VI*) *and osmium*(*IV*) *solutions.* Obtained by dissolving potassium osmate and potassium chloro-osmate in concentrated sodium hydroxide solution and hydrochloric acid respectively.

Standard reagent solution. Obtained by dissolving an appropriate quantity of AHP in 95% v/v ethanol or methanol or in 10% v/v acetic acid. The solutions were kept in coloured glass bottles in a cool place. Under these conditions the solutions remain stable for up to six months.

All other chemicals used were of analytical reagent quality.

Preliminary investigations

On mixing the AHP solution (in alcohol or acetic acid) with osmium(VIII), (VI) or (IV) solutions, an immediate colour development takes place in the cold, the nature of the species formed depending only on the acidity and not on the oxidation state of the osmium.

The absorption spectra of freshly prepared AHP solution in ethanol and of the osmium complexes formed under various conditions are shown in Figs. 1 and 2. The reagent absorbs only in the ultraviolet region, showing maximum absorption at 235 and 300 nm, the corresponding molar absorptivities being $2{\cdot}05 \times 10^{4}$ and $1{\cdot}90 \times 10^{4}$ l. mole^{-1}. cm^{-1}. The absorption maxima of the complexes from a large number of elements at trace concentrations. The method is rapid as the extraction and determination require only 30 min. Concentrations as low as 1·96 μg/ml can be determined. The results are reproducible. The average recovery of gallium is 99·9 ± 0·1% (relative standard deviation 1·0%).

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Table 1. Characteristics of complexes

Characteristics	Os–AHP complex in 50% ethanol		Os–AHP complex in the absence of ethanol	
	3*M* HCl	3*M* NaOH	3*M* CH_3COOH	3*M* NaOH
Colour	Green	Red–violet	Green	Violet
λ_{max}, *nm*	600	540	600	550
Adherence to Beer's law, *ppm*	0–15·3	0–15·3	0–14·3	0–14·3
Molar absorptivity at λ_{max} $l.mole^{-1}.cm^{-1}$	$5{\cdot}2 \times 10^3$	$8{\cdot}4 \times 10^3$	$9{\cdot}0 \times 10^3$	$7{\cdot}0 \times 10^3$
Molar ratio of reagent required for total complexation	4	20	8	10
Composition M:L	1:2	1:3	1:3	1:3

remain unaltered irrespective of the proportions of the reactants, indicating the formation of only one complex.

To find the effect of heating on the completeness of complexation, the solutions were heated on a boiling water-bath and the absorbance was measured after different intervals of time. The absorbance was constant and maximal even without the heating, showing that heating is unnecessary.

Variation in the order of addition of the reactants had no effect. The order used during investigations was osmium solution, interfering ions (if any), AHP, followed by adjustment of the acidity.

Solutions containing osmium and appropriate quantities of AHP were prepared at different pH values (sodium acetate–acetic acid buffer). The complex precipitated at pH between 2 and 8. It was observed that two distinct coloured species are formed at very high and very low pH. The intensity of colour of the complexes remains constant over the range 1·0–6·0*M* hydrochloric acid or sodium hydroxide. Further studies were therefore made with 3*M* acid or alkali.

Effect of reagent concentration, adherence to Beer's law and sensitivity

To a constant amount of osmium solution were added varying molar ratios of AHP at different acidities and in different media. The plot of absorbance (at λ_{max}) *vs.* concentration of the ligand shows that the amount of reagent necessary for complete complexation varies with the conditions and the medium. The range of application of Beer's law and the molar absorptivities were calculated (Table 1). The optimum range is 3–13 ppm.

Composition of the complexes

Various methods, *viz.* continuous variations,[11] mole-ratio[12] and slope-ratio,[13] were used to ascertain the composition of the complexes. The metal combines with the ligand in different stoichiometric ratios under different working conditions (Table 1). Ion-exchange studies showed that the complexes were anionic. In the absence of further evidence, no structure can be proposed for the complexes.

Recommended procedure

To a suitable aliquot, containing 10–100 μg of osmium, in a 10-ml standard flask, add 3 ml of 0·1% AHP solution (in ethanol or 10% acetic acid). Adjust the acidity of the solution to 3*M* by adding conc. hydrochloric or acetic acid, or the alkalinity to 3*M* by adding sodium hydroxide solution. Dilute to the mark, mix, and measure the absorbance at λ_{max} for the complex, *vs.* a water blank. Preparation of a reagent blank is not necessary.

Effect of diverse ions

To a suitable aliquot containing 100 μg of osmium and various amounts of foreign ion, an excess of AHP was added and the recommended procedure followed. The results are summarized in Table 2, the tolerance limit being taken as the concentration causing an error of not more than 3%. The interference of most ions can be avoided by choosing the conditions for colour development.

The interferences caused by various cations, including platinum metals, can be avoided by making use of the common masking agents, *viz.* EDTA, fluoride, citrate, tartrate, *etc.* Typical results are also summarized in Table 2.

Table 2. Effect of diverse species

Foreign species	Os–AHP complex in the presence of 50% ethanol, limit of tolerance, *ppm*		Os–AHP complex in the absence of ethanol, limit of tolerance, *ppm*	
	3*M* HCl	3*M* NaOH	3*M* CH_3COOH	3*M* NaOH
Fluoride	500	500	500	100
Oxalate	500	50	500	400
Tartrate	200	50	400	300
Borate	500	50	50	50
Citrate	80	50	50	50
Phosphate	500	80	500	400
Persulphate	80	100	50	50
Nitrite	20	50	500	400
Cyanide	50	50	50	50
Thiourea	interferes very seriously			
Bromide	80	50	500	500
Iodide	500	50	400	400
Sulphite	500	50	50	80
Thiocyanate	200	50	20	20
Thiosulphate	50	interferes very seriously	50	100
Acetate	500	500	—	—
Chloride	200	250	300	300
Ru(III), Rh(III), Pd(II), Ir(III)	5	5	5(30*)	5(20*)
Pt(IV)	10	50	50	50
Cu(II)	20	50	20(50*)	20(50*)
Hg(II)	20	50	20(50†)	20(50†)
Zn(II)	20	50	100	100
Cd(II)	30	50	20(50*)	20(50*)
Ni(II)	20	25	80	80(100*)
Mn(II)	100	100	200	200
Al(III)	20	25	50	250
Mg(II)	25	50	100	250
Sc(III)	20	25	50	25
Ba(II)	50	50	100	200
Mo(VI)	25	50	20(50*)	25(100*)
Sn(VI)	25	50	20(50§)	25(100§)
Fe(III)	10	25	25(100§)	25(30‡)
In(III)	10	25	100	100
Pb(II)	100	25	100	100
Gd(III)	50	50	100	200
U(VI)	25	100	100	100
Co(II)	25	50	50	50
La(III)	50	100	100	100
EDTA	interferes	interferes	30 μmole	30 μmole

* Masked with 3 ml of 0·01*M* EDTA.
† Masked with 400 ppm of iodide.
§ Masked with 400 ppm of fluoride.
‡ Masked with 100 ppm of fluoride.

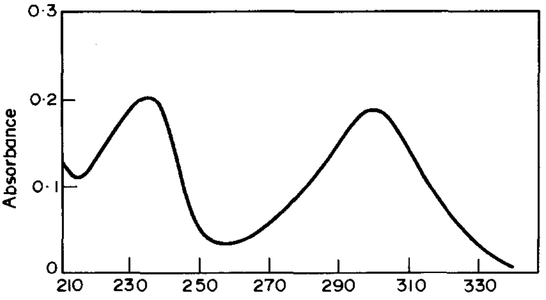

Fig. 1. Absorption spectra of AHP ($1 \times 10^{-5}M$) in ethanol.

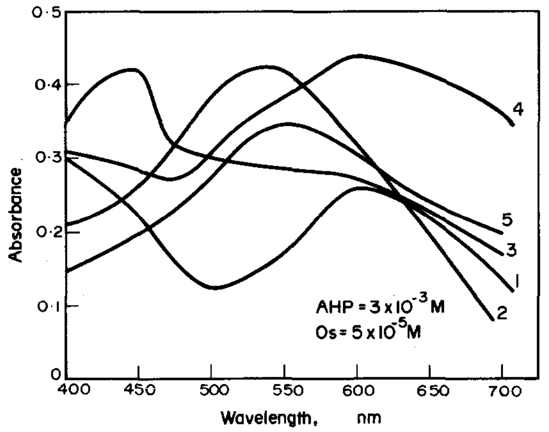

Fig. 2. Absorption spectra of osmium–AHP complex in 1—50% ethanol/$3M$ HCl; 2—50% ethanol/$3M$ NaOH; 3—50% ethanol/pH 4; 4—$3M$ acetic acid; 5—$3M$ NaOH.

Table 3. Determination of osmium in synthetic mixtures in acetic acid medium

Os added, *ppm*	Ir added, *ppm*	Ru added, *ppm*	Pd added, *ppm*	Osmium found, *ppm*	
				$3M$ CH_3COOH	$3M$ NaOH
10·0	11	0·1	0·55	9·85	9·83
10·0	11	2·2	1·40	9·84	9·81
10·0	15	5·5	0·55	9·76	9·78

Determination of osmium in various synthetic mixtures

As naturally occurring ores of osmium are not easily available, synthetic mixtures similar to these in composition were prepared and the amount of osmium was determined by taking an appropriate sample aliquot, adding 3 ml of 0·01M EDTA and 3 ml of 0·1% AHP solution in acetic acid, adjusting the acidity with acetic acid or sodium hydroxide, diluting to 10 ml and measuring the absorbance. The results are summarized in Table 3.

DISCUSSION

Several reagents, such as anthranilic acid,[4] sulphanilic acid,[5] 3-nitroso-2,6-pyridinediol[3] and 2-amino-8-naphthol-3,6-disulphonic acid,[14] have been used for the spectrophotometric determination of osmium. 1-Naphthylamine-3,5,7-trisulphonic acid,[15] though a good analytical reagent, requires at least 4 hr heating for maximum colour development. Other well-known reagents either require controlled conditions of heating and pH or a prior separation of osmium as volatile osmium tetroxide from other platinum metals. Similarly certain reagents, though quite sensitive, lack selectivity and require strict control of pH conditions. AHP overcomes many of these difficulties to a considerable extent.

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Summary—2-Amino-3-hydroxypyridine forms two coloured complexes, green and violet, with osmium, depending on the pH of the solutions. Based on this reaction, a selective and sensitive spectrophotometric method for the determination of osmium (3–13 ppm in the final solution) alone and in the presence of other metal ions has been developed.

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DETERMINATION OF TUNGSTEN WITH IRON(III) AFTER REDUCTION WITH MERCURY IN THIOCYANATE MEDIUM

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For the determination of macro amounts of tungsten gravimetric methods are preferred. In the most frequently used tungstic acid method, the precipitate is contaminated[1a] with antimony, chromium, iron, molybdenum, niobium, phosphorus, silica, vanadium, tantalum and tin present in the sample, and these have to be removed or accounted for. The generally used co-precipitation agent cinchonine is costly. The tungstate precipitation methods suffer from several interferences[2a] and the precipitate should be finally ignited to tungstic oxide. The oxinate method suffers interference from molybdenum, titanium and uranium and is also otherwise unsuitable.[3] All these methods require some hours for a single determination.

The volumetric methods[1b] are based on reduction to W(V) or (III) and reoxidation to W(VI), under an inert atmosphere. Some methods precipitate tungsten as lead tungstate and estimate the lead in the precipitate[4] or in excess,[5] or precipitate tungsten oxinate and estimate the oxine.[6] All these methods are tedious, subject to several interferences and give inconsistent and unreliable results.[2b]

Tungsten(VI) can be reduced to tungsten(V) by mercury metal[7] in hydrochloric acid in the presence of thiocyanate. We now describe a simple titrimetric method for the direct determination of the tungsten(V) with iron(III).

EXPERIMENTAL

Reagents and solutions

Tungsten solution. Sodium tungstate was dissolved to give a mg/ml level solution which was standardized by the oxine method.[8]

Potassium thiocyanate, 5 *M.*

Mercury. Purified with nitric acid.[9a]

Iron(III) solution, ca. 0·01 *M.* Iron(III) chloride was dissolved in 0·1 *M* hydrochloric acid and standardized.[9b] Further dilutions (to 0·05 and 0·02 *M*) were made, the solutions being adjusted to be 4 *M* in hydrochloric acid.

Procedure

Solution containing 5–80 mg of tungsten was placed in a separating funnel, and adjusted to be 0·4 *M* in potassium thiocyanate and 4 *M* in hydrochloric acid, in a final volume of 25 ml. This solution was shaken with 2 ml of mercury for 2 min[7] (3 min if silicic acid was present). The mercury was run off, and the aqueous phase was transferred quantitatively to the titration vessel with 4 *M* hydrochloric acid.

Titration to a visual end-point. A flask was used for the titration, and the solution, made up to about 100 ml with 4 *M* hydrochloric acid (for > 20 mg of tungsten) was titrated with standard iron(III) solution of appropriate concentration, with vigorous mixing by hand or, for > 40 mg of W, magnetically, with dropwise addition at 15–20 sec intervals towards the end-point (red colour of iron thiocyanate).

Titration to a potential end-point. A beaker was used and the titration solution had a volume of about 100 ml and was 7 *M* in hydrochloric acid. It was titrated with standard iron(III) solution, with magnetic stirring. The potential was measured with a tungsten wire electrode against an SCE. Equilibration of potential took 2–3 min.

RESULTS AND DISCUSSION

Tungsten(V) or (III) has to be protected from atmospheric oxidation unless stabilized, *e.g.*, by complexation with thiocyanate. Fluoride and nitrate should be absent.[7] The tungsten(V) in the complex is quantitatively oxidized by iron(III). The thiocyanate is not oxidized and acts as the indicator. Stronger oxidants oxidize the thiocyanate as well.

Titration to a visual end-point. Large amounts of tartrate, citrate, phosphate, acetate and up to 0·5 g of sulphate do not interfere, but oxalate does so slightly (Table 2). The end-point cannot be detected in the presence of EDTA. In the maximum amounts usually encountered in tungsten determinations, iron, nickel, chromium, zirconium, bismuth, antimony, cerium, aluminium, lead and calcium do not interfere (Table 3). Uranium (10 mg) and vanadium (5 mg) are tolerated. Arsenic spoils the mercury, and copper is precipitated as cuprous thiocyanate but up to 5 mg can still be tolerated. Niobium and manganese give high errors. Because of the colour of their thiocyanate complexes, molybdenum, cobalt and rhenium interfere with the end-point. Molybdenum can be tolerated up to only 50 μg. Silicic acid does not interfere if the solution is magnetically stirred during the titration, to prevent adsorption of the iron thiocyanate complex.

Titration to a potential end-point. The tungsten wire electrode gives a sharp potential rise at the end-point. It is poisoned irreversibly by copper, needs regular cleaning[10] and takes 2–3 min to give a constant reading. A platinum electrode does not work. The tungsten electrode is cleaned

Table 1. Titration of tungsten(V) with iron(III)

Tungsten, *mg*	Visual Found, *mg*	Potentiometric Found, *mg*
5·00	5·02	4·99
10·00	9·99	10·01
15·00	14·98	14·98
20·00	19·99	20·01
30·00	29·98	30·07
40·00	39·92	39·94
50·00	49·93	49·93
60·00	60·05	59·97
80·00	79·87	79·87

Table 2. Effect of some anions on titration of 20·00 mg of tungsten(V) with iron(III)

Salt added	Visual end-point Amount added, *g*	 W found, *mg*	 Error, %	Potentiometric end-point Amount added, *g*	 W found, *mg*	 Error, %
Sodium tartrate*	2·0	19·97	−0·15	1·0	19·99	−0·05
Potassium citrate†	2·0	19·99	−0·05	1·0	19·08	−4·6
Sodium phosphate*	2·0	19·99	−0·05	2·0	17·76	−11·2
Sodium acetate†	2·0	20·01	+0·05	1·0	19·97	−0·15
Sodium oxalate†	2·0 (or 1·0)	21·22	+6·1	1·0	18·59	−7·0
Sodium sulphate*	0·5	20·01	+0·05	1·0	19·99	−0·05

* Added before formation of the tungsten thiocyanate complex.

† Added after formation of the tungsten thiocyanate complex.

Table 3. Effect of other elements on determination of 20·00 mg of tungsten with iron(III)

Elements	Visual end-point Amount added, *mg*	 W found, *mg*	 Error, %	Potentiometric end-point Amount, added, *mg*	 W found, *mg*	 Error, %
		19·99	−0·05	—	20·01	+0·05
Ni(II)	50	19·97	−0·15	50	20·05	+0·25
Fe(III)	50	20·01	+0·05	50	20·01	+0·05
Zr(IV)	25	19·97	−0·15	20	20·05	+0·25
Bi(III)	50	19·99	−0·05	20	20·01	+0·05
Sb(III)	20	20·01	+0·05	20	19·97	−0·15
Ce(IV)	20	19·99	−0·05	20	19·97	−0·15
Cr(III)	20	19·99	−0·05	20	19·95	−0·25
Al(III)	20	20·01	+0·05	20	20·66	+3·3
Pb(II)	20	19·99	−0·05	20	20·01	+0·05
Ca(II)	10	19·99	−0·05	10	20·01	+0·05
U(VI)	10	19·99	−0·05	1	19·97	−0·15
V(V)	5	19·99	−0·05	1	19·95	−0·25
As(III)*	5	20·23	+1·15	—	—	—
Mn(II)	20	21·39	+7·0	20	19·97	−0·15
Cu(II)†	5	20·03	+0·15	—	—	—
Nb(V)	10	18·92	−5·4	10	19·97	−0·15
Mo(VI)‡	—	—	—	10	19·97	−0·15
Co(II)‡	—	—	—	20	19·97	−0·15
Re(VII)‡		—	—	1	19·95	−0·25

* Spoils mercury.

† Poisons tungsten wire electrode.

‡ End-point cannot be detected.

by being rubbed occasionally with fine emery paper and washed with hydrochloric acid.

Sulphate, acetate and tartrate do not interfere but citrate, oxalate and phosphate in large amounts interfere increasingly in that order (Table 2). Besides the elements stated as non-interfering in the visual titration, cobalt, rhenium, niobium and manganese also do not interfere (Table 3). Interference by molybdenum is avoided by titration in 9 *M* hydrochloric acid and in the presence of a small amount (0·2–0·5 g) of ammonium, potassium, sodium, calcium or aluminium chloride. In the absence of any of these salts, there is no potential jump even if the acidity is increased to greater than 9 *M* or the chloride concentration to 9 *M* at an acidity of 7 *M*. The salts increase $\Delta E/\Delta V$ in the order $Na^+ < K^+ < Ca^{2+} \sim NH_4^+ < Al^{3+}$.

Titration to a visual end-point takes < 10 min, needs lower acidity, and tolerates citrate and phosphate, whereas that to a potentiometric end-point tolerates molybdenum, cobalt, rhenium, niobium and manganese and more sulphate.

The method gives accurate and reproducible results. In five determinations of 20 mg of tungsten the visual end-point method gave a standard deviation of 0·012 mg.

The wide applicability of the method is shown by satisfactory analysis of several alloys (Table 4).

Table 4. Analysis of various samples

Matrix/sample composition*	Visual end-point W added, *mg*	 W found, *mg*	Potentiometric end-point W added, *mg*	 W found, *mg*
1. Fe(75), Cr(3·8), Mo(0·05), V(1·0)	20·00	20·03	20·00	19·95
2. Fe(75), Cr(6), V(0·3)	20·00	19·99	20·00	20·03
3. Fe(170), Cr(50), Ni(17·5), Mn(1·25)	10·00	10·03	10·00	10·03
4. Fe(90·8), Cr(21·6), Ni(21·6), Mo(2·5), Co(16·6), Mn(1·3), Nb(5·0)	—	—	5·00	4·98
5. Fe(50), Cr(6), Mo(1·5)	—	—	10·00	9·97
6. Ferrotungsten A, 75·2% W†	— —	75·26, 75·16%	— —	75·06, 75·47%
7. Ferrotungsten B, 73·3% W†	— —	73·21, 73·41%	— —	73·41, 73·41%
8. High speed steel BCS 241/1, 19·61% W†	— —	19·75, 19·75%	— —	19·71, 19·83%

* Numbers in brackets are mg of the element in the aliquot analysed. Samples 1–5 are analogous to Fast-cutting steel, High-speed steel, Midvale HR, Heat-resistant alloy and Cristite respectively.

† Reported value.

Acknowledgements—The authors wish to express their sincere thanks to Prof. S. M. Mukherji, Head of the Chemistry Dept., for facilities. S. D. is also grateful to Kurukshetra University for a research fellowship.

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RADIOISOTOPE STUDIES OF CARBOXYL SITES ON STRONG ACID AND STRONG BASE ION-EXCHANGE RESINS DERIVED FROM POLYSTYRENE

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Recent[1,2] mass-spectrometric examination of age-induced deterioration of polystyrene–divinylbenzene copolymer ion-exchangers has indicated the presence of a small number of carboxylic acid functions in addition to the sulphonate or quaternary ammonium sites to which the resin owes most of its exchange capacity. These carboxyl groups may arise from the oxidation of ethyl groups, introduced by formation of the analogous resin from ethylstyrene,[3] a common contaminant of commercial divinylbenzene.[4] Such oxidation can occur at the sulphonation stage of manufacture,[5] although it may continue to occur after sulphonation is complete. It is possible, too, that some divinylbenzene is incorporated into the polymer chain at one end only,[1] leaving a readily oxidized ethylenic group on the polymer. When the resin is subjected to low pressures and moderately high (~150°) temperatures, such as are required for the operation of a mass spectrometer, some of these carboxyl groups become detached from the polymer matrix and are manifested by a peak at $m/e = 44$ in a mass spectrum, corresponding to the formation of the species CO_2^+. Such reactions are discussed fully elsewhere.[1,2] Interpretation of the mass spectra in these terms allows an explanation of hitherto anomalous characteristics of carrier-free radioisotope distribution between ion-exchangers and aqueous phases.

In order to obtain information about the carboxyl exchange function in resins, a study has been made of the distribution of metal ions between aqueous phases at constant ionic strength and the resin, as the pH of the system is varied. Polystyrene–divinylbenzene copolymers having sulphonate or quaternary ammonium functional groups were used. Attempts were made, on the one hand, to introduce additional carboxyl groups by oxidation and, on the other, to eliminate by esterification those already there. For comparison purposes some copolymer lacking either of the aforementioned major functional groups was also examined.

Commercially available resins from the Permutit Co. Ltd., the Dow Chemical Co. and Rohm and Hass were examined in the course of the work described and, although most of the results reported here refer to products from the first-mentioned source, resins from all three manufacturers showed the same general characteristics.

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Commercially available resins from the Permutit Co. Ltd., the Dow Chemical Co. and Rohm and Hass were examined in the course of the work described and, although most of the results reported here refer to products from the first-mentioned source, resins from all three manufacturers showed the same general characteristics.

EXPERIMENTAL

Zeo-Karb 225 (SRC 15, 8% DVB, 100–200 mesh) was washed 3 times with 2*M* hydrochloric acid, then with 2*M* sodium chloride till free from acid and finally with water till free from chloride. It was dried at 80° for 8 hr; capacity 4·18 meq/g.

Bio-Rad AG50WX8 (400 mesh) was converted into the sodium form with 1*M* sodium perchlorate, washed with distilled water and dried at 80°.

De-Acidite FF (SRA 71, 7–9% cross-linked) was treated in sequence with 2*M* hydrochloric acid, water, 1*M* sodium hydroxide, 1*M* sodium perchlorate and water. It was dried at 80°.

Polystyrene resin (8% DVB, 15–50 mesh) was treated in a manner analogous to that used for the Zeo-Karb 225.

Carrier-free ^{144}Ce/^{144}Pr, ^{91}Y and ^{89}Sr were obtained from the Radiochemical Centre, Amersham, and used as supplied.

The distribution measurements were made by adding known amounts of resin (50 mg for cation-exchanger and 100 mg for all others), to clean, dry polyethylene bottles. The appropriate volume of aqueous phase containing the radioisotope and made up to the correct ionic strength (0·5) with sodium perchlorate solution was added to give a total volume of 40 ml. Samples were prepared in batches and equilibrated for 18 hr at 21 ± 0·5°, after which the contents of the polyethylene bottles were transferred to centrifuge tubes and the resin phases separated from the aqueous phases. The supernatant liquid was used for radioassay and the distribution ratio,

$$\phi = \frac{1}{m}\left(\frac{C'_m - C_m}{C_m}\right) - \delta,$$

where C'_m is the count-rate of the aqueous phase per unit volume before and C_m that after equilibration with resin m is the mass of resin, in g, and δ is the swelling factor[6] for the resin, was calculated. The swelling factor has been taken as unity in the present case in view of the experimental conditions used. The pH of each aqueous phase was taken after equilibration with the resin.

Some of the resin samples were treated with acidic potassium permanganate solution as follows: 10 g of conditioned resin were treated with saturated potassium permanganate solution in 1*M* sulphuric acid for 1 hr at 25°. The resin was then well washed with water and treated with nitrous acid to remove the last traces of permanganate, after which the resin was packed into a column, washed with water, 2*M* hydrochloric acid, water, 0·5*M* sodium hydroxide, water, 0·5*M* sodium perchlorate and finally water. The resin was air-dried as before. In an attempt to remove carboxyl groups from other samples, some experiments were done with resin which had been treated with diazomethane to esterify the carboxyl groups. Conditioned resin (5 g) was suspended in ice-cold ether. Diazomethane was liberated by the addition of ethanolic sodium hydroxide solution to *N*-nitroso-*N*-methyltoluene-*p*-sulphonamide at 30° and passed through the suspension of resin in ether for 8 hr; the resin was then filtered off, washed with distilled water and dried at 80° for 8 hr.

Table 1. ϕ obtained at two pH values as a function of varying weights of Zeo-Karb 225 resin equilibrated with a constant volume (40 ml) of 0·5*M* $NaClO_4$ containing carrier-free ^{144}Ce

Experiment	Resin, *g*	C'_m	C_m (pH 3·05)	C_m (pH 5·5)	ϕ (pH 3·05)	ϕ (pH 5·5)
1	0·020	20197	8057	4410	75	179
2	0·040	20197	4897	2252	78	199
3	0·060	20197	3403	1667	83	185
4	0·080	20197	2762	1318	79	179
5	0·100	20197	2207	1045	82	183

RESULTS AND DISCUSSION

Values of ϕ are presented in Table 1 for systems containing free ^{144}Ce(III) and varying weights of Zeo-Karb 225 resin. It is seen that for a given pH, ϕ is independent of the weight of resin used and also of the resin loading which is, however, very light. The results suggest that physical adsorption of a general type is unlikely to be responsible. It may be noted that ϕ is considerably higher at the higher pH, an observation consistent with the creation of additional exchange sites as the pH is increased.

Results for the distribution of ^{144}Ce(III) between Zeo-Karb 225 and 0·5*M* sodium perchlorate over a range of pH are given in Fig. 1. In the pH range 2–3·5, ϕ is nearly constant, which is in keeping with the availability of sulphonate exchange sites, but above pH 4 it rises appreciably with increasing pH. It is seen that addition of very low concentrations of inactive Ce(III) suffices to reduce or eliminate the additional resin capacity, which must consequently be very low.

When the distribution of ^{144}Ce(III) between permanganate-treated Zeo-Karb 225 and 0·5*M* sodium perchlorate is examined (Fig. 2) it is seen that the pH-dependent increase in ϕ occurs at a lower pH; this is consistent with the introduction of additional carboxyl groups, some of which may be more readily ionized than those initially on the resin. Subsequent reaction of permanganate-treated resin with diazomethane did not significantly alter the distribution pattern. The effect of diazomethane-treatment on ϕ for Zeo-Karb untreated with permanganate was also negligible (Fig. 3). In neither instance was the overall resin capacity affected by the treatment. The behaviour of Bio-Rad AG50WX8 is substantially similar to that of Zeo-Karb 225 but the increase in ϕ is not so pronounced in the former (Fig. 4). The anion-exchanger De-Acidite FF exhibits (Fig. 5) behaviour somewhat similar to that of Zeo-Karb 225 and Bio-Rad AG50WX8 with a significant

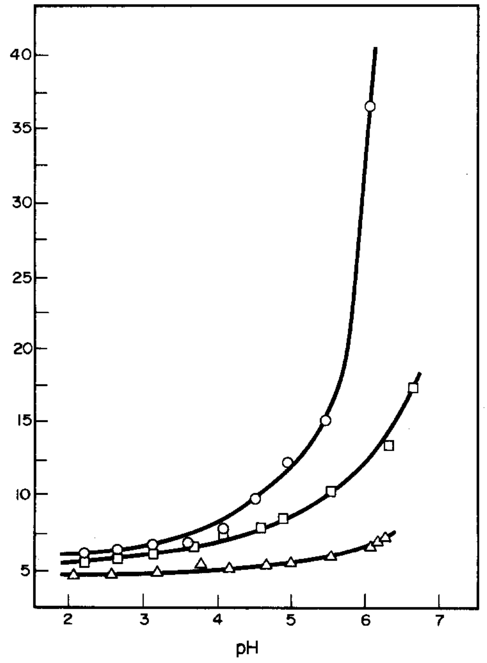

Fig. 1. Distribution of Ce(III) between Zeo-Karb and 0·5*M* $NaClO_4$. ○—Carrier-free ^{144}Ce(III); □—10^{-5}*M* Ce(III); △—5 × 10^{-5}*M* Ce(III).

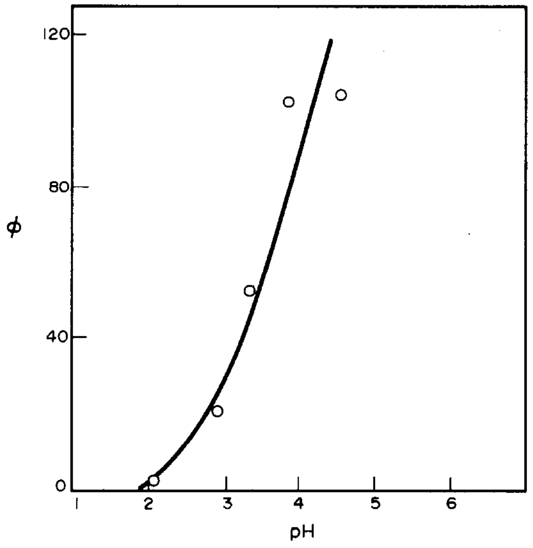

Fig. 2. Distribution of carrier-free ^{144}Ce(III) between Zeo-Karb 225 (treated with $KMnO_4$) and 0·5*M* $NaClO_4$.

suppression of the effect when $10^{-7}M$ carrier is added. The very much lower values of ϕ in this case are consistent with the carboxyl functions under discussion being the only negatively-charged fixed sites on the matrix. It is to be expected that anion-exchangers will exhibit only a slight effect of this kind since even though there may be carboxyl sites within the resin matrix, the Donnan potential should still operate to the exclusion of cations, because the overall fixed-site charge will be positive. Thus the observed cation-capacity probably results essentially from surface sites.

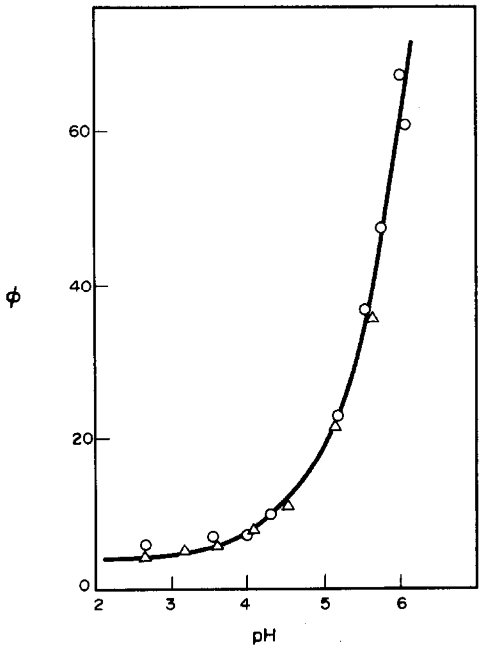

Fig. 3. Distribution of carrier-free ^{144}Ce(III) between Zeo-Karb 225 and 0·5*M* $NaClO_4$. ○—Untreated resin; △—diazomethane-treated resin.

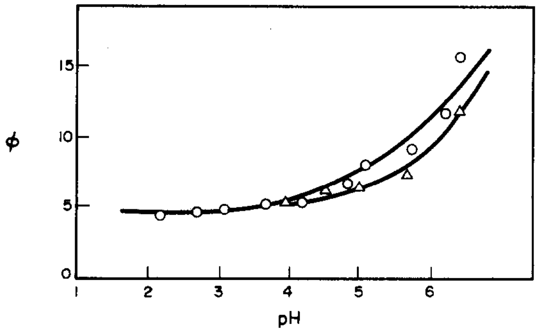

Fig. 4. Distribution of Ce(III) between Bio-Rad AG50WX8 and 0·5*M* $NaClO_4$. ○—Carrier-free ^{144}Ce(III); △—$10^{-6}M$ Ce(III).

In Fig. 6 it is seen that the polystyrene–DVB copolymer beads exhibit a pH-dependent distribution at ϕ-values much lower than those for cation-exchangers, but similar to those for De-Acidite FF. Again, it was found that the effect of treatment with permanganate is to lower the pH at which the increase in ϕ occurs. As with the anion-exchanger but for a different reason, namely lack of resin porosity, this is likely to be a surface effect.

Ce(III) would not be expected to hydrolyse at pH < 6, but if oxidation to Ce(IV) occurred then hydrolysis could perhaps account for the observations reported in Figs. 1–6. Experiments in which a reducing agent (hydroxylamine or hydrazine) was incorporated in the aqueous ^{144}Ce(III) showed that oxidation and subsequent hydrolysis was not responsible. Similar series of experiments were done with ^{89}Sr and ^{91}Y and the various resin samples available, and all results were comparable with those reported for Ce(III) except that, in every case, ϕ was lower and the increase in the region of pH 4–6 was less pronounced for the ^{89}Sr. This behaviour is to be expected if carboxyl groups are responsible.

Earlier processes for the preparation of resins led to the formation of appreciable levels of carboxyl groups on a nominally monofunctional sulphonate cation-exchanger[5] but it is tacitly assumed that more recent techniques produce entirely monofunctional resins. The exhibition of similar cation-exchange behaviour by anion-exchangers and hydrocarbon beads supports the premise that carboxyl groups still persist in polystyrene-based exchangers, but

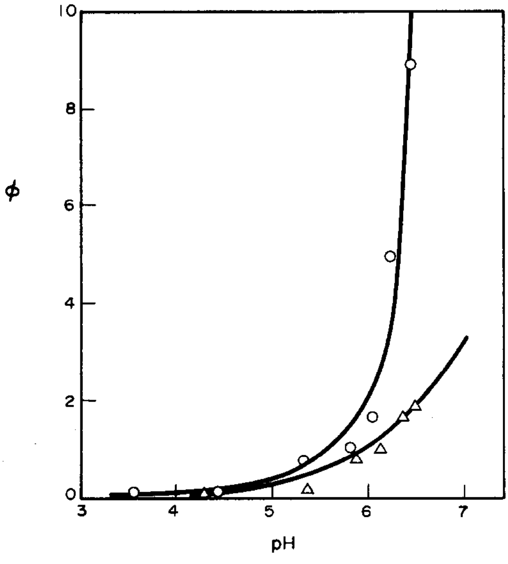

Fig. 5. Distribution of Ce(III) between De-Acidite FF and 0·5*M* $NaClO_4$. ○—Carrier-free ^{144}Ce(III); △—$10^{-7}M$ Ce(III).

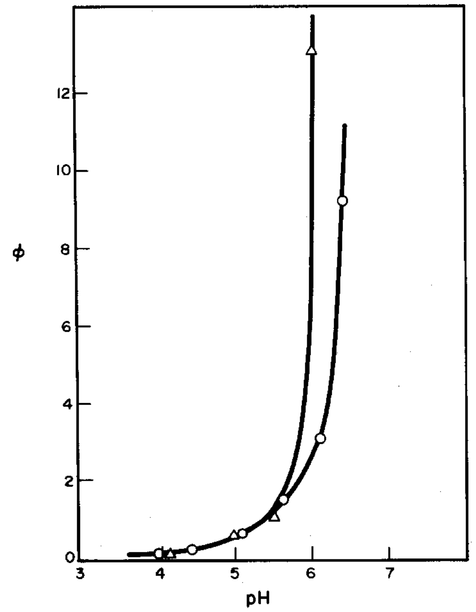

Fig. 6. Distribution of carrier-free ^{144}Ce(III) between hydrocarbon beads and 0·5*M* $NaClO_4$. ○—Untreated hydrocarbon beads; △—hydrocarbon beads treated with $KMnO_4$.

at very low levels. Thus the effect is only likely to be manifest under conditions where (1) there are very small amounts of ion available for exchange, to avoid saturation of the capacity and (2) the cation-exchange is not obscured by a normal exchange function such as is available on sulphonated polystyrenes. Thus evidence from the literature is most likely to come from studies in which anion-exchangers and trace amounts of ions are involved.

The freeing of ^{140}Ba from its daughter ^{140}La by passing the mixture through Dowex-1 in the hydroxide form[7] may well result from retention of the La(III) on carboxyl groups rather than hydroxide precipitation as hitherto assumed. Likewise, the previously obscure[8] affinity of ^{90}Y absorbed from sodium carbonate solutions by Dowex-1 may be explained. Tervalent lanthanides are not appreciably absorbed by a strong base anion-exchanger from nitric acid of a wide concentration range but at low acidity and in the presence of lithium nitrate absorption occurs readily and in an order expected for a cation-exchanger; a separation of ^{140}Ba from ^{140}La by eluting the former with 3–4*M* lithium nitrate was proposed.[9] While other factors such as changes in activity coefficients and electrolyte inversion may be important in this instance, the participation of carboxyl groups cannot be ruled out on the available evidence. Finally, there are several nuclear reactions[10,11] in which the required product-nuclide has a normal oxidation state higher than that of the parent following a change in atomic number, *e.g.* ^{7}Li(p,n)^{7}Be, ^{109}Ag(d,2n)^{109}Cd and ^{116}Cd(n,γ)^{117}Cd → ^{117}In. Carrier-free separations of the required product from the target might usefully be achieved in some instances by using the secondary cation-exchange capacity of an anion-exchanger.

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Summary—The pH-dependent distribution of carrier-free radioisotopes between aqueous phases at constant ionic strength and polystyrene–divinylbenzene type exchangers reveals the presence of a secondary exchange function attributable to carboxyl groups. Cation- and anion-exchangers of the sulphonate and quaternary ammonium types possess this additional cation-exchange capacity which is, however, relatively very low in currently available commercial resins. Its influence on separations involving radioisotopes of high specific activity is discussed.

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LE DOSAGE DE L'ETAIN DANS LES SEDIMENTS PAR SPECTROPHOTOMETRIE D'ABSORPTION ATOMIQUE*

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L'étain dans les sédiments agit comme collecteur de métaux lourds et joue donc le rôle d'indicateur de zones minéralisées en prospection géochimique. On le rencontre[1] dans le réseau silicaté, dans la cassiterite enrobée dans le silicate et dans la cassiterite aisément accessible. Comme c'est sous cette dernière forme qu'il est intéressant du point de vue géochimique et comme sa teneur moyenne[2] dans les sédiments est de l'ordre de 7 ppm, il nous fallait trouver une méthode sensible, précise et rapide nous permettant de le doser sous cette forme dans environ 20000 échantillons par année.

Plusieurs auteurs[3–5] ont utilisé dans leur méthode de l'iodure d'ammonium pour sublimer l'étain. La grande difficulté de cette attaque réside dans le fait qu'il apparaît difficile d'obtenir des résultats répétitifs puisque la température théorique de sublimation[5] de l'oxyde stannique en présence d'iodure d'ammonium se situe entre 425 et 475° et que la température de condensation de l'iodure stannique formé se situe aux environs de 145°. Le danger de perdre une partie du produit de la sublimation est grand si la température du chauffage est trop élevée et par contre un chauffage insuffisant peut conduire à une libération incomplète de l'étain. Ces problèmes ont été résolus grâce à la conception dans nos laboratoires d'un assemblage que nous appelons "appareil de sublimation–condensation". Cet appareil est constitué d'un four "Thermolyne" dont une paroi est remplacée par une plaque de fonte. La température à la surface de la plaque se rapproche de celle que l'on retrouve à l'intérieur du four auquel est superposé un boîtier réfrigéré à l'eau courante. De cette façon, on peut contrôler la température de la sublimation et de la condensation tout en volatisant l'étain de quarante échantillons simultanément. Nous donnons une description détaillée de cet appareil à la figure 1.

PARTIE EXPERIMENTALE

Appareillage

Spectrophotomètre d'absorption atomique Varian Techtron modèle AA-5 couplé à un numériseur DI-30, un brûleur air–acétylène de 10 cm modèle AB-51 de Varian Techtron et une cathode creuse d'étain ASL No. CA 739.

Appareil de sublimation–condensation schématisé à la figure 1.

Conditions opératoires

Longueur d'onde:	224·6 nm
Courant de la cathode:	8 mA
Fente:	150 μm
Débit d'aspiration:	5 ml/min
Position du brûleur:	9
Nature de la flamme:	air–hydrogène riche
Pression d'air:	9·5 l./min à 18 lb/po^2
Débit d'hydrogène:	13·5 l./min à 10 lb/po^2

Réactifs

Acide chlorhydrique concentré.

Acide ascorbique.

Iodure d'ammonium.

Chlorure stannique.

Solution d'acide ascorbique à 1% dans l'acide chlorhydrique 1:4.

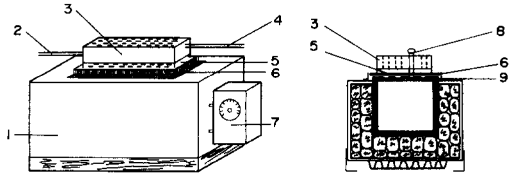
Solution de réglage. Sublimer 50 g d'iodure d'ammonium pendant 20 mn à 550°, reprendre le résidu avec la solution d'acide ascorbique à 1% dans l'acide chlorhydrique 1:4 et étendre à un litre avec la même solution.

Solution d'étain à 1000 μg/ml. Dissoudre 0,295 g de $SnCl_4.5H_2O$ dans 100 ml d'acide chlorhydrique 1:4.

Solutions étalons. Préparer cinq solutions contenant respectivement 0,2, 0,5, 1,0, 2,0 et 3,0 μg/ml d'étain par dilution de la solution à 1000 μg/ml d'étain avec la solution de réglage.

Mode opératoire

Calciner 1,0 g d'échantillon dans un creuset de porcelaine pendant une heure à 550°. Introduire l'échantillon calciné dans une éprouvette en Pyrex de 25 ml et ajouter 0,5 g d'iodure d'ammonium. Mélanger les deux substances en agitant bien l'éprouvette et la déposer dans l'appareil à sublimation–condensation. Laisser sublimer pendant 20 mn à 550°. Retirer l'éprouvette de l'appareil et reprendre le produit de la sublimation avec 10 ml de la solution d'acide ascorbique à 1% dans l'acide chlorhydrique 1:4. Agiter, filtrer sur un papier Whatman No. 40 et recueillir le filtrat dans une autre éprouvette de 25 ml. Régler le numériseur au zéro avec la solution de réglage ou de l'eau déminéralisée et étalonner l'appareil d'absorption atomique. Pour toute dilution de la solution de l'échantillon,



Vue d'ensemble Vue en coupe

Fig. 1. Appareil de sublimation–condensation. *1*—Four "Thermolyne" type 6020 tourné de côté de façon à ce que la porte du four soit dans la partie supérieure; *2*—entrée d'eau froide; *3*—condensateur en acier inoxydable permettant l'introduction de 40 éprouvettes; *4*—sortie d'eau; 5—isolant d'amiante de 1/4-po. d'épaisseur troué en quarante endroits et recouvrant la plaque chauffante; *6*—fer angle retenant l'isolant autour de la plaque chauffante; 7—régulateur de température Dubuque III; *8*—éprouvette en place pour la sublimation; 9—plaque en fonte ayant à sa surface 40 cavités épousant la forme du fond d'une éprouvette (cette plaque occupe la place de la porte du four).

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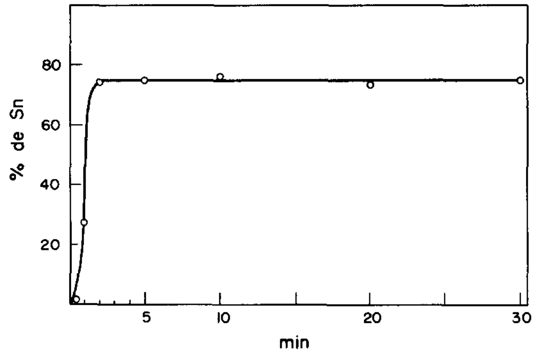

Fig. 2. Influence de la durée de sublimation sur la récupération de l'étain dans un minerai de cassitérite.

utiliser la solution de réglage. Lire directement la concentration d'étain dans l'échantillon sur le numériseur.

RESULTATS ET DISCUSSION

Température et durée de la sublimation

On a mélangé 1 g d'échantillon à 0,5 g d'iodure d'ammonium et on a chauffé pendant 20 mn. Tout comme Heffernan *et al.*,[5] on a observé que la sublimation est complète à 500° et stable jusqu'à au moins 600°. Nous avons opté pour une température de 550° afin d'obtenir une sublimation entière. Pendant la sublimation, la température au milieu de l'éprouvette ne dépasse pas 65° alors qu'elle n'est que de 35° dans la partie supérieure. Le système de réfrigération est donc tout à fait efficace et permet une condensation maximum de l'iodure stannique formé. Comme l'indique la figure 2, une durée de sublimation de 20 mn est amplement suffisante pour obtenir une réaction totale.

Choix et conditions de la flame

On a calculé la sensibilité inverse pour différents types de flamme et les résultats apparaissent au tableau 1. La flamme hydrogène–azote est celle qui nous donne le plus de sensibilité mais les interférences cationiques y sont cependant beaucoup plus importantes qu'avec une flamme air–hydrogène.[6,7] De plus, on obtient un signal plus stable avec une flamme air–hydrogène de sorte que, malgré une sensibilité inférieure, la limite de détection est la même que pour une flamme hydrogène–azote. Ainsi, notre choix s'est porté sur une flamme air–hydrogène et la flamme réductrice s'est avérée la plus sensible.

Etude des interférences

Les interférences d'une part causées par les cations en solutions ont été étudiées par plusieurs auteurs[5,6,8–11] et sont en général peu importantes dans une flamme air–hydrogène; d'autre part, les seuls cations que l'on peut trouver en solution après une sublimation à l'iodure d'ammonium sont peu nombreux et sont ceux qui sont rapidement extractibles à froid dans une solution d'acide chlorhydrique 1:4 ou ceux qui peuvent former des oxydes qui se subliment en laissant des iodures solubles. Pour ces deux raisons notre étude des interférences n'a porté que sur l'influence des produits de la sublimation.

Tableau 1. Sensibilité inverse de l'étain dans différentes flammes

Flamme	Sensibilité inverse en µg/ml pour 1% d'absorption
air–acétylène	33·3
oxyde nitreux–acétylène	25·0
air–hydrogène	2·0
hydrogène–azote	1·0

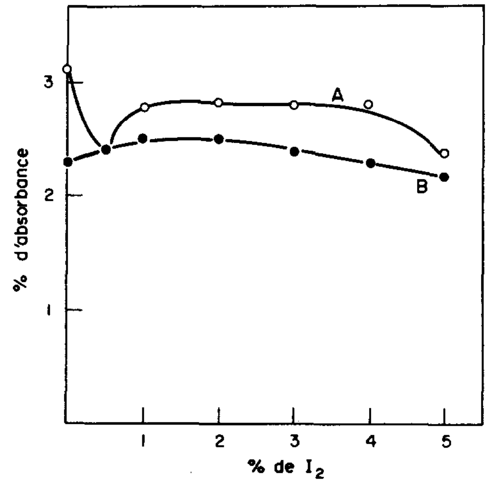

Fig. 3. Influence de I_2 et de l'acide ascorbique sur l'absorbance de l'étain. A—Solution de 5 ppm de Sn + % de I_2. B—Solution de 5 ppm de Sn dans une solution d'acide ascorbique à 1% + % de I_2.

Après la sublimation, on retrouve en solution NH_4^+, I^- et I_2. L'absorbance d'une concentration donnée d'étain augmente linéairement avec la concentration d'ions ammonium tandis qu'elle n'est pas affectée par la présence d'ions iodure. L'influence de l'iode est illustrée à la figure 3.

Dans le but d'augmenter la sensibilité de la méthode, on a concentré l'étain en solution en diminuant le volume recommandé de la solution d'acide chlorhydrique 1:4. Les courbes II et III de la figure 4 représentent les résultats obtenus en reprenant le produit de la sublimation par 5 et 10 ml respectivement de la solution acide. On se rend compte qu'il n'y a rien à gagner à vouloir concentrer la

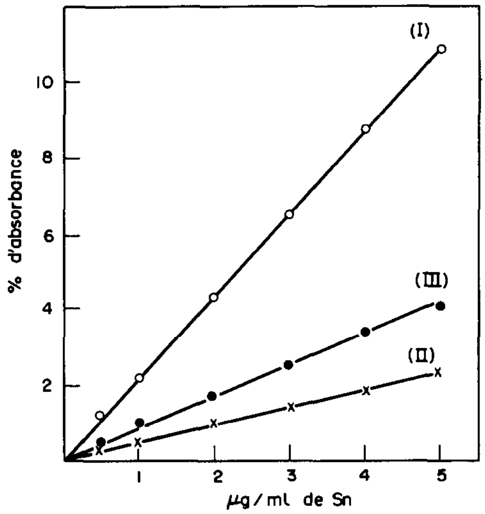

Fig. 4. Influence globale de toutes les substances ajoutées sur l'absorbance de l'étain. I—Etain présent dans une solution d'acide chlorhydrique 1:4. II—Etain présent dans une solution d'acide chlorhydrique 1:4 contenant 7% de NH_4I + 3% I_2 et 1% d'acide ascorbique. III—Etain présent dans une solution d'acide chlorhydrique 1:4 contenant 3·5% de NH_4I + 1·5% I_2 et 1% d'acide ascorbique.

Tableau 2. Récupération des ajouts

Numéro de l'échantillon	Teneur, *ppm*	Ajout, *ppm*	Teneur trouvée, *ppm*
18330	14	0	14
18330	14	2·5	17
18330	14	5·0	19
18330	14	10·0	22
18330	14	15·0	28
18330	14	25·0	36

solution d'étain en diminuant le volume de la solution d'acide. En effet l'accroissement du signal dû à la plus grande concentration d'étain est annulé par la diminution causée par l'augmentation des sels en solution. L'examen de ces trois courbes nous laisse entrevoir que l'influence totale des substances ajoutées est surtout liée à la quantité de sels en solution et non pas aux espèces elles-mêmes. Ceci implique que la quantité d'iodure d'ammonium employée pour la sublimation doit être la même pour chacun des échantillons et que les solutions étalons doivent contenir les mêmes quantités d'ions ajoutés que l'on retrouve dans la solution de reprise des échantillons après sublimation. La courbe III représente donc la courbe d'étalonnage correspondant aux solutions obtenues par la méthode proposée.

Récupération

Une série de sublimation de cassitérite pure a été faite par cette méthode et la récupération variait entre 85 et 100%. De plus des essais sur la récupération d'ajouts ont été effectués et les résultats sont présentés au tableau 2. Nous présentons en outre au tableau 3 une comparaison de nos résultats avec les valeurs recommandées pour une douzaine d'étalons géologiques internationaux et là encore les résultats sont très acceptables. Enfin, le tableau 4 nous indique une reproductibilité satisfaisante de la méthode.

Tableau 3. Dosage de l'étain dans différents étalons géologiques

Echantillon	Valeur admise, *ppm*	Valeur obtenue, *ppm*
AGV-1	4·2	4
BR	8	8
DT-N	5	3
G-2	1·5	1
GH	10	7
GM	4·6	5
GSP-1	6·3	6
JG-1	3	3
Sy-1-0	11	9
Sy-2-0	2·5	4
Sy-3-0	4·8	6
TB-1	6	5

Tableau 4. Reproductibilité de la méthode

Echantillon	Nombre de dosages	Valeur moyenne, *ppm*	Ecart relatif, %
RC-1	133	2·4	25·9
MB-1	79	6·4	15·5
SN-1	30	8·0	13·6
G-1016	12	24·6	7·8

Les résultats présentés ont été obtenus à partir de quatre échantillons dosés pour l'étain par des techniciens différents à des jours différents et avec des appareils différents.

Conclusion

Même si l'addition d'acide ascorbique abaisse légèrement l'absorbance de la solution, elle a pour effet de stabiliser le signal émis et de réduire d'environ 50% l'iode formé donnant ainsi une solution limpide pouvant être atomisée. On doit remarquer en outre que la stabilité des solutions contenant de l'iode n'est que de 2 ou 3 jours. On note en effet une augmentation de l'absorbance d'environ 2% par jour et elle est régulière du moins pour les dix jours qui suivent la préparation des solutions.

Cette méthode a déjà été utilisée pour l'analyse de plus de 20000 échantillons de sédiments de ruisseaux et les résultats se prêtent bien à l'interprétation géochimique grâce à la précision qu'elle peut fournir pour les basses teneurs. Cette méthode pourrait aussi se prêter au dosage de l'étain dans les sols. Nous envisageons actuellement de doser l'antimoine à partir de la même solution et nous devrions présenter des résultats sous peu à ce sujet.

Remerciement—Les auteurs remercient M. Normand Rhéaume pour son ingénieuse assistance technique.

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Résumé—On décrit une méthode simple, rapide et reproductible pour doser 1 à 50 ppm d'étain présent dans des sédiments. L'étain présent dans l'échantillon sous forme de cassiterite est sublimé en présence d'iodure d'ammonium. L'iodure stannique formé est dissous dans une solution d'acide chlorhydrique contenant de l'acide ascorbique. L'étain en solution est finalement dosé par spectrophotométrie d'absorption atomique. Aucune interférence n'a été observée et la méthode a été éprouvée en analysant quelques étalons géologiques. Dans tous les cas les résultats obtenus concordent avec les valeurs recommandées. Un technicien peut analyser 250 échantillons par jour en suivant la méthode proposée.

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DETERMINATION OF ADRENALINE AND NORADRENALINE BY RESONANCE RAMAN SPECTROMETRY

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Conventionally, determination of adrenaline and noradrenaline in urine and other matrices is carried out by fluorimetry after conversion of the catecholamines into the trihydroxyindoles.[1,2] The method suffers from certain disadvantages. First, as with other fluorimetric methods, it is susceptible to interference from a variety of quenching agents. Second, many pharmaceuticals give fluorescent products, which may interfere. Finally, adrenaline and noradrenaline are not differentiated by the procedure. However, adrenaline alone will undergo the initial oxidation in acidic solution, so noradrenaline can be determined by difference.

In the past few years, resonance Raman spectrometry has emerged as a sensitive and selective probe for many molecules of biological interest.[3] Most workers have confined their studies to molecules which themselves can show resonance-enhanced Raman spectra. A few attempts to prepare derivatives suitable for resonance Raman spectrometry have been reported.[4,5]

Moreover, the potential of resonance Raman appears to have been largely overlooked by analytical chemists, although the technique is simple, offers high resolution and freedom from the quenching effects which plague fluorescence.[6] The principal drawback of resonance Raman spectrometry is the fact that conventional spectrometers cannot distinguish between Raman scattering and fluorescence. With the advent of convenient instrumentation for fluorescence-rejecting techniques such as coherent anti-Stokes scattering,[7,8] inverse Raman spectrometry,[9] and time-resolved Raman spectrometry[10,11] the fluorescence problem appears tractable.

In the present communication we report the application of resonance Raman spectrometry to the determination of adrenaline and noradrenaline as the aminochromes. Aerial oxidation of these molecules, catalysed by copper(II), is well known.[12] The technique is simple, applicable to concentrations as low as 1 × $10^{-6}M$ and allows determination of adrenaline and noradrenaline on a single sample.

EXPERIMENTAL

Apparatus

A Spex 1401 double monochromator, a cooled RCA C31034A photomultiplier and both d.c. and photon-counting detection systems were used for these experiments. Slit-widths of 400 μm (9 cm^{-1}) were employed. Scan-rates of 20–50 cm^{-1}/min were used. The excitation source was a Coherent Radiation CR-5 argon-ion laser. Melting point capillaries were used as sample containers, with conventional transverse excitation and observation at 90° to the incident radiation. Absorption spectra were obtained with a Cary 14 spectrophotometer.

Reagents

Adrenaline hydrogen tartrate and noradrenaline hydrogen tartrate were obtained from the Sigma Chemical Company and used as received. Stock solutions of these reagents were stored under refrigeration and replaced at frequent intervals. All other reagents were of ACS reagent grade.

Procedure

The aminochromes were prepared by addition to the catecholamines of stock copper(II) sulphate, ammonium chloride and potassium nitrate solutions to make the solutions 0·01*M* in cupric ion, 0·04*M* in ammonium ion, and 0·05*M* in nitrate. The pH of the resulting solution was adjusted to 5 with ammonia. Raman scattering intensity was measured at 1480 cm^{-1} (adrenaline) and 1430 cm^{-1} (noradrenaline), the nitrate 1050-cm^{-1} line being used as an internal standard. Ar^+ 496·5-nm excitation is optimum, but Ar^+ 488·0 nm may be used.

RESULTS AND DISCUSSION

Absorption spectra of the aminochromes formed are shown in Fig. 1. The compounds have similar spectra, but the adrenaline product shows higher absorption. In the absence of ammonium ion similar spectra were observed, but with lower intensities, implying incomplete oxidation.

The resonance Raman spectra of the adrenaline and noradrenaline aminochromes are presented in Fig. 2. In addition to these bands, weaker bands occur around 1680, 1625, 1100 and 500 cm^{-1}. The two bands of the adrenaline species at 1480 and 1465 cm^{-1} and the single band of noradrenaline at 1430 cm^{-1} allow ready differentiation of these compounds. Interpretation of these spectra is in progress and will be reported at a later date.

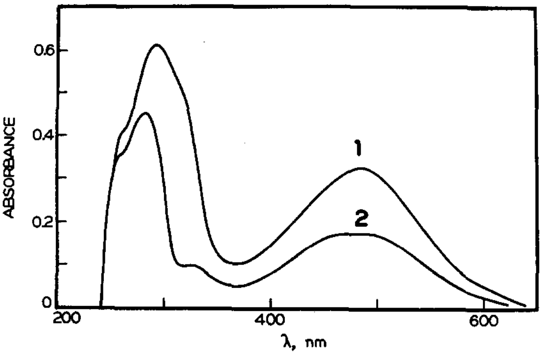

Fig. 1. Absorption spectra of aminochrome systems, pH = 5. 1—1 × $10^{-4}M$ adrenaline; 2—1 × $10^{-4}M$ noradrenaline.

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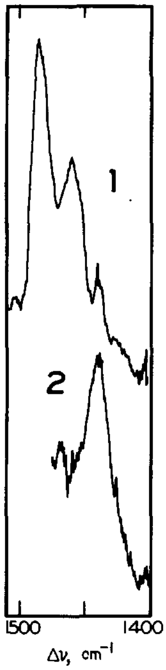

Fig. 2. Resonance Raman spectra of aminochromes, λ_e = 496·5 nm. 1—1 × $10^{-5}M$ adrenaline; 2—1 × $10^{-5}M$ noradrenaline.

Table 1. Concentration dependence of aminochrome resonance Raman scattering

Adrenaline		Noradrenaline	
$C, 10^{-5}M$	$I_{\text{sample}}/I_{\text{NO}_3^-}$	$C, 10^{-5}M$	$I_{\text{sample}}/I_{\text{NO}_3^-}$
0·45	0·032	0·55	0·025
1·05	0·082	1·00	0·045
1·60	0·122	4·0	0·140
2·03	0·158	6·0	0·205
3·00	0·230	7·5	0·260
6·0	$0{\cdot}47_5$	9·0	$0{\cdot}30_5$
7·0	$0{\cdot}56_0$	10·0	$0{\cdot}35_2$
8·0	$0{\cdot}64_2$		
10·0	$0{\cdot}80_5$		

Table 1 shows analytical data for these solutions. The working curve is linear over the range 5×10^{-6}–$2 \times 10^{-4}M$. Above the $10^{-5}M$ level, the precision of the measurements is about ±3%. Although signals are detectable down to about the $10^{-6}M$ level, the noise in our system is too great to allow analytical use of the signals below about $5 \times 10^{-6}M$. More sophisticated signal conditioning could probably lower the detection limits and the limit of the useful concentration range.

Our current studies have been limited to synthetic solutions. We have carried out some preliminary experiments on urine matrices. Prior concentration of the catecholamines by the conventional technique of adsorption on alumina and elution with acid[1] is necessary to bring the concentrations to a usable level. This step also serves to remove fluorescent substances from the sample. Our results show that adrenaline and noradrenaline from urine samples are detectable by this technique. Studies of various clinical specimens are now in progress to determine the relative merits of the resonance Raman and fluorimetric approaches to catecholamine determination.

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Summary—Aminochromes of adrenaline and noradrenaline show resonance Raman scattering at 1480 and 1430 cm^{-1} respectively, with Ar$^+$ excitation. Scattering intensity is a linear function of concentration. Detection limits are $1 \times 10^{-6}M$. Both catecholamines can be determined in a single measurement.

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SUR L'ETAT D'OXYDATION DE L'*o*-TOLIDINE

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(Reçu le 12 février 1974. Révisé le 19 décembre 1974. Accepté le 27 mars 1975)

La benzidine et ses dérivés développent par oxydation des colorations bleue ou jaune.[1–11] Dans le cas de l'*o*-tolidine (diméthyl-3,3′ benzidine), l'oxydation par V^{5+} conduit, suivant le pH, à des colorations variables. La figure 1 montre qu'à pH > 3 la coloration est bleue, tandis qu'elle est jaune à pH inférieur. L'oxydation de la benzidine et ses dérivés, en particulier de l'*o*-tolidine, a fait l'objet de nombreux travaux tendant à élucider le mécanisme de la réaction et la structure des dérivés obtenus. Celle du colorant bleu formé n'était pas encore précisée.

Par spectrophotométrie infrarouge (Unicam SP 200) en nujol, nous avons constaté l'existence des bandes d'absorption caractéristiques de la fonction imine (1560–1570, 1620–1640, 3300–3350 cm^{-1}) ainsi que celles de la fonction $-NH_2$ (660, 680, 1260, 1620–1640, 3200–3500 cm^{-1}). Ces résultats, en accord avec ceux précédemment obtenus,[4–8] confirment pour le dérivé formé une structure de monoquinone imine.

Notre étude a été poursuivie par potentiométrie et photométrie au cours de l'oxydation de l'*o*-tolidine à différents pH par plusieurs oxydants ainsi que de la réduction du dérivé jaune, terme final de la réaction.

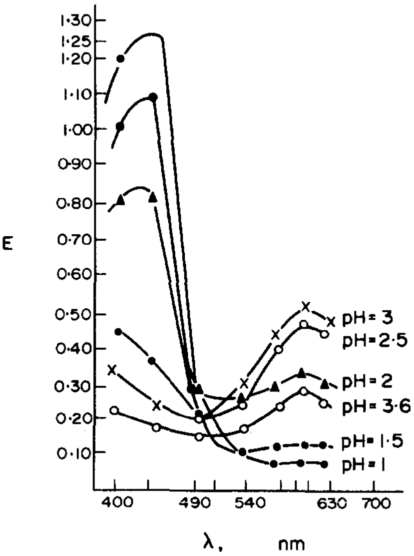


Fig. 1.

Oxydation de l'o-tolidine

Divers oxydants ont été utilisés: $K_2S_2O_8$, I_2, $KMnO_4$, $K_2Cr_2O_7$, $NaNO_2$, NH_4VO_3. Seul, le persulfate a permis la mise en évidence, au cours de l'oxydation quantitative, de deux sauts de potentiel.

(*a*) A pH > 3, par exemple à pH $= 4{,}0$ en tampon acétate–acide acétique, l'oxydation de l'*o*-tolidine en solution 0,005*M* par le persulfate 0,005*M* montre deux virages respectivement pour 2,7 et 5,65 ml de solution oxydante, soit par molécule d'amine l'échange final de deux électrons (figure 2). Les mêmes résultats ont été obtenus en solutions 0,02*M*.

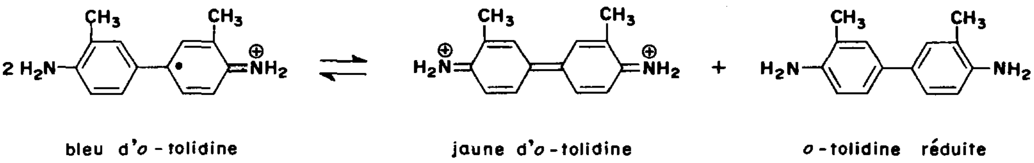
(*b*) A pH < 3, en acide sulfurique par exemple (pH $=$ 1,5–2) pour des solutions 0,01*M* d'*o*-tolidine et de persulfate, le tracé de la courbe de titration (figure 3) montre également deux sauts de potentiel correspondant respectivement à l'échange d'un (virage de la coloration du jaune au brun), puis de deux (virage du brun à l'orange) électrons par mole d'amine.

Lors du premier virage, les colorations différentes obtenues à pH > 3 ou pH < 3 peuvent s'expliquer, à pH < 3, par dismutation de l'*o*-tolidine oxydée en bleu d'*o*-tolidine.

L'oxydation de l'*o*-tolidine (0,005*M*) par des quantités croissantes de persulfate (0,005*M*) a été suivie également par spectrophotométrie à 597 nm (coloration bleu) ou 434 nm (coloration jaune). Les lectures, après 5 minutes, ont permis le tracé du graphique, représentant les valeurs d'extinction en fonction du volume de solution oxydante (figure 4).

On voit que l'extinction due à la coloration jaune (courbe 2) augmente jusqu'à réaction complète et équimoléculaire entre l'*o*-tolidine et $K_2S_2O_8$, la coloration finale est jaune.

L'extinction due à la coloration bleue (courbe 1) qui se forme intermédiairement augmente jusqu'à consommation de 0,5 mole $K_2S_2O_8$ puis diminue: le colorant bleu, état intermédiaire de la réaction s'oxydant ensuite en dérivé jaune.



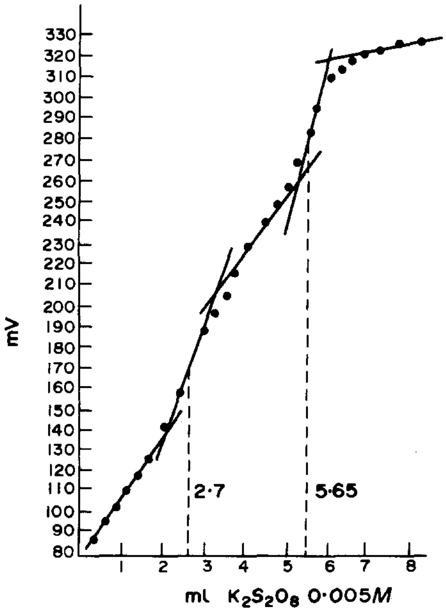


Fig. 2.

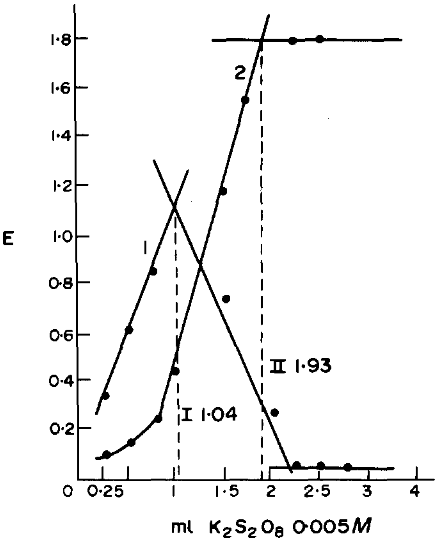


Fig. 4.

Réduction du produit d'oxydation (à pH > 3) de l'o-tolidine (colorant jaune)

Le jaune d'*o*-tolidine a été préparé en traitant 5 ml d'*o*-tolidine 0,005*M* par 2 ml de solution tampon acétate–acide acétique pH = 4,0, 5,65 ml $K_2S_2O_8$ 0,005*M* et 18 ml d'eau.

Par titrage potentiométrique à l'aide de la solution à 1,5% d'iodure de potassium, la courbe de titration montre un seul saut de potentiel (figure 5), la coloration de la solution virant du jaune au bleu.

Le même résultat a été obtenu en titrant potentiométriquement la solution d'*o*-tolidine oxydée par le thiosulfate 0,01*M*. La courbe de titration (figure 6) montre encore un seul saut de potentiel correspondant au virage du jaune au bleu. L'équivalence a également été obtenue avec $Na_2S_2O_3$ 0,1 ou 0,002*M*. Dans tous les cas, la réduction quantitative correspond à l'échange d'un électron.

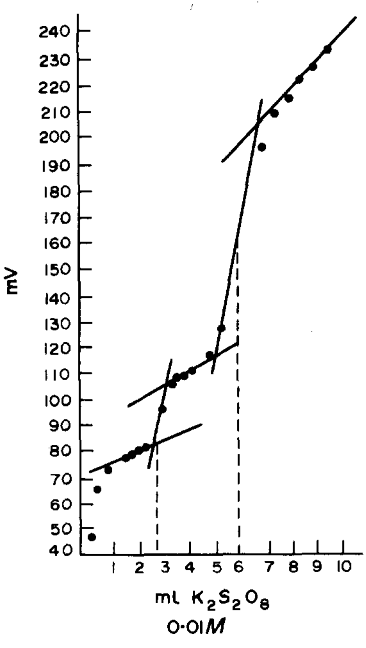
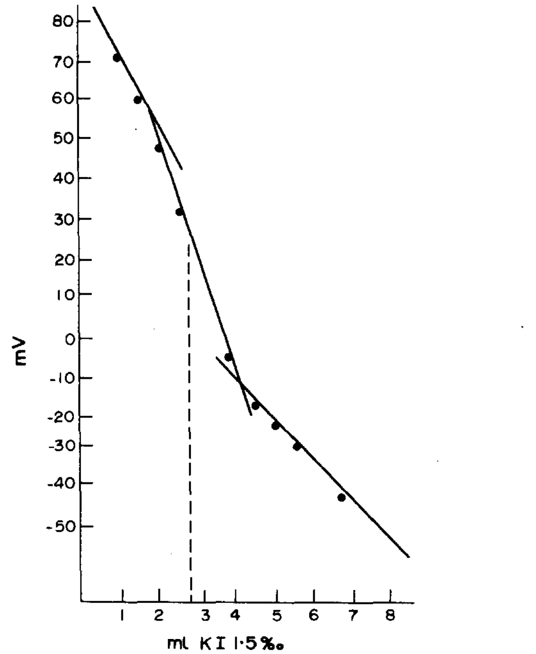


Fig. 3.



2·9ml KI 1·5‰≈25ml KI 0·01M≈10ml KI 0·025M

Fig. 5.

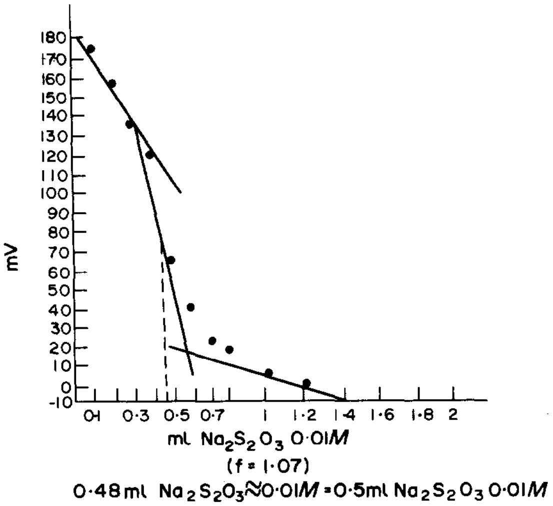
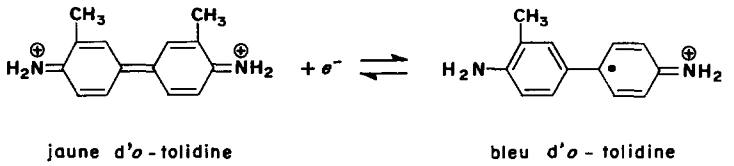


Fig. 6.

Avec les réserves d'usage, on peut proposer le schéma réactionnel suivant:



Conclusion

Pour l'étude de l'*o*-tolidine, c'est avec le persulfate que la mise en évidence des deux sauts de potentiel est la plus nette. A pH > 3, les deux sauts de potentiel correspondent à la formation de deux composés: un colorant bleu, forme intermédiaire d'oxydation avec perte d'un électron, et un colorant jaune correspondant à la perte de deux électrons. A pH < 3, deux sauts de potentiel ont été observés mais la coloration demeure jaune, la forme bleue intermédiairement formée subissant une dismutation. La réduction du jaune d'*o*-tolidine, forme finale d'oxydation, s'effectue par l'iodure ou le thiosulfate avec un seul saut de potentiel correspondant au retour au colorant bleu.

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Résumé—L'oxydation de l'*o*-tolidine s'effectue en deux temps avec formation successive d'un colorant bleu puis d'un colorant jaune correspondant respectivement chacun à la perte d'un électron. La réduction de la forme jaune en colorant bleu a également lieu avec échange d'un électron.

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ANALYTICAL DATA

SENSITIVE TESTS FOR NITRITE THROUGH AZO-DYE FORMATION

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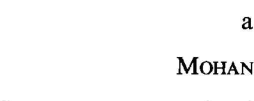
Nitrite reacts with sulphanilic acid, forming the diazonium cation **I**. When the cation is coupled with pyridinols (2-amino-3-pyridinol, 2,3-pyridinediol and 5-chloro-2,3-pyridinediol), the red azo-dyes **II–IV** result. Their formation is used in detection and determination of nitrite (or nitrate after its reduction with zinc dust). The method affords more sensitivity and selectivity than many of the similar methods[1,2] of nitrite detection.

(I)

(II)



(III) when R = H
(IV) when R = Cl

EXPERIMENTAL

Solutions of the pyridinols were prepared by dissolving 500 mg in 100 ml of ethanol. Other solutions employed were: 1% w/v sulphanilic acid in 30% acetic acid, ammonia solution (1 + 1) and 50 μg/ml nitrite (sodium nitrite was used). All other solutions were prepared from reagent grade chemicals in doubly distilled water.

Procedure for detection of nitrite

Place a drop of the nitrite solution on a spot-plate, add 2 or 3 drops of ammonia solution and 1 drop each of the sulphanilic acid and 2-amino-3-pyridinol solutions, whereupon a red colour develops instantaneously. With the other two pyridinols, the order of addition should be nitrite, sulphanilic acid, pyridinol, ammonia.

With 2-amino-3-pyridinol as coupling agent, the tolerance limits (in μg/ml) of various ions are: 10000 each of Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}, $SO_2O_8^{2-}$; 7500 of Al^{3+}; 7000 of F^-, 5000 each of I^-, CNS^-, BO_3^{3-}, PO_4^{3-}; 4000 each of Br^-, SO_3^{2-}, $C_2O_4^{2-}$, tartrate, MoO_4^{2-}, thiourea; 3500 of citrate; 1500 each of Mg^{2+}, In^{3+}, Fe^{3+}; 1000 each of Ca^{2+}, Sr^{2+}, Ba^{2+}; 280 of UO_2^{2+}; 200 of Pb^{2+} and 50 of Sc^{3+}. With 2,3-pyridinediol as coupling agent, they are: 10000 each of Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, $S_2O_8^{2-}$, thiourea; 7500 of $C_2O_4^{2-}$; 7000 of SO_4^{2-}; 5000 each of F^-, tartrate; 4000 of citrate; 3500 of SO_3^{2-}; 2500 each of BO_3^{3-}, PO_4^{3-}; 1200 of In^{3+}; 1000 of Mg^{2+}; 800 each of Ca^{2+}, Sr^{2+}, Ba^{2+}; 120 each of Al^{3+}, UO_2^{2+}, Fe^{3+} and 100 of Sc^{3+}. With 2-chloro-3-pyridinol, the tolerances are: 10000 each of Cl^-, Br^-, I^-, CNS^-, NO_3^-, $S_2O_8^{2-}$, SO_4^{2-}, thiourea; 7500 of $C_2O_4^{2-}$; 5000 each of F^-, SO_3^{2-}, tartrate, citrate; 4000 of BO_3^{3-}; 1000 each of Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, PO_4^{3-}, 600 of UO_2^{2+}; 500 of In^{3+}; 150 each of Mg^{2+}, Fe^{3+} and 100 of Sc^{3+}. In certain cases, the red colour fades after some time, and for determinations, the absorbance should be measured immediately. In presence of Fe^{3+}, the red colour soon changes to that of hydrous ferric oxide. With all pyridinols, Cu^{2+} interfered by producing a violet colour with the dye. Bivalent Zn, Cd, Hg, Co and Ni produced a magenta colour. It seems probable that in these cases the metals displace the hydrogen atom of the —OH group in the dye molecule (**II**, **III** or **IV**) and subsequently co-ordinate through the nitrogen atom of the diazo group marked with an asterisk.

Nitrate determination in water samples

Evaporate the water sample to an appropriate volume. To 1 ml of the sample solution, add 1 ml of ammonia solution, 2 ml each of the sulphanilic acid and 2-amino-3-pyridinol solutions, and finally make up the volume to 10·0 ml. Measure the absorbance at 480 nm. Construct a calibration curve.

The method has been successfully employed in determination of the nitrite content of water samples from wells and pumps.

The limits of identification are 0·02 μg/ml (with 2-animo-3-pyridinol) and 0·01 μg/ml (with the other two pyridinols). The limits of dilution are $1:5 \times 10^7$ (with 2-amino-3-pyridinol) and $1:10^8$ (with the other two pyridinols). The molar absorptivities are $2{\cdot}8 \times 10^4$ $l.mole^{-1}.cm^{-1}$ at 470–485 nm (2-amino-3-pyridinol); $1{\cdot}4 \times 10^4$ at 445–460 nm (2,3-pyridinediol); $2{\cdot}1 \times 10^4$ at 460–475 nm (5-chloro-2,3-pyridinediol).

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Summary—The diazonium cation resulting from the interaction of nitrite with sulphanilic acid is coupled with pyridinols to give red azo-dyes. Compared to many other colour reactions employed for detection of nitrite, the present systems afford greater sensitivity. Many ions do not affect the colour; thus detection and determination are selective. The method is applied in determination of nitrite in water samples.

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PRELIMINARY COMMUNICATIONS

THE DETERMINATION OF WEAK ACIDS IN AQUEOUS SOLUTION BY CATALYTIC THERMOMETRIC TITRIMETRY

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(Received 16 October 1975. Accepted 31 October 1975)

Acetone and acrylonitrile are convenient indicator reagents for use in the determination of weak organic acids in non-aqueous solution by the method of catalytic thermometric titrimetry. The end-points of the titrations are indicated by a sharp rise in temperature caused by the heat evolved in the titrant-catalysed dimerization of acetone[1] and anionic polymerization of acrylonitrile,[2] respectively. Vaughan and Swithenbank[1] have shown that the presence of water in the sample solution has an adverse effect on the end-point sharpness when acetone is used as the thermometric indicator, and it is recommended that the water content of the acetone, which is used as both the indicator and the sample solvent, should not exceed 0.2%. Water and alcohols are regarded as being undesirable impurities in monomers undergoing polymerization by an anionic process because they are proton donors and terminate the growing polymer chains.[3] However, it has been shown[2] that acrylonitrile functions effectively as a thermometric indicator when the solution being titrated contains up to about 1% of water and/or 5% of methanol. The titrants used in conjunction with the acrylonitrile indicator themselves contain alcohols, and the alcohol content of the solution at the end-point is, therefore, dependent on the volume of titrant added.

In the present investigation, it has been established that weak acids can be determined in low concentration in aqueous solution by using the previously-described thermometric procedure with acrylonitrile as the thermometric indicator[2] and a dipolar aprotic

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solvent, dimethyl sulphoxide, as a co-solvent. Titration curves for glycine, cysteine, valine, benzoic acid, phenol, resorcinol, oxalic acid, phosphorous acid, phosphoric acid and boric acid are shown in Fig. 1. It can be seen that sharp end-point inflexions are obtained in the determinations of 0.1 mmole amounts of strong and weak acids in aqueous solution, in concentrations ranging from 1 to 10%. The volume of the 0.5M titrant required to neutralize 0.1 mmole of a dibasic acid is 0.4 ml, while the volume of water in a 1% aqueous sample is about 1 ml. If an aqueous 0.5M titrant were used for the titration of a 2% aqueous sample, containing about 0.5 ml of water, the solution after neutralization would contain less than 1 ml of water. Thus the possibility arises of using aqueous titrants, and this was investigated. In Fig. 2 are shown the titration curves obtained when 2% aqueous solutions of arginine, phenol, resorcinol, benzoic acid, phosphorous acid and phosphoric acid are titrated with 0.5M aqueous potassium hydroxide. The end-point inflexions are distinct but there is a sharp rise in temperature preceding the inflexion, *i.e.*, during the neutralization of the acid. This can be attributed to the exothermic heat of mixing of the water in the titrant with the dimethyl sulphoxide in the titration solution. In contrast, the addition of propan-2-ol to a mixture of water, dimethyl sulphoxide and acrylonitrile results in a fall in temperature at the neutralization stage in most of the titrations shown in Fig. 1.

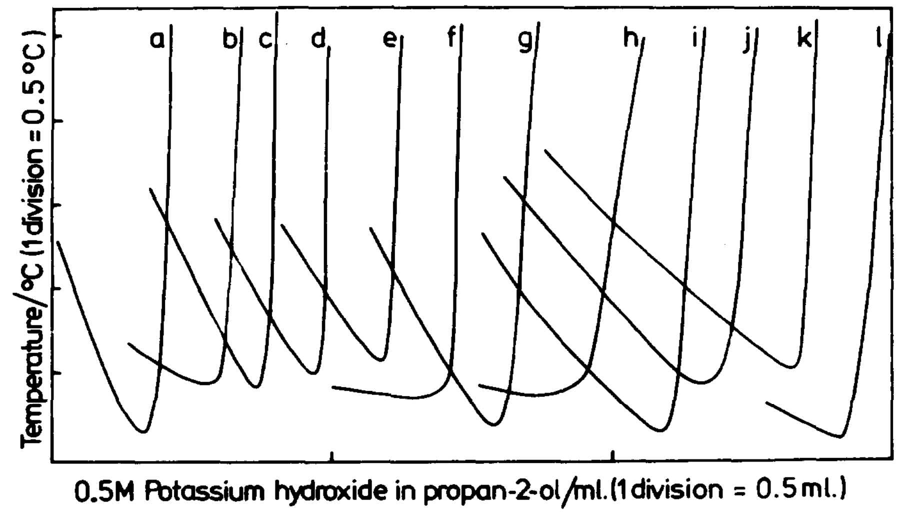

Fig. 1. The catalytic thermometric titration of acids in aqueous solution with 0.5M potassium hydroxide in propan-2-ol.

a, glycine (1.5%);[*] b, cysteine (2%); c, valine (2%); d, benzoic acid (2%); e, phenol (2%); f, phenol (10%); g, resorcinol (2%); h, resorcinol (10%); i, oxalic acid (2%); j, phosphoric acid (1%); k, phosphorous acid (1.1%); l, boric acid (1%).

Conditions: titrant is added at 0.2 ml/min to a mixture of the aqueous sample containing 0.1 mmole of the acid, 4 ml of dimethyl sulphoxide and 2 ml of acrylonitrile.

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[*] Concentration in aqueous solution.

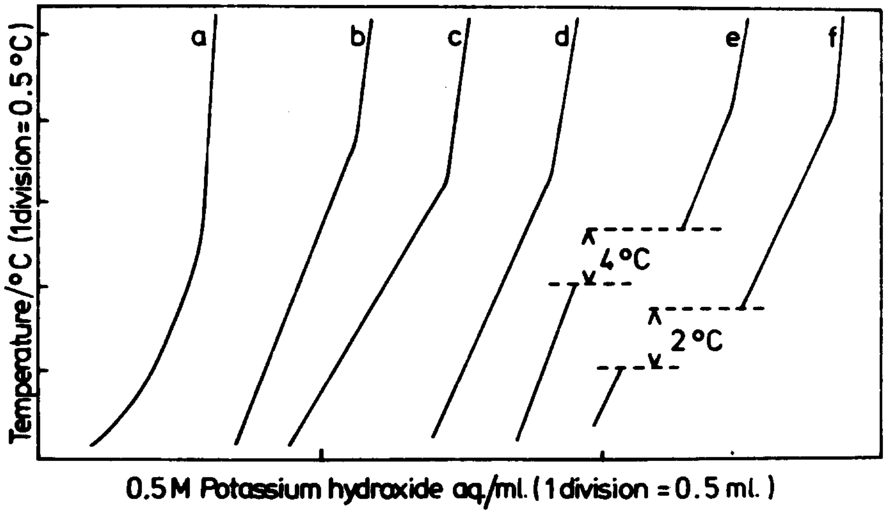

Fig. 2. The catalytic thermometric titration of acids in aqueous solution with 0.5M aqueous potassium hydroxide.

Conditions: as in Fig. 1, apart from the titrant. The acid samples are 2% aqueous solutions. a, arginine; b, phenol; c, resorcinol; d, benzoic acid; e, phosphoric acid; f, phosphorous acid.

It has been established[4] that the measured reaction stoichiometry of resorcinol is dependent on the titrant and the solvent system when the catalytic thermometric procedure is used. Thus, resorcinol is determined as a monofunctional acid in solvents that promote the ionization of the potassium hydroxide titrant, and as a difunctional acid in solvents in which potassium hydroxide exists mainly as an ion-pair. In the solvent mixtures used in the present study, resorcinol shows an intermediate reaction stoichiometry of about 1.5, although a value of 1 might have been expected in the presence of the strongly cation-solvating dimethyl sulphoxide. Apparently, hydrogen bonding with water reduces the ionizing power of the former solvent. The effect of the proportions of water, dimethyl sulphoxide and acrylonitrile on the measured reaction stoichiometry when resorcinol is determined in these mixtures will be discussed in a later contribution. In the present study, phosphoric, phosphorous and oxalic acids are titrated as dibasic acids while boric acid is determined as a monobasic one.

One advantage of using this catalytic thermometric procedure in preference to visual-indicator or potentiometric titrimetry is that weak acids in aqueous solution can be titrated directly. Before determining very weak acids by the visual-indicator or potentiometric methods it is usually necessary to enhance their acidities, either by extracting them into an appropriate non-aqueous solvent, as in the case of phenols, or by adding reagents, such as formaldehyde to amino-acids and mannitol to boric acid.

The exothermic reaction marking the end-point in the titrations is unlikely to be a simple anionic polymerization process because, as noted above, water and alcohols terminate the growing polymer chains. Zilkha and Feit[5,6] have shown that chain transfer and cyanoethylation reactions occur when sodium and potassium alkoxides are used as catalysts for the polymerization of acrylonitrile in the presence of methanol, and they identified the cyanoethylation product of methanol and acrylonitrile in the polymerization mixtures. In their evaluation of quaternary ammonium hydroxides as polymerisation catalysts, they deduced that water can function as a chain transfer reagent in the polymerization of acrylonitrile. The results of these investigations suggest that chain transfer and cyanoethylation reactions, involving water and/or propan-2-ol, are responsible for the temperature rise marking the end-point in the titrations discussed in the present communication.

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A NOVEL COLOUR REACTION FOR ALDEHYDES AND KETONES

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During some experiments with ethanolamine it was found that when formaldehyde was added to it, followed by formic acid, the reaction was exothermic with instantaneous production of a yellow colour. This novel colour reaction was further investigated, with different aliphatic and aromatic aldehydes and mineral acids. The substances tested included reducing sugars (glucose, galactose, xylose, ribose and lactose), aliphatic aldehydes (formaldehyde, butyraldehyde, crotonaldehyde, citronellal and acrolein), heterocyclic aldehydes (furfural), aromatic aldehydes (benzaldehyde, *o*- and *p*-hydroxybenzaldehyde, vanillin, *p*-dimethylaminobenzaldehyde, anisaldehyde and cinnamaldehyde) and ketones (acetone, methyl isobutyl ketone, dimedone, quinone, and levulinic acid). All gave a positive reaction.

The colour was obtained whether the aldehyde or ketone was first treated with ethanolamine, followed by formic acid, or formic acid was reacted with ethanolamine followed by the aldehyde or ketone, but the intensity was higher by the first method. Addition of excess of formic acid or slight warming increased the sensitivity. At low concentrations, a yellow colour was usually obtained, but at higher concentrations of formaldehyde, crotonaldehyde, cinnamaldehyde and furfural, an intense red colour was obtained. Addition of alkali generally decreased the colour intensity; in some cases the colour disappeared. Electron-releasing groups such as hydroxyl, dimethylamino or a double bond conjugated with the carbonyl group, increased the sensitivity. Thus *p*-dimethylaminobenzaldehyde, cinnamaldehyde and crotonaldehyde gave very sensitive reactions, the first being detectable even at the 0.5-μg level.

Amino-acids, phenols (*o*-aminophenol, catechin, catechol, pyrogallol), esters (ethyl acetate), amides (dimethylformamide, asparagine, glutamine), hydrazines, uric acid, alcohols (inositol, geraniol, linalool) and formic acid gave no reaction.

Investigations of the analytical use and the mechanism of this colour reaction are in progress. The colour reaction does not involve quinone formation since aliphatic compounds also gave a positive reaction. It is very likely that the reaction proceeds *via* Schiff's base formation, since no colour reaction was observed when the product obtained after addition of aldehyde to ethanolamine was reduced with $LiAlH_4$. Probably the Schiff's base is rapidly converted into oxazolidine derivatives[1] which react with formic acid to form coloured compounds. The reaction appears to be greatly accelerated in the presence of formic acid, which could not be replaced by mineral acids, and no colour was obtained without it.

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CHROMATOGRAPHIC SEPARATION OF OPTICAL ISOMERS BY MEANS OF OUTER-SPHERE COMPLEX FORMATION REACTIONS

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It was shown earlier that there are differences between the stability constants of outer-sphere complexes formed between the D- and L-forms of an asymmetric anion and an optically active cobalt(III) cation.[1,2] This type of stereoselective complex formation reactions has not so far been used for chromatographic separation of optical isomers.

In our experiments the outer-sphere complex-formation reactions between the optically active $[Co(en)_3]^{3+}$ cation (en = ethylenediamine) and the D- and L-forms of aspartic and mandelic acids were investigated by potentiometric titration and ion-exchange methods, and the stability constants of the outer-sphere complexes were determined. For aspartic acid the stability constants were log $\underline{K}_1$ = 3.06 ± 0.01 for the D-aspartate complex, and log $\underline{K}_1$ = 2.24 ± 0.01 for the L-aspartate complex.

On the basis of the difference between the stability constants of these complexes a new ligand-displacement chromatographic method was developed for the separation of the optical isomers of aspartic and mandelic acid. From the results of our experiments it was established that the nature and concentration of the displacement anion (sulphate, chloride, perchlorate) in the eluent, and the pH, are very important factors affecting the selectivity and efficiency of separation of the optical isomers.

Figure 1 shows the separation of the D- and L-forms of aspartic acid on a weakly acidic cation-exchange resin column loaded with the D-form of optically active $[Co(en)_3]^{3+}$. Stepwise elution with 0.116 and 0.715$\underline{M}$ sodium sulphate was used for the separation. The mandelic acid isomers were similarly resolved.

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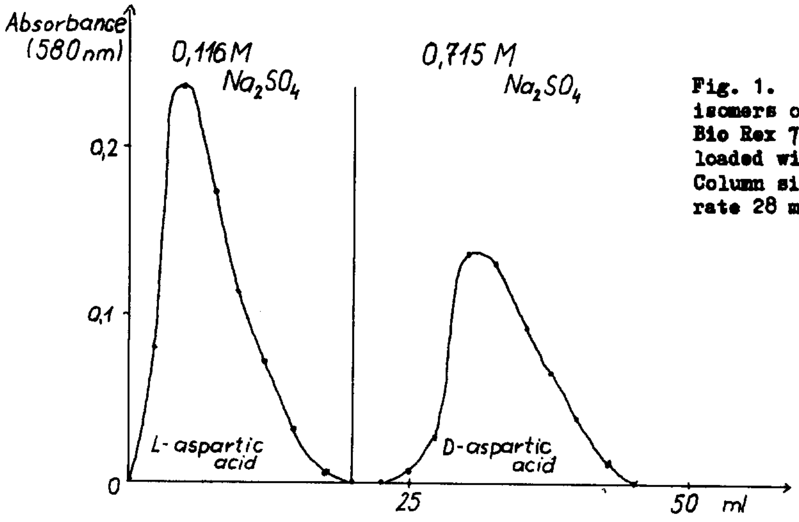

Fig. 1. Separation of optical isomers of aspartic acid on a Bio Rex 70 cation-exchange column loaded with D-$[Co(en)_3]^{3+}$ cations. Column size 7.2 x 0.6 mm; flow-rate 28 ml/hr.

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LETTERS TO THE EDITOR

COLORIMETRIC DETERMINATION OF NYSTATIN

SIR,

Recently a communication[1] dealing with a new colorimetric method for analysis of the polyene antibiotic nystatin was published. That communication, I feel, highlights and reflects some important facts pertaining to nystatin which are of particular interest to analysts and require pointing out.

Most publications (including that of Amer *et al.*) give the impression that nystatin is a single compound. This, in fact, is not true, as is reflected by the work of Shenin[2] and Borowski *et al.*[3] Furthermore, the ratio and (possibly) the nature of the constituents is variable.[4] Nystatin is a natural metabolite of micro-organisms arising through secondary metabolism, which means that there is a high likelihood of impurities being associated with the substance.

None of the literature on analysis of nystatin defines the composition of the substance tested. Hence comparisons of methods of analysis should be treated with caution. The literature also contains little or nothing on the intermediate products of the chemical reactions used for qualitative and quantitative analysis of nystatin. If the nature of nystatin were better known then more sensitive and specific methods of analysis could be devised.

Some authors[5,6] have reported mass spectrometry studies and given fragmentation schemes based (apparently) on the assumption that nystatin is a single compound. The interpretation of these results is therefore also open to question.

Two other factors are worthy of mention. First, it has been reported that nystatin is surface-active and forms micelles.[7] Care should therefore be taken when spectrophotometric experiments are conducted. Secondly, much of the work reported on the molecular mode of action of nystatin has been done with material of undefined composition.[8,9]

In my opinion any reported work (particularly of an analytical nature) should try to include the composition of the nystatin used.

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IMPROVEMENT IN SAMPLE PREPARATION FOR ALPHA LIQUID-SCINTILLATION SPECTROSCOPY

SIR,

Since the publication of our paper,[1] "Plutonium and Uranium Determination in Environmental Samples: Combined Solvent Extraction - Liquid Scintillation Method," we have developed an improvement in one of the analytical steps that results in a simplification of the procedure as well as a considerable increase in its reliability and reproducibility.

In Procedure, the paragraph entitled Fuming with perchloric acid, a method is described for converting a mixed nitrate-perchlorate system into the perchlorate, in which essentially all the perchloric acid is evaporated to yield a lithium perchlorate fusion. We have now replaced this step with an evaporation at controlled temperature. We found that the fusion step occasionally resulted in the removal of so much perchloric acid that some of the plutonium was converted into a form not amenable to recovery by extraction into the scintillator containing di(2-ethylhexyl)phosphoric acid (i.e., the extractive scintillator). We suspect that the plutonium was being precipitated as an oxide or hydrous oxide since it is possible to precipitate iron oxide during the lithium perchlorate fusion. Results obtained over a period of a few months in our laboratory indicate that an experienced operator fails to recover 100% of the plutonium about one out of ten times in this step; the failure rate is somewhat higher for an inexperienced operator.

Our present procedure, which eliminates the difficulty associated with the fusion step, is as follows. The 0.3M tertiary amine nitrate solution is stripped with an equal volume of a solution that is 1.5M in lithium perchlorate and 0.325 - 0.350M in perchloric acid. In the stripping operation the amine nitrate is converted into perchlorate, releasing an equivalent amount of nitric acid to the aqueous phase. The strip solution is then heated by radiant heaters at a controlled temperature of 150 - 170° for 30 - 60 min to remove the nitric acid. While still warm, the concentrated product (about a quarter of the original volume) is diluted approximately 1:1 with a 2.5% w/v solution of sodium peroxysulphate. The final solution is approximately 3M in perchlorate and 0.05 - 0.10M in perchloric acid. Plutonium is extracted directly from this solution into the extractive scintillator. The organic scintillator sample prepared in this way has good pulse-height, pulse-shape, and energy resolution characteristics. Plutonium recovery by this procedure has routinely been 100%, within counting statistics. A similar procedure has been designed for obtaining plutonium and other alpha-emitting nuclides in a perchlorate medium for extraction into an extractive scintillator for gross alpha-counting in a beta liquid-scintillation counter, and a method of stripping from this scintillator and re-extracting into a scintillator for alpha spectroscopy has been developed. These procedures will be reported more fully in a forthcoming publication.

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25 September 1975

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TALANTA MINI-REVIEW*

CHEMICAL PHASE-ANALYSIS OF ORES AND ROCKS

A REVIEW OF METHODS

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Summary—The methods employed in the chemical phase-analysis of rocks, ores and their treatment products are reviewed. An attempt has been made to be critical, selective and thorough in the choice of methods available in the literature, in order to provide a convenient manual for workers interested in this aspect of analytical chemistry.

Chemical phase-analysis (also called rational or practical analysis) is the determination, by a chemical dissolution technique, of the distribution of an element in an ore or rock on the basis of minerals or oxidation states. The goal of the analysis is the selective dissolution of one or more minerals present in the ore, but because no solvent is completely selective in its action, a quantitative separation is seldom achieved and it is necessary to correct the result to allow for the partial dissolution of other minerals. Because the reactivity of a mineral with a particular solvent varies from specimen to specimen, a truly constant correction is not possible and an error of 1–10% is considered to be acceptable.

The importance of chemical phase-analysis to the mining industry, *e.g.*, in process control, and to hydrometallurgists has ensured its being a valuable aspect of analytical chemistry. Chemical phase-analysis has enjoyed an appreciable increase in interest since 1960. Reviews, both comprehensive and partial, have appeared at irregular intervals in the literature of the Soviet Union[1–6] but unfortunately English translations are not available and access to the original is often difficult. The need for a review in English was apparent.

During the preparation of this manuscript, a book entitled "Chemical Phase Analysis" appeared in print.[7] Although there must of necessity be some duplication, the aim and contents of the present review and of the book are significantly different. This review considers only the phase-analysis of ores and rocks and is intended for publication in the open literature as a guide for analysts to the methods employed. The references given herein were selected on the following basis. Emphasis was placed on methods developed within the past 25 yr. Most older methods have since been modified (and are included in the modified form) or appear in standard analytical texts such as Low,[8] Hillebrand and Lundell,[9] and Maxwell.[10] References to Soviet journals which are not readily available to Western readers are omitted wherever subsequent publication of the method has occurred in a more widely circulated journal.

References in this review are made to the English edition of Soviet journals wherever possible. Recourse to the Russian edition was necessary where the English edition either does not exist for the complete series of a journal or was not reasonably accessible to the reviewer.

Finally it must be mentioned that information on procedures of chemical phase-analysis may be hidden away in the body of papers and is, therefore, effectively inaccessible because titles and references do not convey its existence. It is suggested, therefore, that future authors should strive to prevent the recurrence of this problem by deliberate mention of chemical phase-analysis either in the abstract or, preferably, in the title of their publication.

SUMMARY OF METHODS

Aluminium

The bauxite minerals, gibbsite $Al(OH)_3$, boehmite, $AlO(OH)$, and diaspore, $AlO(OH)$, can be determined on the basis of different rates of dissolution in potassium hydroxide solution or sulphuric acid under controlled conditions.[11,12] Sodium hydroxide solution and hydrochloric acid can be used if only the gibbsite component is determined.[13,14] Gibbsite, boehmite and diaspore can be separated by successive chlorinations with carbon tetrachloride vapour at 400, 500 and 600° respectively.[15] The $AlCl_3$ formed at each temperature is distilled and collected in ammonia

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* For reprints of this Review see Publisher's announcement near end of this issue. TALMR2.

solution. The accuracy of the method is improved if the result for a mineral is corrected for the partial conversion of other minerals at a particular temperature.[16]

Aluminium phosphate minerals such as crandallite, millesite, *etc.*, are easily separated from kaolinite by dissolution in boiling hydrochloric acid (1 + 1).[17] Approximately 1% of the aluminium in kaolinite also dissolves.

Antimony

Antimony oxides and sulphides in ores can be separated by treatment with tartaric acid.[18] The sulphides are not attacked. A method for selectively determining Sb, Sb_2O_3, Sb_2S_3 and $Sb_2O_4 + Sb_2O_5$ in pyrometallurgical samples has been developed.[19] The method is subject to an error of 2–3%.

Beryllium

A method of determining certain beryllium minerals in beryllium ores and concentrates has been described.[20] Helvine, $3(Mn,Fe)O.3BeO.SiO_2.MnS$, and danalite, $3(Fe,Zn,Mn)O.3BeO.3SiO_2.(Fe,Zn)S$, are dissolved in 3% hydrochloric acid. However, 5–15% of the beryllium vesuvianite, $2(Mg,Mn,Zn)O.6CaO.4BeO.Al_2O_3.6SiO_2$, also dissolves. The residue is roasted at 700–800° and the remainder of the vesuvianite becomes soluble in hydrochloric acid (1 + 1). Beryl, $3BeO.Al_2O_3.6SiO_2$, and chrysoberyl, $BeO.Al_2O_3$, are determined in the final residue after fusion.

Bismuth

Bismuth oxide minerals can be extracted from ores by treatment with a 5% thiourea solution in 0·5N sulphuric acid[21] or a 3% phenylacetic acid solution in 0·4M hydrochloric acid.[22] Native bismuth in the residue is dissolved with 0·1M silver nitrate in 0·5–1·0M nitric acid. Bismuth sulphides are then decomposed with nitric acid or hydrofluoric acid–nitric acid mixture. An error of approximately 20% is obtained for individual bismuth components.

Calcium

Free CaO is extractable from $Ca_3(PO_4)_2$, CaF_2, $CaCO_3$, $CaSO_4$ or calcium silicate ores with an aqueous sucrose solution.[23,24] Calcite, $CaCO_3$, can be selectively dissolved in the presence of fluorite, CaF_2, by 5–10% acetic acid.[25,26] Approximately 0·3% of the fluorite also dissolves and, therefore, the appropriate correction should be made to the calcite result. This method is applicable to both fluorspars and complex sulphide ores.

Carbon

Carbonate and carbonaceous carbon in rocks and ores is readily determined. Carbonates are decomposed by heating with hydrochloric or phosphoric acid and the liberated carbon dioxide is absorbed in dilute barium hydroxide solution[27] or in a preweighed tube containing anhydrous magnesium perchlorate.[28] The residue may be treated with chromium trioxide in phosphoric acid to oxidize the carbonaceous carbon to carbon dioxide,[27] or the carbonaceous carbon may be assumed to be the difference between the total and carbonate carbon. The latter method becomes unsatisfactory when the sample contains much carbonate carbon and little carbonaceous material.[28]

Copper

Native copper, cuprite and tenorite. Cuprite, Cu_2O, can be selectively extracted from ores which contain native copper and tenorite, CuO, by dilute hydrochloric acid in ethanol plus stannous chloride,[29] or by a hot saturated potassium iodide solution.[30] The native copper is then dissolved with a solution of ferric chloride in 3M hydrochloric acid. Tenorite is given by the difference between the total copper and cuprite + native copper.

Cuprite can also be extracted with a 1% aqueous solution of unithiol, sodium 2,3-dimercaptopropane-1-sulphonate.[31] The residue is treated with a 1% solution of unithiol in 5% ammonium chloride to extract tenorite. The native copper is dissolved in nitric acid. The cuprite result must be corrected to take into account the solubility of tenorite and native copper, 5 and 8% respectively, in the 1% unithiol solution.

Copper sulphides and oxidation products. Oxidized copper minerals can be extracted from sulphide ores with a reagent consisting of 2 g of sodium sulphite and 1 g of phenylacetic acid in 20 ml of acetone and 100 ml 3% H_2SO_4.[32] Native copper in the residue is dissolved in 15% ammonium carbonate or bicarbonate solution. The copper sulphides may be dissolved in acid or analysed for mineral phases as in the next section.

Treatment of copper ores with a 1% unithiol solution dissolves azurite, $Cu_3(CO_3)_2(OH)_2$, malachite, $Cu_2(CO_3)(OH)_2$, and cuprite.[33] Chrysocolla, $Cu_2H_2Si_2O_5(OH)_4$, can be extracted from the residue with a 2% sodium sulphite solution in 3% sulphuric acid or extracted together with tenorite with a 1% solution of unithiol in 5% hydrochloric acid. Copper sulphides are unattacked. An error of 3–8%, depending on the copper content of the ore, is expected.

Malachite can be extracted from copper ores with a 10% sodium potassium tartrate solution in 10% sodium hydroxide solution in a nitrogen atmosphere.[34] The residue is treated with this reagent in an oxygen atmosphere to dissolve cuprite. The residue contains the copper sulphides.

Copper sulphides. The following methods apply to copper sulphide ores from which oxidized forms of the copper sulphides are either absent or have been previously extracted (*vide supra*). Successive treatment of the ore with 2% ferric sulphate in 5% sulphuric acid and a saturated silver sulphate solution in 5% acetic acid will dissolve bornite, Cu_5FeS_4, and chalcocite, Cu_2S.[34] The residue is treated with a 1:1 hydrochloric acid–nitric acid mixture to dissolve chalcopyrite, $CuFeS_2$.

Bornite, chalcocite and covellite, CuS, can also be extracted from ores with a 2–3% potassium cyanide solution[35,36] or with an acidic solution of thiourea.[37,38] Only 0·07% of the chalcopyrite dissolves. The analytical results are corrected to take into account either the incomplete dissolution of the mineral(s) being determined or partial dissolution of other minerals. The phase-analysis for malachite, chalcocite, covellite and chalcopyrite by the successive use of sulphuric acid, ferric sulphate in sulphuric acid and potassium cyanide has been critically assessed and errors arising from the partial selectivity of the solvents have been estimated.[39]

Chalcocite can be separated from bornite, covellite and chalcopyrite by a 5% solution of unithiol in 5% ammonia solution.[40] A correction for the slight solubility of the last three minerals must be made. An error of 3–9%, depending on mineralogical composition, is expected. Chalcocite can be determined in mixtures with bornite by dissolution in neutral silver nitrate solution.[41] This method, however, is only semiquantitative. A scheme has been devised whereby a copper ore may be analysed for chalcocite, covellite, bornite, chalcopyrite, stannite [Cu_2FeSnS_4], bournonite [$PbCuSbS_2$] and the tetrahedrite–tennantite group [$(Cu,Fe)_{12}(As,Sb)_4S_{13}$].[42]

Germanium

The germanium compounds that are present in coal-ash may be determined[43] if the sample is treated successively with 0·1*M* ammonia to dissolve GeO_2 (including that in solid solution with SiO_2), 0·3*M* EDTA to dissolve $CaGeO_3$ and $MgGeO_3$, 3*M* sodium hydroxide to dissolve aluminium germanates, and 1*M* oxalic acid to dissolve $Fe_6Ge_2O_{13}$. The final residue, which consists of silica and mullite, $3Al_2O_3 . GeO_2 . SiO_2$, is dissolved in nitric acid, hydrofluoric acid and phosphoric acid. The result for a particular germanium compound must be corrected to take into account the partial solubility of other germanium compounds in the solvent.

Indium

Indium compounds in metallurgical dusts can be determined as follows.[44] The dust is treated successively with water to extract $In_2(SO_4)_3$, a 3% bromine solution in methanol to dissolve In_2S_3 and 3*M* hydrochloric acid to dissolve In_2O_3. The components are determined with an error of approximately 3%.

Iron

Fe, FeO, Fe_2O_3 and Fe_3O_4 in reduced ores. Metallic iron can be selectively extracted from reduced iron ores with a solution of mercuric chloride in water[45] or alcohol,[46–48] by aqueous copper sulphate solution,[49–52] ammonium dithiocyanatoargentate[53] or lead chloride[54] or by bromine in alcohol.[55–58] The use of bromine in alcohol is superior to that of mercuric chloride or silver thiocyanate.[59] Further, the use of bromine in methanol is preferable to that in ethanol.[60]

Metallic iron can also be determined indirectly (*a*) by conversion into FeS and subsequent determination of H_2S on acid treatment[61] and (*b*) measurement of the hydrogen evolved by the dissolution of metallic iron in an acid.[62] The latter technique gives a metallic iron content with an error less than 3%.

To determine FeO and Fe_2O_3 in reduced iron ores, a sample from which metallic iron has been removed is dissolved in hydrochloric acid in an inert atmosphere.[46,56,57] The iron(II) in solution is determined either by titration with dichromate[46] or vanadate,[57] or spectrophotometrically.[56] The same solution is analysed for total iron, and iron(III) is obtained by difference. The error in determining each oxidation state is 1–2%.

Free FeO can be distinguished from Fe(II) in magnetite, Fe_3O_4.[48] Metallic and total FeO are extracted from the sample with a 6% ferric chloride solution. The metallic iron is readily determined (*vide supra*) to give total FeO. Another sample is treated successively with ethanolic stannous chloride and a 4% ferric chloride solution to dissolve Fe_2O_3 and metallic iron. The magnetite in the residue is collected magnetically and dissolved in hydrochloric acid in an inert atmosphere. The Fe(II) in the magnetite is determined as stated above. The error in these determinations is 1–5%.

Magnetite is selectively extracted from mixtures with hematite, Fe_2O_3, by 1% hydrochloric acid in phosphoric acid and an oxidant such as hydrogen peroxide or permanganate.[63,64] Approximately 1% of the hematite iron is also dissolved.

Ferrous and ferric iron in rocks and ores. For the determination of ferrous iron, the sample is decomposed with sulphuric–hydrofluoric acid mixture either with the exclusion of air and direct determination of ferrous iron[65–68] or in the presence of a known excess of ammonium vanadate,[69,70] potassium permanganate,[71,72] potassium dichromate[73] or silver perchlorate[74] and indirect determination of ferrous iron by back-titration of the oxidant. The sample decomposition in the presence of excess of ammonium vanadate was found to be very reliable.[75] For samples that dissolve in the acid mixture with great difficulty, fusion with sodium fluoroborate is recommended.[76,77] The use of platinum crucibles, however, yields low results for ferrous iron.[78] It should be noted that the determination of ferrous iron is subject to error in the presence of Ti(III), V(III), Mn(IV), sulphides and organic matter.

Ferric iron in rocks and ores is, in general, assumed to be the difference between the total and ferrous iron. Ferric iron in acid-soluble samples can, however, be determined directly.[79,80] After dissolution of the sample in hydrochloric acid (1 + 1) in an inert atmosphere, ferric iron is titrated with EDTA at pH 1·2–2·0. The error is 0·6–3% depending on the iron content and nature of the sample. The presence of Bi, Tl and large amounts of Cu interferes in the titration. Sulphides and higher oxides of Mn and V interfere during decomposition.

Iron oxides in iron sulphide ores. Hydrogen will easily reduce iron in iron oxides, silicates and other oxygen-bearing minerals to metallic iron but it will only slightly attack pyrite.[81] The metallic iron may then be removed by aqueous copper sulphate solution. Magnetite is easily separated from chalcopyrite with phosphoric acid.[82] Pyrrhotite can be extracted from mixtures with FeO and Fe_2O_3 by bromine in alcohol.[83]

Iron sulphide ores. Pyrrhotite can be determined in the presence of pyrite by dissolution in 4% stannous chloride solution in 6*M* hydrochloric acid.[84] The inertness of pyrite to this reagent is variable, however, and appreciable errors can arise.[85] Pyrrhotite, chalcopyrite and bornite can be extracted from ores with bromine in methanol.[86] Pyrite in the residue is dissolved by hydrogen peroxide in methanol. An error of approximately 2% is obtained.

Lead

A method for the determination of lead minerals in ores has been developed.[87,88] The sample is treated with 25% sodium chloride solution to dissolve anglesite, $PbSO_4$, and then with 15% ammonium acetate solution in 3% acetic acid to dissolve cerussite, $PbCO_3$. Successive treatment of the residue with 2% sodium hydroxide solution and ammonium acetate solution extracts the combined lead of crocoite, $PbCrO_4$, and wulfenite, $PbMoO_4$. Mimetite, $Pb_5(AsO_4)_3Cl$, pyromorphite, $Pb_5(PO_4)_3Cl$, and vanadinite, $Pb_5(VO_4)_3Cl$, are then extracted with a 25% solution of sodium chloride in 0·5% hydrochloric acid [containing approximately 5 mg of mercury(II) per litre to inhibit the dissolution of galena].[88] The galena, PbS, in the residue may be dissolved either with a 25% solution of sodium chloride in 6% ferric chloride solution or with hydrogen peroxide.[88] The final residue contains beaverite, $Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6$, beudantite, $PbFe_3(AsO_4)(SO_4)(OH)_6$, and plumbojarosite, $PbFe_6(SO_4)_4(OH)_{12}$ and is dissolved in hydrochloric acid (1 + 3).

The determination of cerussite by 15% ammonium acetate in 3% acetic acid gives high results for ores containing galena, pyrite and organic matter.[89] The addition of ascorbic acid will suppress the oxidation and dissolution of galena.

Galena may be determined in mixtures with betekhinite, $Cu_{10}(Fe,Pb)S_6$, by dissolution with 4% hydrogen peroxide in 4*M* ammonium acetate in 5% acetic acid.[90] Because of the slight dissolution of betekhinite in this reagent, the determination is subject to an error of 1–4%.

Manganese

Manganese carbonate minerals can be selectively dissolved in the presence of manganite, MnO_2, by 6*N* ammonium sulphate acidified with sulphuric acid to pH 2.[91] Manganite in the residue is dissolved with a 2% solution of sulphosalicylic acid in 0·1–1·0*N* sulphuric acid.

The treatment of carbonate–oxide ores with 1% acetic acid completely dissolves manganocalcite, $(Mn,Ca)CO_3$, and 7–8% of rhodochrosite, $MnCO_3$, and oligonite, $(Fe,Mn)CO_3$.[92] The complete dissolution of rhodochrosite and oligonite is accomplished with 8% sulphuric acid. Manganese oxides are separated from manganese silicates in the residue, with 15% hydrochloric acid. The results for manganocalcite, rhodochrosite and oligonite must be adjusted to take into account the 7–8% solubility of the last two in 1% acetic acid.

Mercury

Mercury compounds in pyro- and hydrometallurgical products may be determined semiquantitatively.[93] Leaching of the sample with 5% nitric acid selectively dissolves HgO. Metallic mercury in the residue is extracted with nitric acid (2 + 1). HgS in the residue is then dissolved in a 5% sodium hydroxide–5% sodium sulphide solution. The compounds may be determined with an error of less than 20%.

Molybdenum

Molybdenum oxide, MoO_3, can be extracted from roasted molybdenite ore with 20–50% ammonia solution.[94,95] The molybdenite, MoS_2, in the residue is then roasted to MoO_3 and determined as above or is assumed to be given by the difference between total Mo and the MoO_3.[94]

The partial roasting of MoS_2 at 450–550° gives a product which contains Mo(IV) and Mo(VI) as well as sulphide and sulphate.[96] Mo(VI) compounds, MoO_3 and MoO_2SO_4, are dissolved in boiling 20% sodium hydroxide solution. Mo(IV) can be determined in the residue. Sulphate is extracted from the roasted MoS_2 on heating with 15% hydrochloric acid. Sulphide in the residue is determined by oxidation to sulphate.

Nickel, cobalt

Chondritic meteorites (and lateritic nickel ores) can be analysed for the metallic, sulphide and silicate phases of nickel and cobalt.[97] Metallic nickel and cobalt are dissolved in a 12% solution of mercuric chloride in 6% ammonium chloride solution, in an inert atmosphere. The sulphides are extracted from the residue with 2% bromine in methanol. The silicates are decomposed with hydrofluoric acid. The error in the determination is approximately 1%.

Ascorbic acid–hydrogen peroxide selectively dissolves Ni, Co and Cu sulphide minerals in rocks.[98] A total and sulphide-phase metal determination permits the calculation of the distribution of metal(s) over the mineral phases in the rock.

Silicon (*quartz in silicates*)

Quartz in silicates may be determined as follows.[99] The sample is roasted at 600–650° and treated with a 1:3 mixture of nitric and hydrochloric acids to dissolve oxide minerals. The residue is heated to 250–275° with freshly prepared pyrophosphoric acid to dissolve the silicates. The quartz is then dissolved with hydrofluoric–sulphuric acid mixture. An error of 0·5% is claimed.

Quartz may also be determined in rocks by pyrosulphate fusion followed by fluorosilicic acid treatment.[100] The latter must be repeated if much feldspar is present in the sample. A decrease in the recovery of quartz with each dissolution stage must be taken into account in calculating the result for quartz. Both pyrophyllite, $Al_2Si_4O_{10}(OH)_2$ and zircon, $ZrSiO_4$, offer significant resistance to this procedure.

Sulphur

Elemental sulphur in ores and minerals. Karchmer[101] has reviewed several methods for the determination of elemental sulphur. In addition, spectrophotometric[102,103] and chromatographic[104,105] methods are available. In the spectrophotometric method, the elemental sulphur is extracted from the sample with a solvent such as carbon disulphide or acetone and the absorbance due to sulphur is measured at the appropriate wavelength. The presence of other sulphur compounds may interfere. Also sulphur, if present in the amorphous form, may be incompletely dissolved.[101]

After extraction from the sample with acetone, elemental sulphur is determined by thin-layer chromatography.[105] A carbon disulphide extract of the sample may be analysed for both elemental and xanthate sulphur.[104] Total sulphur in the extract (in a fixed volume of carbon disulphide) is determined by oxidation of all sulphur compounds to sulphur dioxide. Xanthate sulphur is determined in a second portion of extract by thermal decomposition of all combined-sulphur compounds. All measurements are by gas chromatography. Elemental sulphur is the difference between total and xanthate sulphur.

Sulphide. Sulphide in the presence of sulphate is usually determined by evolution of hydrogen sulphide on treatment of the sample with acid.[82,106] Sulphate may then be determined directly as barium sulphate or as the difference between total and sulphide sulphur. Sulphide may also be determined by pyrolysis of the sample, mixed with reduced copper, at 700° in a stream of nitrogen.[107] Oxidized forms of sulphur are converted into sulphur dioxide, which is collected. Sulphide forms CuS which, of course, gives hydrogen sulphide on addition of acid.

Pyrrhotite sulphur can be determined in the presence of pyrite sulphur by its evolution as hydrogen sulphide by a 4% stannous chloride solution in hydrochloric acid (1 + 1).[84] This reagent may, however, also partially decompose pyrite and it is recommended that a solution of hydrazine in 4*N* sulphuric acid be used instead.[85]

Tantalum, niobium

A mixture of hydrofluoric and hydrochloric acids, used at slightly elevated pressure, decomposes pyrochlore, $(Na,Ca)_2(Ta,Nb)_2O_6(OH,F)$, and microlite, $(Na,Ca)_2(Ta,Nb)_2O_6(O,OH,F)$, but only slightly attacks simpsonite, $Al_4(Ta,Nb)_3(O,OH,F)_{14}$.[108] Hydrofluoric acid (4*M*) dissolves 98% of microlite but only 7–15% of columbite–tantalite.[109] Correction for the degree of dissolution of these minerals in this reagent permits the determination of the distribution of Ta_2O_5 and Nb_2O_5 in microlite and columbite–tantalite, $(Fe,Mn)(Ta,Nb)_2O_6$, with an error of 2–6%.

Tin

A method has been developed for differentiating and determining free cassiterite, SnO_2, cassiterite occluded in the silicate lattice and silicate-bound tin in rocks.[110] The sample is decomposed with a 2:1 hydrofluoric–hydrochloric acid mixture and subsequently heated with ammonium iodide to give total tin. Lattice-bound tin is determined by decomposition with the same acid mixture and subsequent heating with hydriodic acid to dissolve the freshly formed tin oxide. The rock is heated with ammonium iodide to determine the free cassiterite. The difference between total and free cassiterite and lattice-bound tin is the occluded cassiterite. An error of 5–20%, depending on tin content, is obtained.

Stannite, Cu_2FeSnS_4, may be selectively decomposed in the presence of cassiterite with concentrated nitric acid,[111] bromine in ethanol or carbon tetrachloride[112] or sodium nitrate in glacial acetic acid.[113] The cassiterite may be determined directly in the residue or by difference between total and stannite tin. The error in the determination is 1–2%.

Titanium

Ilmenite, $FeTiO_3$, titanomagnetite, $(Fe,Ti)_3O_4$ and sphene $CaTiSO_5$, may be extracted from mixtures with rutile, TiO_2, with a 2% solution of sodium fluoride in 8 *M* hydrochloric acid.[114] Because 1–2% of the rutile also dissolves, the results for these minerals must be corrected accordingly. Sphene can be determined in the presence of ilmenite and titanomagnetite. The sample is reduced in a stream of hydrogen at 880° and then treated with 1*M* hydrochloric acid to dissolve iron oxides. Subsequent treatment with a 1·5% solution of sodium fluoride in 8*M* hydrochloric acid dissolves sphene, leaving ilmenite and titanomagnetite in the residue. Rutile, if present, also remains in the residue but may be determined as above. The error in these determinations is 1–10%, depending on the mineral and its content in the ore.

Tungsten

Members of the wolframite group, ferberite, $FeWO_4$, and huebnerite, $MnWO_4$, can be determined in scheelite.[115] The sample is first roasted at 400° to oxidize all ferrous minerals soluble in hydrochloric acid, other than wolframite, to their ferric counterparts, and is then completely dissolved in concentrated hydrochloric acid, in an inert atmosphere. Ferrous iron in the solution represents ferberite. Also, experimental studies[115] indicate that huebnerite is the only manganese mineral of appreciable amount in scheelite and, therefore, the determination of manganese will yield the huebnerite content of the scheelite.

Uranium

The ratio of U(IV) to U(VI) in rocks and ores can be evaluated.[116,117] The sample is decomposed with a non-oxidizing acid in an inert atmosphere. U(IV) is precipitated with cupferron, Ti(IV) being used as carrier, and is determined by fluorimetry.[118] Otherwise, U(VI) is separated from U(IV) by extraction as an anionic phosphate complex with a 5% solution of tri-n-octylamine in benzene[116] or xylene.[117] A total uranium determination gives by difference the amount of the oxidation state of uranium not determined directly. The error in the determination is 2–3%.

Zinc

Oxidized zinc minerals such as smithsonite, $ZnCO_3$, willemite, Zn_2SiO_4 and hemimorphite, $Zn_4Si_2O_7(OH)_2 . H_2O$, are easily separated from sphalerite, ZnS, by dissolution in boiling 5% acetic acid.[119] The result must be corrected for the 5–10% of ZnS which also dissolves. The error in this determination is 10–15% for the oxidized minerals and 2–5% for ZnS. ZnS is easily determined in the presence of zinc spinel by dissolution in acidic hydrogen peroxide.[120] The error in the determination is approximately 3%.

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AN AUTOMATED SUBMICROGRAM DETERMINATION OF SELENIUM IN VEGETATION BY QUARTZ-TUBE FURNACE ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—An automated method for the determination of submicrogram amounts of selenium in vegetation is described. A weighed sample of vegetation is digested with a 4:1 nitric–perchloric acid mixture, and made up to a known volume. The digested sample is placed in a Technicon sampler and reacted with sodium borohydride solution. The selenium converted into the gaseous hydride is swept by an argon stream into a gas–liquid separator. The mixed gas stream is passed through a heated quartz cell, positioned in the light-path of an atomic-absorption spectrophotometer. The absorption by the atomized selenium is recorded. The method is capable of analysing 50 samples a day by the use of a calibration curve or 25 a day by the standard addition technique. A relative standard deviation of better than 10% and a detection limit of 0·025 μg/g were obtained.

There is a need for a simple, precise and fast method for determining selenium in biological materials for pollution monitoring and surveillance. The most commonly used and recommended method for trace levels of selenium is based on the formation of the piazselenol complex with diaminonaphthalene and its subsequent extraction into a non-polar solvent such as hexane. The fluorescence of the extract is measured at a specific wavelength.[1,2] The method involves time-consuming procedures such as distillation with bromine before the complexation, or coprecipitation with arsenic.[3] It demands more than average analytical skills to obtain accurate results and is not ideally suited for high-volume routine work.

The application of flame atomic-absorption techniques to selenium determination has been reported.[4] The sensitivities of the various flame methods are not sufficient to measure selenium levels much below 1 ppm. Improved sensitivities have been achieved by directing the flame into long tubes held in the path of the hollow-cathode light-beam,[3] but the stability of the signals deteriorates and offsets the advantage.

Dagnall *et al.*[5] measured the atomic fluorescence of selenium and obtained a limit of detection of 0·1 μg/ml.

Better sensitivities were achieved by the carbon-rod atomization technique designed around the principle of the graphite furnace described by L'vov,[6] Massmann,[7] and West.[8] Baird *et al.*[9] have determined selenium in different matrices by this technique. The technique is not very precise and is subject to matrix interferences that are difficult to control.

The ability of selenium and a few other elements of groups IVA, VA and VIA of the periodic table to form volatile hydrides, has been used recently for their separation and measurement by atomic-absorption spectrophotometry.[10–12] The subject has been recently discussed in a paper on the determination of arsenic in air particulate matter.[13] The present method uses a similar approach for the determination of selenium in vegetation samples.

EXPERIMENTAL

Reagents

Sodium borohydride (Fisher Scientific Company, 98% pure) solution, 1% w/v in distilled water; perchloric acid, 70%; nitric acid, conc.; hydrochloric acid, conc. All the acids used were analytical-reagent grade. A 4:1 mixture of nitric and perchloric acids was used for sample decomposition.

A 1000-ppm stock solution of selenium was prepared by dissolving 1 g of selenium (analytical-reagent grade) in a minimum quantity of hot nitric acid and diluting to 1 litre with distilled water.

Apparatus

Aluminium metal blocks, 26 × 11 × 4 cm, drilled with 40 holes (3 cm deep) to accommodate 18 × 150 mm test-tubes, were used as test-tube holders as well as a uniform means of heating for sample decomposition.

The sampler, with a 40-sample capacity, and the proportioning pump used were obtained from Technicon Corporation. Other components used were a gas–liquid separator, a 0–2 l./min flowmeter in the argon line and appropriate tubings, connectors and mixing coils to build the proportioning pump manifold. The complete system is illustrated in Fig. 1.

A Varian Techtron model AA5 atomic-absorption spectrophotometer equipped with an ASL selenium hollow-cathode lamp and a (W & W Electronics, Switzerland) linear–log integrating recorder was used. The recorder range was set at 2 mV full-scale deflection. The quartz tube was 10 cm long and 10 mm in internal diameter with a 17-cm long and 4-mm bore inlet tube fused at the mid-point. The quartz tube had hooks, 0·5 cm from each end, to serve as anchors for the heating wire. It was wound with approximately 2 m of No. 75 chromel-C heating wire

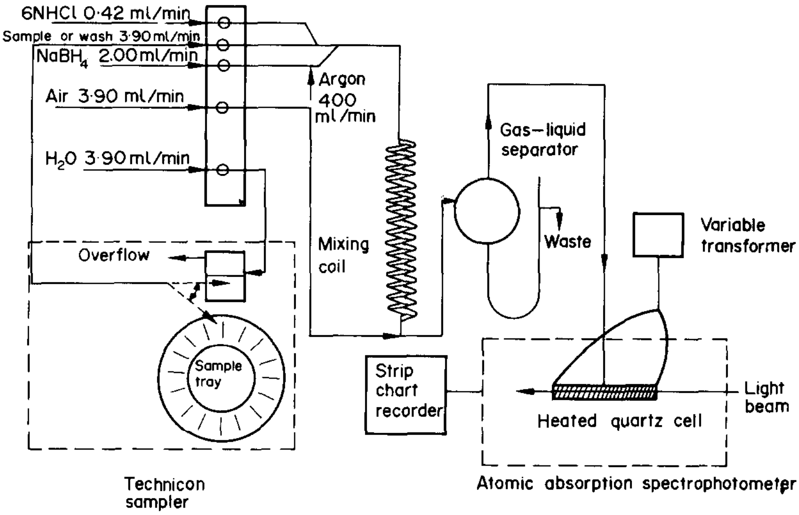

Fig. 1. Diagram of autoanalysis system for selenium determination.

(resistance 3·48 Ω/m) and insulated by wrapping with asbestos tape and a layer of asbestos cord. Insulated terminals were provided for the power supply. The finished cell was mounted on the burner head of the spectrophotometer and secured by metal clips. This allowed the use of burner alignment controls to position the quartz cell in the optical path. The temperature of the heated cell was controlled by means of a 0–140 V variable transformer.

Procedure

Exactly 0·200-g portions of vegetation samples previously dried at 80° and ground to 40-mesh were weighed in duplicate into 18 × 150 mm borosilicate glass test-tubes calibrated at the 10-ml mark and placed in the aluminium block. Then 0·100 ml of 1·00-ppm selenium standard solution was dispensed into one tube of each pair from a 2-ml microburette or with an Eppendorf pipette, and 4 ml of nitric–perchloric acid mixture were added to each test-tube. The aluminium block containing 40 test-tubes was heated at 125° surface temperature until the organic matter was completely oxidized or, preferably, overnight. Distilled water was then added to the test-tubes to bring the volume to within 1 ml of the calibration mark. The contents of the test-tubes were allowed to cool to room temperature and the volumes were brought to the 10-ml mark with distilled water. The test-tubes were sealed with "parafilm" and the contents were thoroughly mixed. Blanks and standards were incorporated in the batch and taken through the entire decomposition procedure.

The solutions were poured into sample-cups held in the sampler tray. The instrumental parameters were optimized and are shown in Tables 1 and 2. The entire system, except the sampler, was turned on and allowed to equilibrate, with the reagents being pumped, the argon flow adjusted to optimum, and the sampling probe taking up distilled water from the wash-well. The recorder pen was set at the base-line and the sampler was then switched on for unattended operation.

Table 1. Atomic-absorption spectrophotometer settings (Techtron model AA-5)

Wavelength	196·0 nm
Slit	300 μm
Lamp current	10 mA
Mode	absorbance
Scale expand	no expansion
Damping	4 (maximum)
Exhaust vent	closed
Recorder sensitivity	2 mV full-scale deflection
Recorder chart speed	5 mm/min

The zero-selenium vegetation sample was prepared by taking a low selenium sample through the prescribed digestion procedure with added amounts of bromine and hydrobromic acid to volatilize any selenium. The halides were fumed off and the digested material was treated like a normally decomposed sample.

The concentration of selenium in the samples was calculated by using the following expression:

$$\mathrm{Se}(\mu g/g) = \frac{cb}{(a-b)W}$$

where a = peak height due to sample + added selenium
b = peak height due to sample only
c = the amount of added Se (μg)
W = weight of the sample (g)

RESULTS AND DISCUSSION

Effect of acid matrix on selenium signal

The absorbance of a 10-ppb (parts per billion) selenium standard in various acid matrices was determined to ascertain their suitability for hydride generation and to select the acid concentration for optimum performance. Table 3 contains the results of this

Table 2. Technicon system

Sampler	
Sample tray	40-position
Cam	2-lobe
Sample time	1 min
Wash time	2 min
Proportioning pump	
Sample or wash	3·90 ml/min
6*M* HCl	0·42 ml/min
Sodium borohydride solution	2·00 ml/min
Air	3·90 ml/min
Distilled water	3·90 ml/min
Reaction coil	29-turn, 1·8-cm diam.
Argon flow	400 ml/min

Table 3. Effect of various acid matrices on A.A. signal

Acid	Absorbance for 10 ppb selenium in 20% acid solution
H_2SO_4 (B&A Reagent A.C.S. 96%)	0·042
HCl (B&A Reagent A.C.S. 37%)	0·051
HNO_3 (Mallinckrodt 70%)	0·0078
Fuming HNO_3 (Fisher Reagent A.C.S. 90%)	0·0055
$HClO_4$ (Fisher Reagent A.C.S. 70%)	0·023
H_2SO_4–HCl (1:4)	0·054
$HClO_4$–HNO_4 (1:4)	0·0035

study. Hydrochloric acid seems to be the best for the purpose. Figure 2 shows that 6*M* is about the optimum concentration. However, it was the least suitable acid for sample decomposition. Various acid mixtures were tried for sample decomposition. Halogen acids had to be excluded from this operation because of the volatility of selenium in such media. The choice was narrowed down to the use of sulphuric–nitric or perchloric–nitric acid mixtures. After preliminary experimentation, it was decided to use a 4:1 mixture of perchloric and nitric acids for the digestion of vegetation because it gave relatively complete digestion of organics at reasonably low temperature. A stream of 6*M* hydrochloric acid was introduced into the system just before the confluence of sample and the sodium borohydride streams to provide a suitable medium for proper hydride generation.

Effect of sodium borohydride concentration on selenium signal

Figure 3 shows that 0·5% w/v sodium borohydride concentration is the optimum, but a 1% solution was used in this work because sodium borohydride in solution undergoes gradual breakdown with time. The potency of a 1% solution was adequate after 4–5 days of storage under refrigeration. One pellet of sodium hydroxide added for each 100 ml of sodium borohydride solution slowed down the rate of decomposition.

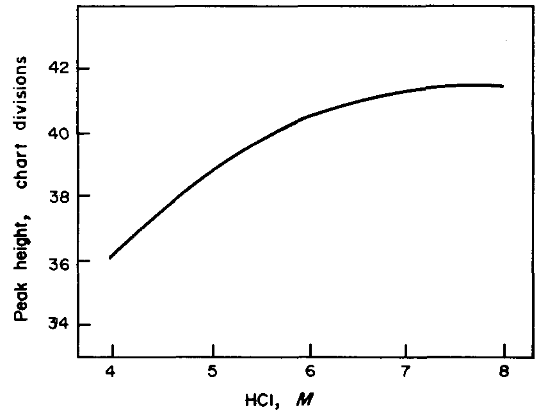

Fig. 2. Effect of HCl concentration on sensitivity (10-ppb Se standard).

Effect of argon flow and cell temperature

The argon flow-rate adjustment is very critical in this method. Too low a flow yields good sensitivity but noisy signals while too high a flow-rate considerably reduces the sensitivity. The temperature of the quartz cell is also important as too high a temperature causes loss of sensitivity. This is apparent from Figs. 4 and 5. The argon flow-rate chosen as best

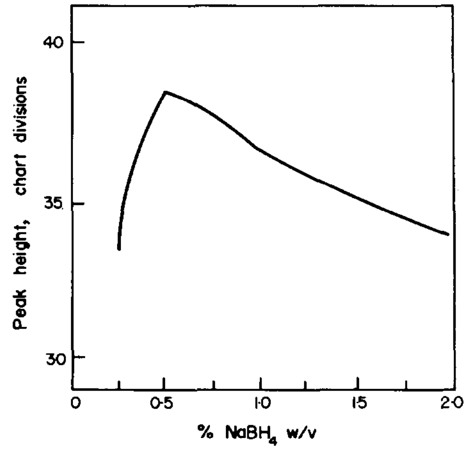

Fig. 3. Effect of $NaBH_4$ concentration on sensitivity (10-ppb Se standard).

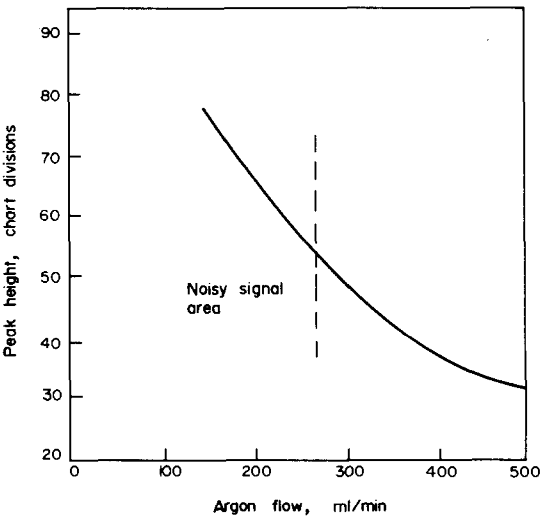

Fig. 4. Effect of argon flow-rate on sensitivity (10-ppb Se standard).

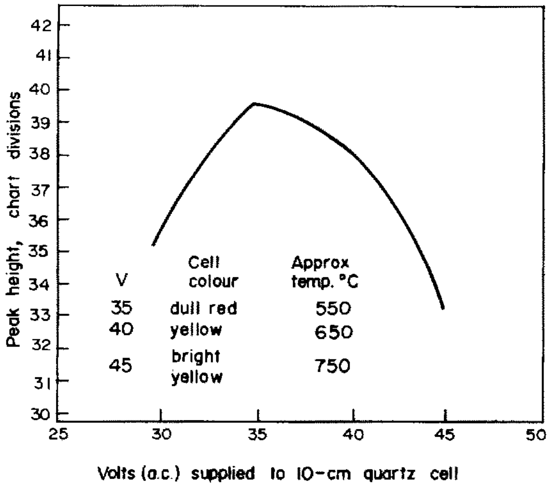

Fig. 5. Effect of quartz cell temperature on sensitivity (10-ppb Se standard).

compromise between signal and noise was around 400 ml/min. The optimum temperature range was 570 ± 20°, controlled by means of a variable transformer.

Effect of quartz-cell size on selenium signal

Three other cells were tried besides the one used in this work. Two open-ended cells 16 and 28 cm in length, constructed in the same way as the 10-cm cell, were investigated. A 16-cm cell with end-windows of quartz and having an inlet and an outlet tube adjacent to the ends, was also studied. All were operated at the specified temperature (570 ± 20°). It was expected that the 28-cm cell would give rise to the highest peak, but the 10-cm cell generated a signal which was 25% higher than that from either the 16-cm or the 28-cm cell under similar conditions of operation. The latter two gave about the same peak heights. The 16-cm cell with quartz windows generated a negligible peak which was lower by an order of magnitude than that obtained with the 10-cm cell. These observations suggest that the effective path-length is perhaps determined by the burning hydrogen slug inside the cell rather than by the length of the cell. The entrained air–hydrogen flame is visible at the two ends of the open cells. The addition of an air-line to the manifold is necessary and improves the signal strength considerably. The cell with quartz windows does not show any burning hydrogen slug inside the cell, which is probably the cause of the weaker signal. The removal of the air-line reduces the signal by approximately 50%.

Table 4. Effect of interfering elements on selenium determination

Element added, *ppm*	Recovery, %
K 20	107
P 20	107
Fe 20	81
Al 20	99
Cu 2	21
Pb 2	86
As 2	83
As 20	26
Ni 2	80
Bi 2	90
Bi 20	53
Sb 2	78
Sb 20	49

Indicated element was added to a 20-ppb selenium solution in $HClO_4$-HNO_3. A 20-ppb Se solution was run alongside as the reference standard.

Effect of the oxidation state on selenium signal

The absorbance signals of 5, 10 and 20 ppb Se(IV) and Se(VI) standards were recorded under similar experimental conditions. Se(VI) was prepared from Se(IV) by oxidation with potassium permanganate. The Se(VI) absorbance signals were approximately 66% lower than the corresponding Se(IV) signals.

Vegetation samples spiked with 100 ng of Se(IV) and Se(VI) were taken through the digestion procedure and the absorbance signals were recorded. Six replicate measurements gave the ratio of signal peak-

Table 5. Performance of standard addition *vs.* standard curve methods of computation for same sample with interfering elements added (final volume 10 ml)

	Cu, Zn, Mn, Pb, Ni added, *μg* of each	Peak height *chart divisions**	Difference per 10 ppb Se, *chart divisions*	Se, *μg/g* Std. addn.	Std. curve
Sample	0	45·5	33·5	0·68	0·70
Sample + 100 ng Se	0	79·0			
Sample	5	48·0	34·0	0·71	0·74
Sample + 100 ng Se	5	82·0			
Sample	10	37·0	29·5	0·63	0·62
Sample + 100 ng Se	10	66·5			
Sample	20	24·0	21·0	0·57	0·37
Sample + 100 ng Se	20	45·0			
Sample	40	12·0	8·0	0·75	0·18
Sample + 100 ng Se	40	20·0			
Sample	60	9·0	6·0	0·75	0·14
Sample + 100 ng Se	60	15·0			
Sample	100	6·5	5·0	0·65	0·095
Sample + 100 ng Se	100	11·5			
50 ng Se	0	15·5		Mean = 0·677 μg/g	
100 ng Se	0	32·5		S.D. = 0·066 μg/g	
200 ng Se	0	66·0		R.S.D. = 9·8%	
Blank	0	0·0			

* 100 chart divisions = 0·200 Absorbance.

Table 6. Within-run and day-to-day precision of the selenium measurement

Sample No.	Se, *μg/g*			Date analysed	Mean, *μg/g*	S.D., *μg/g*	R.S.D., %
6328W	0·39	0·48	0·40	30/7/74	0·42	0·041	9·8
	0·37	0·40		31/7/74			
	0·40	0·40		6/8/74			
	0·42	0·39		8/8/74			
	0·45	0·45		22/8/74			
	0·52	0·45		26/8/74			
6020W	0·28	0·33	0·31	all on 25/7/74	0·293	0·021	7·2
	0·28	0·29	0·29				
	0·26	0·31	0·29				

heights due to the added amounts of Se(IV) and Se(VI) of 1·2:1, suggesting that the vegetation matrix caused some conversion of Se(VI) into Se(IV). However, selenium is known to occur in its most common oxidation state (*i.e.*, +IV) in its organo-complexes.

Interferences

Some of the interfering elements likely to occur in decomposed vegetation, and their effect on selenium determination are given in Table 4. Copper happens to be the worst interferent, causing strong signal depression at the 2-ppm level. This concentration corresponds to 100 ppm of copper in the solid sample. Levels higher than this are unlikely to occur in normal vegetation samples. Up to a 10-fold amount of copper and other metals in solution may be compensated for by the addition technique, as evidenced by the results in Table 5.

Attempts were made to eliminate interfering metals by an on-line ion-exchange technique, but the results were not very encouraging. Dowex 50W, a strong acid cation-exchange resin, was used to cope with the relatively high acidity of the sample stream, but without much success. Separation of selenium by co-precipitation and distillation was found to be cumbersome and time-consuming.

All results were obtained without background correction because when a hydrogen lamp was used there was no absorption at 196 nm. Standard solutions were run with and without digestion, to study loss of selenium during decomposition. No significant losses were observed.

Zero-selenium vegetation samples were run to confirm the absence of background interference.

Precision and accuracy

The standard curve was linear up to 30 ppb. The range may be extended by using different sample aliquots or adequate dilution. Undigested and digested standards gave signal peaks of equal height, suggesting that there is no loss of selenium due to volatility.

The 5, 10 and 15 ppb selenium peaks were high enough for a 0·5 ppb level to be easily measured, giving a peak of two chart divisions above the baseline noise. This corresponds to a selenium level of 0·025 μg/g in a vegetation sample, based on a 0·2-g sample in 10 ml of solution. The difference in peak-heights for samples with and without addition of selenium (10 ppb) was the same as the peak height for the digested 10–ppb standards. Thus in the majority of cases, there is no evidence of interference due to matrix background. Problems could arise, however, with vegetation samples contaminated with interfering metals such as copper, nickel, *etc.* Table 5 clearly illustrates this point and at the same time demonstrates the value of the standard addition technique in compensating for these interferences.

The relative standard deviation (R.S.D.) by the standard addition technique shown in Table 5 is 9·8% which is quite satisfactory. Triplicate analyses of 52 different vegetation samples by the standard addition technique, run in batches of seven a day, gave an overall S.D. of 0·025 μg/g, calculated as the square root of the mean variance. The highest and the lowest

Table 7. Comparison of the automated method results with those of fluorimetric and neutron-activation methods

	Se, *ppm*		
Sample No.	Present method	N.A.	Fluorimetric
5524W	0·11	0·14 ± 0·03	0·10
5537W	0·47	0·41 ± 0·08	0·40
5580W	0·15	0·14 ± 0·03	0·15
5713W	0·15	0·13 ± 0·03	0·14
5740W	0·06	0·07 ± 0·02	0·05
5956W	0·11	0·12 ± 0·03	0·10
5963W	0·42	—	0·47
5974W	0·67	0·56 ± 0·09	0·56

mean Se values were 0·673 and 0·027 μg/g. Individual relative standard deviations ranged from 0 to 28%, but showed no correlation with the selenium content. The analyses of NBS Orchard Leaves standard gave results in good agreement with the certified value. Table 6 contains information which supplements these findings and also suggests that within-run precision is better than day-to-day precision. The use of an electrodeless discharge lamp and R106 photomultiplier tube instead of R213 may considerably increase the signal-to-noise ratio.

Table 7 shows a satisfactory overall agreement between results obtained by this method and those obtained by neutron activation and fluorimetry. These samples were selected for this study because the neutron activation data were already available. The fluorimetric method used was a modification of the AOAC[14] procedure using diaminonaphthalene complexation. The results for a further 18 samples showed equally good agreement between the fluorimetric and atomic-absorption results.

Results were calculated from both peak-height measurement and integration of the area under the peaks. No significant differences were found. The peak-height method was used for convenience. The readability of peak heights is poor at low selenium levels and in these cases area-integration might give slightly better results.

Conclusions

The method described is faster than the conventional procedures, suitable for handling a large volume of samples, and sufficiently sensitive and accurate for determination of submicrogram quantities of selenium in vegetation and possibly other types of matrices. A single-point standard-addition compensates for interferences, although most uncontaminated samples can be analysed twice as fast by the use of a calibration curve. The argon flow-rate is critical within narrow limits. The high signal-to-noise ratio obtained allows further amplification of the signal should lower detection limits be desired. The method can be performed on a semiautomatic basis by manual presentation of the sample solution to the system.

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ANWENDBARKEIT DER FLAMMENLOSEN ATOMABSORPTION IN DER MESSENDEN KOMPLEXCHEMIE—II*

ÜBER LÖSLICHKEIT, STABILITÄT UND VERTEILUNG DES Cd-OXINATES

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Zusammenfassung—Die Atomabsorption in einer Graphitrohrküvette wurde zur Bestimmung der Löslichkeit des Cadmiumoxinates bei verschiedenen freien Oxinatkonzentrationen [L] verwendet. Die Löslichkeitskurve $\log[\mathrm{Cd}]_t$, pL kann mit den Bildungskonstanten β_1, β_2, β_3 und dem Löslichkeitsprodukt K_{s0}, deren Logarithmen der Reihe nach 7,34, 13,44, 17,96 und −21,39 (μ = 0,1, Tetramethylammoniumnitrat, 25°) betragen, beschrieben werden. In mit Wasser gesättigtem Chloroform tritt neben dem $\mathrm{CdL_2(H_2O)_2}$ bei höheren Oxinkonzentrationen ($[\mathrm{HL}]_0 > 5\cdot 10^{-2}M$) $\mathrm{CdL_2(HL)_2}$ auf. Die Logarithmen der Sättigungskonzentration $[\mathrm{CdL_2(H_2O)_2}]_{o,s}$ bzw. der Adduktbildungskonstante β_A^o in der organischen Phase betragen −6,88 bzw. 3,33. Die Rolle des Dihydrates bei der Extraktion von Cd(II) wird diskutiert.

Die Anwendbarkeit der flammenlosen Atomabsorption zum Studium des Extraktionsgleichgewichtes von Cu(II)-Oxinat in Anwesenheit von 0,1*M* Tetramethylammoniumnitrat wurde kürzlich bewiesen.[1] Da atomabsorptiometrisch wie auch radiochemisch die totale Metallkonzentration $[\mathrm{M}]_t$ erhalten wird, muß zur Ermittlung von Stabilitätskonstanten schwerlöslicher Komplexe ein Zweiphasen-System untersucht werden. Prinzipiell hat man zwei Möglichkeiten: entweder die Ermittlung des Verteilungsverhältnisses $q = [\mathrm{M}]_{t,o}/[\mathrm{M}]_t$ (o: organische Phase) zwischen zwei flüssigen Phasen, in Abhängigkeit der freien Ligandkonzentration [L], oder die Bestimmung der Löslichkeit bei verschiedenen [L]-Werten. Die Auswertung der beiden Kurven $\log q$, pL bzw. $\log[\mathrm{M}]_t$, pL liefert dann die Gleichgewichtskonstanten. Extraktionsmessungen haben den Vorteil, daß sich im allgemeinen ein konstanter *q*-Wert schnell einstellt. Schwierigkeiten treten aber dann auf, wenn sich während der Verteilung des Metalls eine in beiden Phasen schwerlösliche Verbindung bildet. Das war der Fall in dem hier untersuchten System. Wenn Cd(II) mit Oxin extrahiert wird, bildet sich an der Phasengrenze ein Niederschlag[2] von $\mathrm{CdL_2\cdot 2H_2O}$. Wasserfreies $\mathrm{CdL_2}$ löst sich in Chloroform, welches Oxin enthält und an Wasser gesättigt ist. Die Lösung ist aber nicht stabil und es bildet sich fortwährend $\mathrm{CdL_2\cdot 2H_2O}$.

Abbildung 1 zeigt die zeitliche Abnahme der Konzentration des gelösten Cadmiums bezogen auf die Anfangskonzentration. Die Letztere sinkt innerhalb von 2 bis 3 Stunden auf *ca.* die Hälfte, wobei die Abnahmegeschwindigkeit in erster Linie von der Oxinkonzentration abhängt. 10^{-4}M $\mathrm{CdL_2}$-Lösungen sind über längere Zeit nur bei sehr hohen Oxinkonzentrationen ($[\mathrm{HL}]_0 > 0{,}5M$) haltbar. Die Anwendung von so stark konzentrierten HL-Lösungen bei Gleichgewichtsstudien ist jedoch ungünstig. Man muß nämlich annehmen, daß die Aktivität des Oxins mit seiner Konzentration nicht mehr übereinstimmt. Wie die Abb. 1 zeigt, bildet sich die feste Phase relativ langsam. Bei den Extraktions-bzw. Rückextraktionsversuchen kann sich daher ein partielles Gleichgewicht zwischen den beiden flüssigen Phasen einstellen, sodaß nach einigen Minuten ein konstantes *q* beobachtet wird. Mit einer 0,1*M* Oxinlösung konnte man[3] sogar bei einer Extraktionsdauer von einigen Minuten, Extraktionsausbeuten von 100% erzielen.

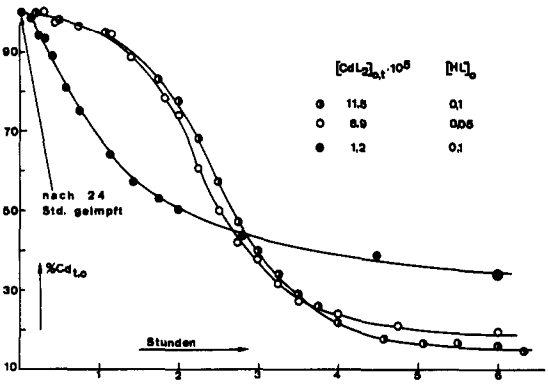

Abb. 1. Zeitliche Abnahme der Cadmiumkonzentration in Lösungen des entwässerten Cd-Oxinates in oxinhaltigem Chloroform.

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* Part I—*Talanta*, 1974, **21**, 539.

Nach unserer Ansicht ist es jedoch thermodynamisch sinnvoller, die Gleichgewichtsversuche ausgehend aus der stabilsten Verbindung $CdL_2 \cdot 2H_2O$ durchzuführen. Mit dieser schwerlöslichen Verbindung können aber nur Löslichkeitsuntersuchungen angestellt werden, d.h. es muß die zweite der oben genannten Möglichkeiten realisiert werden.

Löslichkeitsbestimmungen zwecks Bestimmung von Stabilitätskonstanten wurden bereits an einer ähnlichen Verbindung ($ZnL_2 \cdot 2H_2O$) radiochemisch[4] durchgeführt. Nach unserer Kenntnis wurden die Bruttostabilitätskonstanten β_2 und β_3 von Cd–Oxinat in rein wäßrigem Medium bisher noch nicht bestimmt. In der Datensammlung[5] "Stability Constants" wird für log β_2 ein geschätzter Wert[6] von (2 log $\beta_1 - 1$) angegeben. Bisher wurden auch die Löslichkeit des $CdL_2 \cdot 2H_2O$ in Chloroform sowie seine Verteilung zwischen Chloroform und Wasser nicht untersucht. Wie später gezeigt wird, sind aber diese Daten für die Interpretation von Verteilungsmessungen sehr wichtig. Zudem kann Cadmium mit der flammenlosen Atomabsorption in einer Graphitrohrküvette sehr empfindlich bestimmt werden. Daher schien uns das System $CdL_2 \cdot 2H_2O/H_2O$ bzw. $CHCl_3$ sehr geeignet um die Anwendbarkeit der Atomabsorption in der messenden Komplexchemie weiter zu prüfen.

EXPERIMENTELLER TEIL

Apparatives

Verwendeter Atomabsorptionsspektrophotometer, pH-Einstabmesskette und pH-Meter wurden bereits beschrieben.[1] Zur Messung der optischen Dichte von CdL_2-Lösungen diente ein Einstrahl-Spektrophotometer (Unicam).

Chemikalien

$CdL_2 \cdot 2H_2O$ und CdL_2 wurden nach gravimetrischen Standardmethoden hergestellt. Man benutzte doppeltdestilliertes Wasser, Tetramethylammoniumnitrat[1] $[Me_4N]NO_3$, $[Me_4N]OH$ und HNO_3, welche sich bei der Prüfung in der Graphitrohrküvette als Cd-frei erwiesen. Chloroform (Merck) wurde kurz vor dem Gebrauch durch Ausschütteln mit Wasser alkoholfrei gewaschen und mit Wasser gesättigt.

Abnahme des Cd-Gehaltes frisch präparierter CdL_2-Lösungen

Es wurden verschieden konzentrierte Oxinlösungen (0,05 und 0,1M) in alkoholfreiem, an Wasser gesättigtem Chloroform hergestellt. In einem Teil der Lösungen wurde CdL_2 gelöst, und mit der übrigen Lösung füllte man die Referenzküvette. Die Abnahme der Cadmium konzentration (s. Abb. 1) wurde in der Küvette durch Messung der optischen Dichte bei 380 und 390 nm direkt verfolgt. Die gemessenen optischen Dichten D_{380} und D_{390} mußten allerdings korrigiert werden, da sich während der Messungen festes $CdL_2 \cdot 2H_2O$ bildete, welches Lichtstreuung verursachte. Die relative Konzentration wurde mit $(D_\lambda\text{-}D_{\lambda,s})/D_{\lambda,a}$ gleichgesetzt, wobei $D_{\lambda,a}$ die anfängliche optische Dichte bei der betreffenden Wellenlänge und $D_{\lambda,s}$ den Beitrag der Lichtstreuung bei der gleichen Wellenlänge bedeuten. Zur Ermittlung von $D_{\lambda,s}$ wurde angenommen, daß das Raleigh'sche Gesetz näherungsweise gilt, d.h. daß zwischen $D_{\lambda,s}$ und log λ eine lineare Beziehung besteht. Für die lineare Extrapolation benötigte Koeffizienten ermittelte man durch die gleichzeitige Messung der optischen Dichte bei den zusätzlichen Wellenlängen von 500 und 600 nm, bei welchen das gelöste Cadmiumoxinat kein Licht mehr absorbiert. Proben aus sämtlichen Lösungen wurden nach gewisser Zeit (*ca.* 2 Wochen) an einem Membranfilter (Sartorius 11605, Porengröße 0,6 μm) filtriert gewogen, das Lösungsmittel abgedampft und die Rückstände in soviel Salpetersäre aufgelöst, daß nach Protonierung des Oxins noch 0,1M freie Salpetersäure vorlag. Der Cadmiumgehalt wurde schließlich nach dem unten beschriebenen Programm atomabsorptiometrisch ermittelt (log $[Cd]_{t,o}$ wird in Abb. 4 mit Gleichgewichtsdaten verglichen).

Atomabsorptiometrische Bestimmung von Cadmium in der Graphitrohrküvette

$[Me_4N]NO_3$ wurde[1] als Inertsalz bei der Rückextraktion von Cu(II)–Oxinat gewählt, da es sich bei 400° bis 500° aus der Küvette verflüchtigte und die Cu-Bestimmung nicht störte.

Allerdings mußte—wegen sich widersprechenden Angaben[7–11] über die Flüchtigkeit von Cadmium—geprüft werden, ob eine Zersetzungsstufe mit einer Temperatur zwischen 400° und 500° genügend tief liegt damit keine nennenswerten Cadmiumverluste auftreten. Um dies festzustellen, wurden Cadmiumbestimmungen mit je 10 bzw. 20 μl einer $5 \cdot 10^{-8}M$ $Cd(NO_3)_2$-Lösung in 0,1M Salpetersäure mit dem folgenden Programm ausgeführt: 1. Trocknen: 96°, 30–60 Sek; 2. Abdampfen von HNO_3: 136°, 30 Sek; 3. Thermische Zersetzung durch Temperaturerhöhung von 138° auf T_4 während *ca.* 60 Sek; 4. Vervollständigung der thermischen Zersetzung: T_4, 60 Sek; 5. Atomisierung:[12] 1900° 10 Sek.

Zur Berechnung der Cd-Verluste, welche in der 4-ten Stufe auftraten, wurde eine Eichung bei $T_4 = 300°$ (% Verlust = 0) vorgenommen, wobei die Peakhöhen (% ABS) bezogen[1] auf die Basislinie bei T_4 verwendet wurden. Diese Versuche zeigten, daß merkliche Cadmiumverluste erst oberhalb 500° auftraten. Alle späteren Bestimmungen wurden mit $T_4 = 450°$ ausgeführt. Zur Berechnung der Cadmiummenge Q mußte jeweils die entsprechende optische Dichte D in ein parabolisches Eichpolynom $Q = a + bD + cD^2$ eingesetzt werden, da eine Linearität zwischen Q und D nicht einmal in einem engen Meßbereich bestand.

Mit diesem Programm wurden nun Eichkurven bei verschiedenen Lampenströmen aufgenommen. Der Einfluß des Lampenstromes auf die Eichkurven ist sehr ausgeprägt (s. Abb. 2). Die starke Abnahme der meßbaren optischen Dichte mit der zunehmenden Belastung der Hohlkathodenlampe wird vermutlich durch Selbstabsorptionsverbreiterung der Emissionslinie verursacht. Man arbeitete in der Regel mit Lampenströmen von 9–10 mA, da hier zwischen Empfindlichkeit und Schwankung des Basissignals das

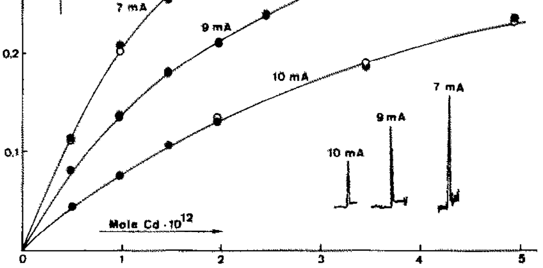


Abb. 2. Einfluß vom Strom der Hohlkathodenlampe auf die Empfindlichkeit der Cadmiumbestimmung in der Graphitrohrküvette.

günstigste Verhältnis vorlag. $[Me_4N]\,NO_3$ beeinflußt nicht in nachweisbarem Maß die gemessenen optischen Dichten. In der Folge wurden daher Eichlösungen ohne $[Me_4N]NO_3$ verwendet.

Auf die ständige Benützung des Deuterium-Untergrundkompensators wurde ebenfalls verzichtet, da offensichtlich keine nicht-spezifische Absorption vorlag. Gelegentlich wurden jedoch mit der Deuteriumlampe Kontrollmessungen durchgeführt.

Ausführung der Löslichkeitsbestimmungen im Wasser

Es wurden 10 bis 30 mg $CdL_2 \cdot 2H_2O$ in je 10 ml einer Oxinlösung beigegeben, deren pH-Wert mit HNO_3 bzw. $[Me_4N]OH$ und deren ionale Stärke mit $[Me_4N]NO_3$ auf 0,1 eingestellt war. Vorversuche auf einer Schüttelmaschine mit *ca.* 200 Schüttelbewegungen pro Minute zeigten, daß ein Gleichgewicht zwischen fester und flüssiger Phase innerhalb einer nützlichen Frist—besonders im neutralen und alkalischen Gebiet—mit genügender Genauigkeit nicht angenähert werden konnte. Alle Löslichkeitsbestimmungen wurden daher unter den folgenden standardisierten Meßbedingungen ausgeführt.

Je 6 der anfangs genannten Ansätze wurden in Pillengläsern von *ca.* 30-ml Fassungsvermögen auf einem Gestell, welches mit einem Vibromischer in Bewegung gehalten wurde, 5 Tage bei 25° equilibriert. Die Pillengläser enthielten noch zusätzlich zur besseren Dispergierung der festen Phase in der Lösung einige kleine Glasperlen. Der Vibromischer wurde mit einer solchen Amplitude betrieben, daß das feste Oxinat ständig in Dispersion blieb. Diese Technik gewährleistete eine recht schnelle Einstellung des Auflösungsgleichgewichtes. Dieses wurde in meisten Fällen nach 24 Stunden erreicht. In allen Fällen wurde $[Cd]_t$ nach 3 Tagen konstant und war für verschiedene $CdL_2 \cdot 2H_2O$-Präparate und verschiedene $CdL_2 \cdot 2H_2O$-Mengen innerhalb der Fehlergrenzen bei gleichem pL-Wert immer dieselbe. Man erhielt zudem eine sehr gute Reproduzierbarkeit. Die durchschnittliche, einfache Standardabweichung einer Meßserie unter standardisierten Versuchsbedingungen betrug 6,2% und niemals wurde 10% überschritten. Diese entspricht einer einfachen Standardabweichung des log $[Cd]_t$-Wertes von 0,028.

Nach Ablauf von 5 Tagen wurden die pH-Werte gemessen (für Eichung der Meßkette s. Zitat[1]). Die durchschnittliche, einfache Standardabweichung σ(pH) innerhalb einer Serie (6 Ansätze) mit je gleicher Konzentration an $[HL]_t$ und HNO_3 bzw. $[Me_4N]OH$ betrug bei genügender Pufferkapazität (pH $< 5{,}8$ bzw. pH $> 8{,}9$) 0,013. Da diese ungefähr dem Meßfehler der pH-Messung in einer und derselben Lösung entspricht, wurde pL mit dem Mittelwert der pH-Werte innerhalb einer Serie berechnet, wobei die kürzlich ermittelten[1] Protonierungskonstanten K_1 und K_2 von L^- benutzt wurden. Nach dem Fehlerfortpflanzungsgesetz beträgt die Reproduzierbarkeit [$= \sigma$(pL)] 2σ(pH) für pH $< 4{,}3$, und 1σ (pH) für pH > 9 [für dazwischenliegende pH-Werte: 2σ (pH) $> \sigma$(pL) $> 1\sigma$ (pH)].

Nach erfolgter pH-Messung wurden die Proben nochmals 6 Stunden equilibriert und hierauf durch einen Membranfilter (Sartorius 11107, Porengrösße 0,2 μm) abfiltriert und das Filtrat durch Zugabe von konz. Salpetersäure auf 0,1*M* angesäuert. Obwohl in saurer Lösung keine Cadmiumverluste infolge Cd-Absorption an Gefäßwänden auftreten,[13] wurden die atomabsorptiometrischen Cd-Bestimmungen gleich anschliessend ausgeführt. Nötigenfalls wurden die angesäuerten Filtrate mit 0,1*M* Salpetersäure weiterverdünnt. Die Konzentration der Eichlösungen wurde jeweils der zu bestimmenden Cadmiumkonzentration angepaßt, sodaß für gleiches Einspritzvolumen der zu analysierenden Proben bzw. der Eichlösung ungefähr gleich große Absorptionssignale resultierten. Jede Probe wurde mehrfach eingespritzt, wobei die eingespritzten Cadmiummengen variiert wurden.

Bei der Ausführung der Löslichkeitsbestimmungen wurde der Kontaminationsgefahr besondere Aufmerksamkeit geschenkt: sämtliche benutzten Glaswaren wurden mit einer Säuremischung von je 2*M* Salpeter- und Salzsäure vorgereinigt und mit doppelt-destilliertem Wasser gespült. Weiterhin wurde das Referenzelektrolyt der kombinierten pH-Elektrode häufig gewechselt.

Bestimmung der Löslichkeit von $CdL_2 \cdot 2H_2O$ in Chloroform

Die Löslichkeitsversuche wurden genau auf die selbe Art und Weise wie in wäßrigem Medium durchgeführt. Es wurde die eingesetzte Oxinkonzentration $[HL]_0$ variiert, wobei je zwei Ansätze mit der gleichen $[HL]_0$-Konzentration jedoch mit verschiedenen $CdL_2 \cdot 2H_2O$-Einwaagen gemacht wurden. Die Filtrierung der Proben erfolgte ebenfalls durch ein Membranfilter (Sartorius 11605, Porengröße 0,6 μm).

RESULTATE UND DISKUSSION

Der Logarithmus der atomabsorptiometrisch bestimmten, totalen Cadmiumkonzentration log $[Cd]_t$ im Wasser ist in Abb. 3 gegen den negativen Logarithmus der freien Oxinatkonzentration pL aufgetragen. Da die Löslichkeit nicht nur bei kleinen, sondern auch bei hohen Konzentrationen [L] des freien Oxinations L^- zunimmt, muß neben den Partikeln Cd^{2+}, CdL^+ und CdL_2 auch das koordinativ gesättigte CdL_3^- berücksichtigt werden. Die Löslichkeit beträgt daher bei einer bestimmten Oxinatkonzentration:

$$\begin{aligned}[Cd]_t &= [Cd] + [CdL] + [CdL_2] + [CdL_3] \\ &= K_{s0}/[L]^2 + \beta_1 \cdot K_{s0}/[L] \\ &\quad + \beta_2 \cdot K_{s0} + \beta_3 \cdot K_{s0} \cdot [L] \qquad (1)\end{aligned}$$

In dieser Gleichung bedeutet K_{s0} das Löslichkeitsprodukt des Cd–Oxinates ($= [Cd]\,.\,[L]^2$) und β_n die Bruttostabilitätskonstante ($= Cd(L)_n/[Cd]\,.\,[L]^n$ mit $n = 1, 2, 3$).

Die Ermittlung dieser Konstanten aus den Löslichkeitsdaten erfolgte rechnerisch, wobei aber gewisse

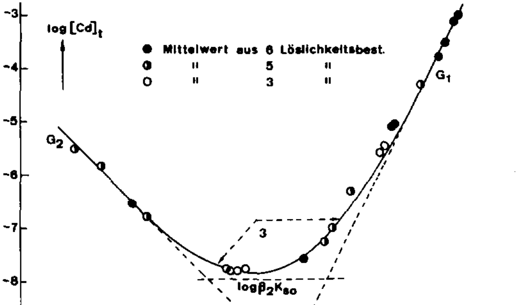


Abb. 3. Löslichkeit des Cd-Oxinates ($CdL_2 \cdot 2H_2O$) als Funktion der Konzentration des freien Oxinations (25°C, $\mu = 0{,}1$).

Aspekte der graphischen "curve fitting"-Methode von Sillén[14] berücksichtigt wurden. Die Auswertung und die Abschätzung der Reproduzierbarkeit (Standardabweichung, σ) von den Konstanten sollen nun kurz beschrieben werden.

Wenn unter den Partikeln Cd^{2+} stark dominiert, hängt log $[Cd]_t$ von pL gemäß Gleichung (1) linear ab (Assymptote A_1):

$$\log [Cd] = \log K_{s0} + 2 \cdot pL \qquad (A_1)$$

Die Punkte in stark sauerem Gebiet mit $pL > 8{,}2$ (s. Abb. 3) ergaben eine Neigung von 1,90 ± 0,12, was die Molzahl 2 des Oxinations pro Cd in der Auflösungsreaktion eindeutig bestätigt.

Bei sehr hohen Oxinatkonzentrationen herrscht CdL_3^- vor, sodaß die Funktion $\log[Cd]_t$, pL die Assymptote A_2 annähert:

$$\log[CdL_3] = \log \beta_3 \cdot K_{s0} - pL \qquad (A_2)$$

Die Messungen mit $pL < 4{,}5$ (s. Abb. 4) liegen an einer Regressionsgerade mit der Neigung von −0,95 ± 0,09. Das Cadmiumoxinat geht also in diesem Gebiet durch Aufnahme von 1 Mol Oxination pro Cd in Lösung. Damit ist die Arbeitshypothese gemäß Gleichung (1) bestätigt und kann beibehalten werden.

Zur Bestimmung von log β_3 und log K_{s0} werden die Assymptoten A_1 und A_2 durch die Geraden G_1 und G_2 angenähert, deren Schwerpunkte $(\bar{x}_1, \bar{y}_1)$ und $(\bar{x}_2, \bar{y}_2)$ aus den oben genannten Punkten bestimmt und deren Neigung 2 bzw. −1 gesetzt wird:

$$y_1 = \log[Cd]_{t,1} = \bar{y}_1 + 2 \cdot (x_1 - \bar{x}_1) \qquad (G_1)$$

$$y_2 = \log[Cd]_{t,2} = \bar{y}_2 - (x_2 - \bar{x}_2) \qquad (G_2)$$

Hierbei wurde pL im Gebiet G_1 bzw. G_2 mit x_1 bzw. x_2 bezeichnet.

Der Schnittpunkt S_{12} der beiden Geraden G_1 und G_2 fällt innerhalb der Fehlergrenzen mit dem Schnittpunkt der beiden Assymptoten A_1 und A_2 zusammen. Für diesen gemeinsamen Punkt gilt daher die folgende Beziehung [2]:

$$3 \cdot pL_{12} = \log \beta_3 = 2 \cdot \bar{x}_1 - \bar{y}_1 + \bar{x}_2 + \bar{y}_2 \qquad (2)$$

Die Schwerpunkte $(\bar{x}_1, \bar{y}_1)$ und $(\bar{x}_2, \bar{y}_2)$ betrugen (8,916 ± 0,026, −3,554 ± 0,030) und (2,741 ± 0,013, − 6,164 ± 0,051). Gleichung (2) ergab mit diesen Werten log β_3 zu 17,96 ± 0,08.

Da der Ordinatenabschnitt y_1^0 der Geraden G_1 mit dem Ordinatenabschnitt der Assymptote A_1 innerhalb der Fehlergrenzen zusammenfällt, gilt Beziehung (3), welche zur Berechnung von log K_{s0} verwendet wird:

$$y_1^0 = \log K_{s0} = \bar{y}_1 - 2 \cdot \bar{x}_1 \quad (= -21{,}39 \pm 0{,}06) \quad (3)$$

Der Ordinatenabschnitt y_2^0 der Geraden G_2 beträgt:

$$y_2^0 = \log K_{s0} \cdot \beta_3 = \bar{y}_2 + \bar{x}_2 \quad (= -3{,}42 \pm 0{,}05) \quad (4)$$

[Diese Beziehung ermöglicht natürlich keine Kontrolle der bereits erhaltenen Werte für β_3 und K_{s0}, da sie von Beziehung (2) nicht unabhängig ist].

Der gefundene Wert für log K_{s0} stimmt mit dem Literaturwert[15] von −21,96 ($\mu = 0$, 25°) überein, welcher in einer Fällungstitration potentiometrisch bestimmt wurde.

Um β_1 und β_2 zu erhalten substrahiert man [Cd] und $[CdL_3]$ von $[Cd]_t$ und ermittelt die Koeffizienten A und B der resultierenden Beziehung (5):

$$[Cd]_t - K_{s0}/[L]^2 - K_{s0} \cdot \beta_3 \cdot [L] = A + B \cdot \frac{1}{[L]} \qquad (5)$$

A bzw. B bedeutet $\beta_2 \cdot K_{s0}$ bzw. $\beta_1 \cdot K_{s0}$. Damit A genügend genau erhalten wird, dürfen nur Punkte einbezogen werden, für welche $[Cd]_t$ die minimale Löslichkeit $[Cd]_{t,min}$ nicht mehr als (5–10)-fach überschreitet (s. Meßbereich 3 in Abb. 4).

$$\log \beta_2 = \log (A/K_{s0}) \pm \{[0{,}434 \cdot \sigma(A)/A]^2 + [\sigma(\log K_{s0})]^2\}^{1/2} \qquad (6)$$

$$\log \beta_1 = \log (B/K_{s0}) \pm \{[0{,}434 \cdot \sigma(B)/B]^2 + [\sigma(\log K_{s0})]^2\}^{1/2} \qquad (7)$$

Mit den Meßpunkten im Gebiet 3 erhielt man log β_2 zu 13,44 ± 0,08 und log β_1 zu 7,34 ± 0,07.

Aus Fällungstitrationen[6,15] ermittelte man für log β_1 die Werte 7,2 ($\mu = 0{,}01$, 20°) bzw. 7,78 ($\mu = 0$, 20°). Der abgeschätzte Wert[6] für log β_2 von 13,4 ($\mu = 0{,}01$, 20°) stimmt erstaunlich gut mit dem hier experimentell bestimmten Wert überein.

Die erhaltenen Konstanten wurden schließlich in Gleichung (1) eingesetzt und $\log[Cd]_t$ berechnet (s. voll ausgezogene Linie in Abb. 3). Die berechnete Kurve ergibt eine recht gute Übereinstimmung mit den experimentellen Punkten und zeigt ein Minimum bei pL = 5,4. Das gelöste Cd ist hier zu 75, 15 bzw. 10 Mol % in Form von CdL_2, CdL^+ bzw. CdL_3^- vorhanden. Die Assymptote log $\beta_2 \cdot K_{s0}$ (s. Abb. 3) kann daher durch experimentell bestimmte Punkte nicht angenähert werden, was eine graphische Bestimmung von log β_2 und log β_1 verunmöglicht. Im allgemeinen ist die graphische Auswertung anwendbar, wenn (log β_2/β_1 − log β_3/β_2) größer als 2 ist, wie z.B. im Falle[4] von Zn(II).

Die Resultate von den Löslichkeitsversuchen in

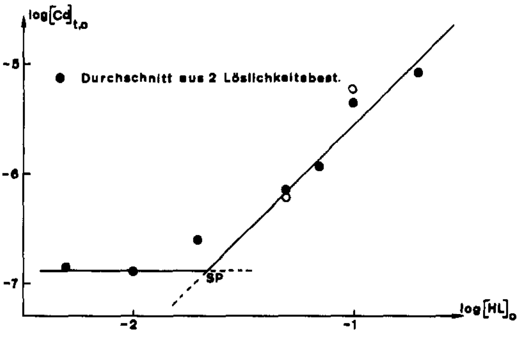


Abb. 4. Löslichkeit des Cd-Oxinates ($CdL_2 \cdot 2H_2O$) in Chloroform in Abhängigkeit der Oxinkonzentration (25°C).

Chloroform sind in Abb. 4 eingezeichnet, und die Auswertung wurde folgendermaßen durchgeführt.

Die totale Cadmiumkonzentration $[Cd]_{t,o}$ einer Chloroformlösung, welche sich mit der festen Phase $CdL_2 \cdot 2H_2O$ im Gleichgewicht befindet, an Wasser gesättigt ist und deren Oxinkonzentration $[HL]_o$ beträgt, Kann wie folgt beschrieben werden:

$$[Cd]_{t,o} = [CdL_2]_o + [CdL_2HL]_o + [CdL_2(HL)_2]_o \qquad (8)$$

Bei höheren $[HL]_o$-Konzentrationen dominiert das Diaddukt, sodaß sich die Funktion $\log[Cd]_{t,o}$, $\log[HL]_o$ der Assymptote A_1^o annähert:

$$\log[Cd]_{t,o}([HL]_o \to \infty) = \log[CdL_2]_{o,s} + \log\beta_A^o + 2\cdot\log[HL]_o \qquad (A_1^o)$$

Hier bedeuten:
$\beta_A^o = [CdL_2(HL)_2]_o/[CdL_2]_o \cdot [HL]_o^2$, die Adduktbildungskonstante in der organischen Phase; $[CdL_2]_{o,s}$, die Sättigungskonzentration des Dihydrates in Chloroform.

Bei sehr niedrigen $[HL]_o$-Konzentrationen wird $[Cd]_{t,o}$ von der $[HL]_o$-Konzentration unabhängig und man erhält eine zweite Assymptote:

$$\log[Cd]_{t,o}([HL]_o \to 0) = \log[CdL_2]_{o,s} \qquad (A_2^o)$$

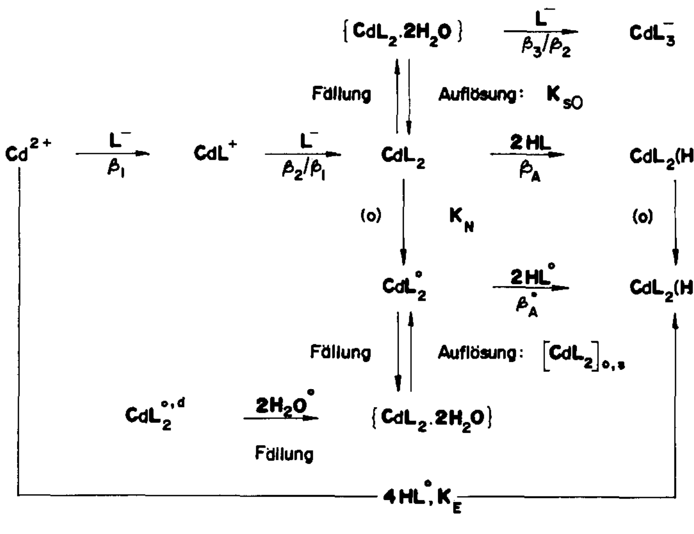
Der Schnittpunkt SP beider Assymptoten liefert die Adduktbildungskonstante:

$$\log\ \beta_A^o = -2\cdot\log[HL]_{o,SP} \qquad (9)$$

Die Neigung der Geraden $\log[Cd]_{t,o}$, $\log\ [HL]_o$ bei $\log[HL]_o \geq -1{,}3$ beträgt 1,85 ± 0,39 d.h. 2 innerhalb der Fehlergrenzen, was die Bildung der Spezies $CdL_2(HL)_2$ bestätigt. Bei $-2{,}3 \leq \log[HL]_o \leq -2$ wird $[Cd]_{t,o}$ von der Oxinkonzentration unabhängig und entspricht $[CdL_2]_{o,s}$ ($\log[CdL_2]_{o,s} = -6{,}882 \pm 0{,}056$). Bei $\log[HL]_o \leq -2{,}3$ erhält man schlecht reproduzierbare Werte für $[Cd]_{t,o}$, was wahrscheinlich auf die Entstehung neuer Spezies durch hydrolytische Spaltung zurückzuführen ist. Zur Berechnung von log β_A^o aus der Beziehung (9) wurden die Assymptoten A_1^o und A_2^o wie vorne durch Geraden mit der Neigung 2 bzw. 0 und den experimentell bestimmten Schwerpunkten ($-1{,}039 \pm 0{,}028$, $-5{,}628 \pm 0{,}086$) bzw. ($-2{,}150 \pm 0{,}029$, $-6{,}882 \pm 0{,}056$) angenähert. Man erhielt aus dem Schnittpunkt dieser Geraden log β_A^o zu 3,33 ± 0,16. Die abgeschätzte Standardabweichung enthält den fortgepflanzten Fehler von $\log[CdL]_{o,s}$ und vom Schwerpunkt der A_1^o repräsentierenden Geraden. Der Verlauf von $\log[Cd]_{t,o}$, $\log[HL]_o$ in der Nähe des Schnittpunktes deutet darauf hin, daß die Spezies $CdL_2 \cdot HL$ in vernachlässigbar kleiner Konzentration auftritt. Eine Ermittlung ihrer Adduktbildungskonstante ist daher nicht möglich. Das Auftreten der Spezies $CdL_2(HL)_2$ wurde bei Extraktionsversuchen[3,16,17] ebenfalls beobachtet. Die Stabilität des Adduktes konnte jedoch aus Verteilungsmessungen nicht ermittelt werden. Merkwürdigerweise bildet sich beim Zn-Oxinat nur ein Monoaddukt[18,19] mit dem Logarithmus 2,17 der Adduktbildungskonstante.

In Abb. 4 sind auch zwei $\log[Cd]_{t,o}$-Werte eingezeichnet, welche in der Mutterlauge von $CdL_2 \cdot 2H_2O$-Fällungen aus Lösungen von wasserfreiem Cadmiumoxinat (s. auch Abb. 1) gemessen wurden. Da man durch Fällung bzw. Auflösung praktisch die gleichen $[Cd]_{t,o}$-Werte erhielt, handelt es sich bei diesen Angaben mit absoluter Sicherheit um Gleichgewichtskonzentrationen.

Mit den ermittelten Daten kann nun auch die Verteilung von Cadmiumoxinat zwischen Chloroform (o, organische Phase) und Wasser (kein Index) richtig interpretiert werden. Die folgende Skizze zeigt die wichtigsten Stufen der Komplexbildung, ausgehend vom Aquokomplex Cd^{2+} bzw. vom dehydratisierten Cd–Oxinat $CdL_2^{o,d}$.



Die bisher nicht difinierten Konstanten bedeuten:

$\beta_A = [CdL_2(HL)_2]/[CdL_2]\cdot[HL]^2$ = die Adduktbildungskonstante im Wasser.

$K_N = [CdL_2]_o/[CdL_2]$ = Nernst'-sche Verteilungskonstante des neutralen Komplexes.

$K_A = [CdL_2(HL)_2]_o/[CdL_2(HL)_2]$ = Nernst'-sche Verteilungskonstante des Diadduktes.

$K_E = [CdL_2(HL)_2]_o\cdot[H]^2/[Cd]\cdot[HL]_o^4$ = Extraktionskonstante.

Die Extraktion von Cd(II) kann entweder durch Verteilung des neutralen Komplexes CdL_2 mit anschliessender Adduktbildung in der organischen Phase, oder durch primäre Adduktbildung in der wäßrigen Phase mit nachfolgender Verteilung des Adduktes beschrieben werden. Obwohl die zweite Möglichkeit bisher bevorzugt wurde,[16,17] schlagen wir den ersten Reaktionsweg vor, da dieser über experimentell nachweisbare Stufen verläuft.

In dieser Arbeit konnten β_1, β_2, β_3, K_{s0} und β_A^o sowie die Sättigungskonzentration $[CdL_2]_{o,s}$ in der organischen Phase aus Löslichkeitsversuchen ermittelt werden. Zudem kann K_N aus diesen Daten berechnet werden. Die Verteilung von CdL_2 stellt sich nämlich so ein, daß seine Aktivität bezogen auf den gemeinsamen Standardzustand des festen Oxinates in beiden Phasen gleich wird. Somit kann K_N dem Verhältnis der beiden Sättigungskonzentration $[CdL_2]_{o,s}$ bzw. $[CdL_2]_s$ gleichgesetzt werden:

$$\begin{aligned} K_N &= [CdL_2]_{o,s}/[CdL_2]_s \\ &= [Cd]_{t,o}([HL]_o \rightarrow 0)/K_{s0}\cdot\beta_2 \qquad (10) \end{aligned}$$

$[CdL_2]_{o,s}$ bekommt man durch Extrapolation der bei verschiedenen $[HL]_o$-Konzentrationen bestimmten Löslichkeiten von $CdL_2.2H_2O$ in Chloroform. Die direkte Bestimmung scheitert an der Hydrolyse (s. vorne) des Cadmiumoxinates in Abwesenheit von Oxin. Mit den bereits mitgeteilten Daten erhielt man für log K_N 1,07 ± 0,11. Bei dieser Fehlerangabe handelt es sich um einen maximalen Fehler, da er durch Fehlerfortpflanzung abgeschätzt wurde. Der niedrige K_N-Wert deutet darauf hin, daß sich eine hydratisierte Spezies zwischen den beiden Phasen verteilt. Wenn man die Koordinationszahl 6 als gegeben annimmt, kann es sich nur um $CdL_2(H_2O)_2$ handeln. K_N bedeutet daher die Verteilungskonstante $[CdL_2(H_2O)_2]_o/[CdL_2(H_2O)_2]$. Wir verzichteten jedoch auf Angabe der koordinierten Wassermoleküle, da diese in der messenden Komplexchemie gewöhnlich weggelassen werden. Ähnlich verhält sich das Zinkoxinat mit einem K_N-Wert[19] von $10^{1,41}$. Dagegen dürfte bei Kupferoxinat kein Wasser als Ligand vorhanden sein, da der K_N-Wert[1] $10^{3,38}$ beträgt.

Eine Bestimmung von K_N durch Extraktion kann nicht ausgeführt werden, da CdL_2 bei keinem [L], $[HL]_o$-Wertepaar als in beiden Phasen gleichzeitig dominierende Partikel auftritt. Diese Bedingung trifft auf $CdL_2(HL)_2$ noch weniger zu, da die Konzentration von HL im Wasser nicht genügend hoch gewählt werden kann. [HL] beträgt maximal $5\cdot10^{-3}M$, sodaß die Adduktbildungskonstante im Wasser mindestens $10^{6,6}$ betragen sollte, damit das Verhältnis $[CdL_2(HL)_2]/[CdL_2]$ auf 100 steigt. Es ist aber sehr unwahrscheinlich, daß die Adduktbildungskonstante in Wasser mehr als 1000-mal größer ist als in Chloroform. Die Zerlegung der leicht meßbaren Extraktionskonstante K_E in β_2, β_A und K_A kann daher nicht durchgeführt werden. Die Auftrennung von K_E wurde trotzdem versucht,[16,17] wobei ein K_A-Wert von $10^{4,1}$ verwendet wurde, welcher als Verteilungsverhältnis q_{Cd} $(= [Cd]_{t,o}/[Cd]_t)$ ermittelt worden ist und somit sicherlich zu niedrig ist. Gleichzeitig ist das angegebene Produkt $\beta_2.\beta_A$ $(=K_c$ im Zitat[17]) zu hoch. Nichtsdestoweniger stimmt das Produkt $K_A.\beta_2.\beta_A$ bzw. K_E. Nach unserer Ansicht sollte K_A bei $CdL_2(HL)_2$ wesentlich größer sein als bei einem Monoaddukt, wie z. B. ZnL_2HL bzw. ZnL'_2HL' (HL' = 8-Hydroxychinaldin), welche einen abgeschätzten, minimalen K_A-Wert[18] von $10^{3,6}$ bzw. $10^{4,8}$ besitzen. Das Zentralion ist nämlich in $CdL_2(HL)_2$ vollständig vom voluminösen in Chloroform gut löslichen Oxin umhüllt, was einen grossen K_A-Wert ergeben sollte.

Um unsere Daten mit Literaturangaben zu vergleichen berechneten wir daher mit den hier bestimmten β_2, β_A^o und K_N die Extraktionskonstante K_E:

$$\begin{aligned} K_E &= \beta_2\cdot\beta_A\cdot K_A/K_{HL}^4\, K_1^2 \\ &= \beta_2\cdot\beta_A^o\cdot K_N/K_{HL}^2\cdot K_1^2 \qquad (11) \end{aligned}$$

wobei K_{HL} $(= [HL]_o/[HL])$ die Nernst'-sche Verteilungskonstante des Oxins ist. Diese Beziehung ergibt für log K_E −6,5 Radiochemisch[3,17] wurden aus Verteilungsmessungen Werte von −6,1 bzw. −5,3 gefunden.

Eine wichtige Regel kann nun für die Anreicherung von Cd(II) aus verdünnten Lösungen durch Extraktion mit einer HL-haltiger Chloroformlösung abgeleitet werden: $[Cd]_{t,o}$ darf im Laufe der Extraktion den Wert $[CdL_2]_{o,s}\cdot(1 + \beta_A^o\cdot[HL]_o^2)$ nicht überschreiten, da sonst eine Fällung von $CdL_2.2H_2O$ auftreten kann. Die Entstehung der festen Phase geht allerdings kinetisch sehr träge vor sich, sodaß in einer "schnellen Extraktion" höhere Anreicherungen erreicht werden können. Anreicherungsmethoden, welche mit übersättigten Lösungen arbeiten, sind jedoch störanfällig, da der plötzliche Beginn einer Kristallisation von vielen zufälligen Faktoren abhängt.

Entwässertes Cd(II)-Oxinat löst sich in H_2O- und HL-haltigem Chloroform relativ gut. Es handelt sich auch hier um übersättigte Lösungen, falls die Cadmiumkonzentration $[Cd]_{t,o}$ den oben angegebenen Grenzwert überschreitet (d.h. $[Cd]_{t,o} > 10^{-6,88}\cdot(1 + 10^{3,33}\cdot[HL]_o^2)$). Dies konnte durch ein Impf-Experiment eindeutig bewiesen werden: eine $1{,}2\cdot10^{-5}M$ Lösung von dehydratisiertem Cd-Oxinat, in Chloroform welches an Wasser gesättigt und an HL 0,1*M* war, zeigte während 24 Stunden keine Abnahme des Cd-Gehaltes. Nach dem Impfen mit $CdL_2\cdot2H_2O$ sank aber $[Cd]_{t,o}$ innerhalb von *ca.* 2 Stunden auf die Hälfte (s. Abb. 1).

Wie aus der vorliegenden Arbeit ersichtlich ist, können aus Löslichkeitsbestimmungen alle benötigten Informationen gewonnen werden, welche zur Ausarbeitung von Fällungs- bzw. Extraktionsmethoden für die Anreicherung von Metallionen notwendig sind. Aus Löslichkeitsversuchen kann beurteilt werden, ob eine einzige Spezies gleichzeitig in zwei verschiedenen Lösungsmitteln bei einer bestimmten Ligandkonzentration die dominierende Partikel ist, und damit ihre Nernst'-sche Verteilungskonstante als Verteilungsverhältnis des Metalls direkt bestimmt werden kann. Dadurch können Unsicherheiten bei der Interpretation von Verteilungsdaten vermieden werden.

Das Hauptproblem besteht bei Löslichkeitsuntersuchungen in der genügenden Annäherung des Gleichgewichtes zwischen der Lösung und der festen Phase. Dies wird am besten erreicht, wenn die feste Phase in kristalliner Form vorgegeben wird. So vermeidet man nämlich die Bildung von übersättigter Lösungen, und die Trennung der Phasen nach dem Equilibrieren gestaltet sich auch leichter. Zur Separation beider Phasen sollten unbedingt Membran-Filter eingesetzt werden, da diese eine sichere und schnelle Trennung ermöglichen. Die Bestimmung des aufgelösten Metalls kann in vielen Fällen mit flammenloser Atomabsorption durchgeführt werden. Jedenfalls hat sich diese Technik für die Bestimmung von Cadmium sehr gut bewährt.

Danksagung—Der Eidg. Stiftung zur Förderung Schweizerischer Volkswirtschaft durch wissenschaftliche Forschung danken wir für finanzielle Unterstützung.

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ELECTROREDUCTION OF URANIUM (VI) AT A PLATINUM ELECTRODE AND ITS ANALYTICAL APPLICATIONS

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Summary—Under normal conditions, the reduction of uranium(VI) at a platinum electrode, in acid solutions, is masked by the reduction of the hydrogen ion. If the working electrode is subjected to hydrogen evolution (at a current density of about 7 A/cm^2 for 90–120 min) the H_{ads} on the platinum surface, acting as a bridge in the electron transfer, shifts the reduction wave of uranium(VI), in 1*M* sulphuric acid solutions, to potentials ($E_{1/2} \simeq -0{\cdot}03$ V) less negative than that of the hydrogen discharge (about $-0{\cdot}25$ V). The wave corresponding to the reduction of uranium(VI) to uranium(IV) is well shaped, diffusion-controlled, and can be used for the determination of uranium down to $2 \times 10^{-5}M$ or $3 \times 10^{-6}M$ if a rotating electrode is used. Interferences arise from those ions with similar $E_{1/2}$ [*i.e.*, Cu(II) and Bi(III)], or from those such as permanganate and dichromate, which oxidize the H_{ads} on the platinum electrode. Because of the time required for the electrode pretreatment, the determination is time-consuming but in some respects it appears a useful improvement over the DME.

A mercury electrode is often used for the polarographic or coulometric determination of uranium(VI),[1] but sometimes it is preferable to use solid electrodes.[2,3] Zittel and Miller[4] have employed graphite, in the pyrolytic and glassy carbon form; the latter provides the better definition. Inconclusive results have been obtained with a boron carbide electrode.[5]

The platinum electrode, the commonest among solid electrodes, has severe limitations because of the evolution of hydrogen at the potential needed for the reduction of uranium(VI). A ring platinum electrode[2] has been used for the determination of uranium(VI) in sulphuric acid solutions at pH 3·2. Davies *et al.*[3] have reported a coulometric determination of uranium(VI) in hydrochloric acid media with a platinum-gauze electrode, but they resorted to a small amount of bismuth(III) to increase the hydrogen overvoltage at the electrode.

The present note demonstrates that the platinum electrode, both smooth and platinized, can be used for the direct determination of uranium(VI) in strongly acidic solutions and in the presence of diverse ions, when it has been subjected to a vigorous reduction. A rotating platinum electrode or one with periodical renewal of the diffusion layer has been employed. It is possible by combining this and an earlier method,[6] to determine simultaneously uranium(VI) and uranium(IV), whereas, with rare exceptions, the DME fails.

The proposed techniques are sensitive, easy to work and give good reproducibility in various acidic media.

EXPERIMENTAL

Apparatus

The voltammetric behaviour of uranium was investigated in a cell with periodically renewed diffusion-layer electrode (DLPRE).[8] The voltammograms for analytical applications were also measured with a rotating platinum electrode.

The dropping mercury electrode used had the following characteristics: $m = 1{\cdot}24$ mg/sec, $t_d = 4{\cdot}75$ sec.

The mean voltammetric currents were recorded with a three-electrode system. Electrochemical measurements were made with a PAR Mod. 170 Electrochemistry System. The potentiostatic current–time curves were measured on the screen of a Tektronix Type 502 dual-beam oscilloscope.

The reference electrode was a saturated mercury(I) sulphate electrode connected with the polarographic cell through a glass bridge with a sintered filter, filled with saturated sodium sulphate solution. The auxiliary electrode was a platinum electrode with an area of 1 cm^2. The platinum working microelectrode, when necessary, was platinized by cathodic treatment at a current density of 1·2 A/cm^2 in a 3% solution of chloroplatinic acid containing 0·025% of lead acetate.

Unless otherwise specified, measurements were performed at 25 ± 0·1°. The ionic strength was kept constant with an inert salt. Solutions were deaerated with purified nitrogen. All potentials reported are referred to the saturated calomel electrode.

Reagents

All chemicals used were of reagent grade.

Uranium(IV) solutions were prepared by electrolytic reduction of uranium(VI) at a mercury-pool electrode, and standardized by permanganate titration.

Preliminary work

Effects of the pretreatment of the smooth platinum electrode. The current–voltage curve (scan-rate 60 mV/min) from +0·225 to −0·300 V, at a smooth platinum electrode (DLPRE), of deaerated 1*M* sulphuric acid solution is shown in Fig. 1B, curve a.

To see whether the hydrogen evolution really makes it impossible to obtain a reduction wave for uranium(VI) at the platinum electrode, we tried to pretreat the electrode so as to displace the hydrogen discharge to more negative potentials. The pretreatment consisted of: (*a*) cleaning of the electrode in hot nitric acid (1 + 1) for about 10 min;

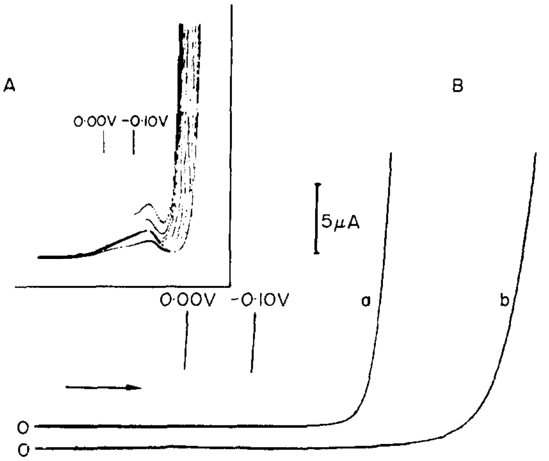

Fig. 1. A: Voltammograms of 1*M* HNO_3 during pretreatment. B: Voltammograms of 1*M* H_2SO_4 before (curve a) and after (curve b) pretreatment.

(*b*) dipping the electrode in the polarographic cell containing deaerated 1*M* nitric acid and making repeated recordings of the current–voltage curves in the cited potential range with a slow scan-rate (≤ 30 mV/min). In the course of this tedious operation (it took 3–4 hr), the hydrogen discharge shifted towards negative potentials, by about 0·1–0·2 V as seen in Fig. 1A, which shows the electroreduction of platinum oxides. The comparable curve for deaerated 1*M* sulphuric acid solution is curve b in Fig. 1B.

When a platinum electrode, so pretreated, is dipped in a deaerated 1*M* sulphuric acid solution, $7 \times 10^{-4}M$ in uranium(VI), the voltammogram shown in Fig. 2 (curve a) is obtained.

Under the same conditions, the reduction at the DME takes place at the same potential (Fig. 2, curve b). This seems to confirm the impossibility of obtaining a reduction wave for uranium(VI) at the platinum electrode; however, if the electrode is polarized at -2 V for 1 min (at a current density of about 4 A/cm^2) the well-shaped cathodic wave shown in Fig. 2 (curve c, $E_{1/2} = -0{\cdot}080$ V) is obtained temporarily.

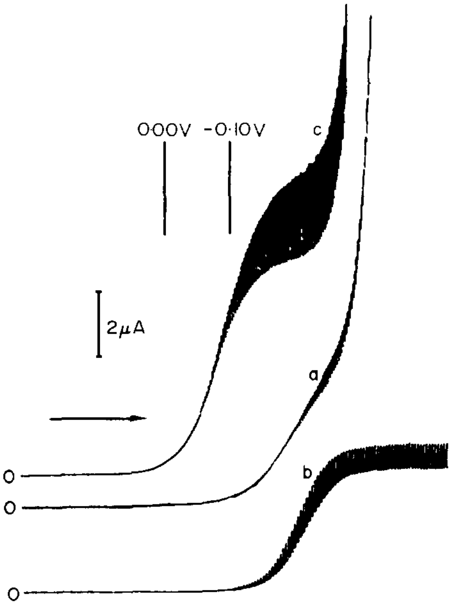

Fig. 2. Voltammetric curves of $7 \times 10^{-4}M$ uranium(VI) after the pretreatment of Fig. 1 (curve a) and the subsequent cathodic treatment at -2 V for 1 min (curve c); the same solution polarographed with DME (curve b).

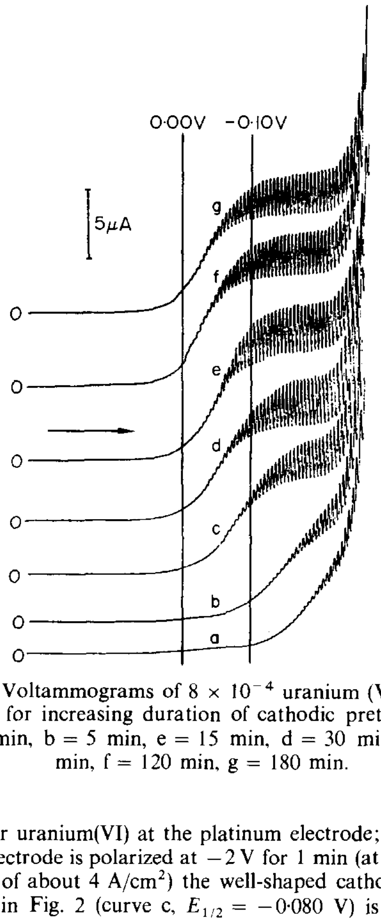

Fig. 3. Voltammograms of 8×10^{-4} uranium (VI) in 1*M* H_2SO_4 for increasing duration of cathodic pretreatment: a = 0 min, b = 5 min, e = 15 min, d = 30 min, e = 60 min, f = 120 min, g = 180 min.

The polarization may be carried out after pretreatment in nitric acid or directly in the sulphuric acid solution of uranium(VI). The latter is easier and was the procedure adopted.

We assume that hydrogen adsorbed on the electrode surface plays an important role in the detection of the cathodic wave of uranium(VI).

Figure 3 shows the voltammograms obtained with a smooth platinum electrode in a deaerated 1*M* sulphuric acid solution that is $8 \times 10^{-4}M$ in uranium(VI), when the applied voltage changes from $+0{\cdot}225$ to $-0{\cdot}300$ V, (scan-rate 60 mV/min) after hydrogen evolution at about $-3{\cdot}2$ V (at a current density of 7 A/cm^2) for the periods indicated in Table 1. As deducible from Fig. 3 and Table 1, the reduction wave of uranium(VI) is already well shaped after hydrogen evolution for 60 min, and after 120 min there is no sensible improvement. Essentially the same results

Table 1. Effect of the electrode hydrogenation on the reduction wave of uranium(VI)

Curve in Fig. 3	Hydrogenation time, *min*	$E_{1/2}$, *V*	$\bar{i}_d$, *μA*
a	0	not detectable	—
b	5	hardly useful	—
c	15	−0·082	8·40
d	30	−0·063	8·75
e	60	−0·052	8·80
f	120	−0·032	8·75
g	180	−0·031	8·70

Electrolyte: 1*M* H_2SO_4, $8 \times 10^{-4}M$ UO_2^{2+}.

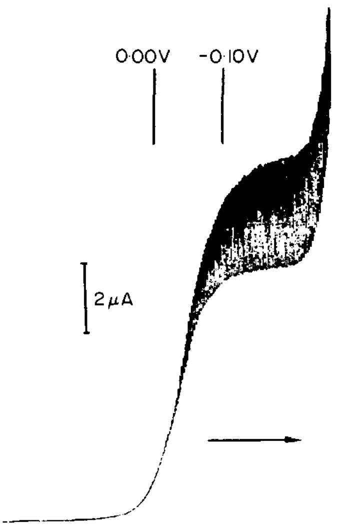

Fig. 4. Voltammograms of $8 \times 10^{-4}M$ uranium(VI) in $1M$ H_2SO_4 under optimal condition of pretreatment.

are obtained when the hydrogen evolution is performed with current densities of 5–9 A/cm^2; at lower current densities a more protracted time of prehydrogenation is necessary.

Under these conditions no anodic current arises from hydrated oxides of uranium.[9,10]

The cathodic wave for uranium(VI), obtained through sufficiently prolonged hydrogen evolution (120 min) is well shaped (Fig. 4) ($E_{1/2} = -0{\cdot}032$ V), and strictly proportional to uranium(VI) concentration down to $2 \times 10^{-5}M$. The best-shaped waves were obtained when the curves were registered for increasingly negative potentials, after the working electrode had been held for 1 min at the starting potential of $+0{\cdot}225$ V.

Potentiostatic curves obtained at potential values between $-0{\cdot}030$ and $-0{\cdot}200$ V show that the mean reduction currents of uranyl ions remain practically constant for about 80 min, when the platinum electrode has been prehydrogenated at a current density of about 7 A/cm^2 for at least 90 min. Then gradually the cathodic wave shifts towards negative potentials, so that it is necessary to repeat the hydrogenation cycle. The regenerative cycle (type B) described by Gilman[11] is not sufficient to give a well-formed cathodic wave of uranium(VI).

Effect of the supporting electrolyte. Various supporting electrolytes, including hydrochloric, nitric, perchloric and phosphoric acids, were tried with the prehydrogenated electrode.

Hydrochloric acid and its mixtures with other acids suppressed the reduction wave of uranium(VI); this can be attributed to the complexing action of chloride ions on platinum oxides,[12] and consequent modification of the electrode surface.

In perchloric acid the cathodic wave of uranium(VI) is sufficiently well-shaped and diffusion-controlled; however, it is very near to the hydrogen discharge (in $2M$ perchloric acid $E_{1/2} = -0{\cdot}105$ V).

The same results were obtained for nitric acid medium, in the presence of sulphamic acid.

Phosphoric acid gives a well-formed and diffusion-controlled cathodic wave for the reduction of uranium(VI) (in $0{\cdot}66M$ phosphoric acid $E_{1/2} = 0{\cdot}00$ V), but in this electrolyte, seemingly, the hydrogen is not so strongly adsorbed on the electrode surface as for sulphuric acid medium and subjection to a new hydrogen evolution does not provide quite reproducible results.

Concentrations of sulphuric acid greater than $1M$ were tested and good results were obtained up to $5M$ (in $4M$ sulphuric acid $E_{1/2} = +0{\cdot}015$ V); however, when the electrode prehydrogenation is performed in such strongly acidic solutions, it is best to minimize the effects of oxygen by screening the platinum counter-electrode from the solution with a sintered disk.

Effect of platinizing the electrode. Electrodes which have been platinized for 2–8 sec behave like the smooth electrode and do not shorten the hydrogenation times required. Electrodes platinized for >15 sec distort the wave because the capacity of the electrode–solution condenser system is too high.

Procedure for the pretreatment of the electrode

In order to obtain a well-formed cathodic wave for uranium(VI) at a platinum electrode it is necessary to hydrogenate the electrode itself. Such a pretreatment must be carried out in sulphuric acid with or without uranium(VI). During the voltammetric measurements it is convenient to avoid any handling of the solution that may cause the electrode to come into contact with air, because of the possible oxidation of adsorbed hydrogen.

The best conditions are the following: with nitrogen passing through a known volume of $1M$ sulphuric acid, keep the assembly (DLPRE or RPE) at constant cathodic current and a current density of about 7 A/cm^2 for at least 90 min.

In the rest of this paper any reference to the electrode pretreatment means such experimental conditions.

RESULTS AND DISCUSSION

Voltammetric behaviour

The reduction of uranium(VI) at a pretreated platinum electrode is diffusion-controlled, as shown by the dependence of the mean limiting current on the concentration of uranium(VI), and on the temperature over the range 20–55°. The temperature coefficient of the half-wave potential of the cathodic wave is $+1{\cdot}93$ mV/deg. The mean limiting diffusion current increases by 1·45%/deg.

The oscillographic investigation shows the limiting current follows the equation[8]

$$\overline{i_d} = KC$$

where

$$K = nFAD/r + nF\,AD^{1/2}(2t_{tot}^{1/2} - 1{\cdot}5t_p^{1/2})/\pi^{1/2}t_{tot}$$

and n, F, A, D, C have their usual meaning, t_p is the washing period of the electrode (0·025 sec), t_{tot} the period between two subsequent washings (5 sec), and r the radius of the platinum sphere (0·0972 cm). Substitution of the value of D obtained from a DME[13,14] in the same solution, allowed evaluation of n from which it was concluded that the uranium(VI) reduction is represented by:

$$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$$

The ratio $\Delta E/\Delta \log i/(\overline{i_d} - i)$ is 50 mV, whereas 29·5 mV is expected for a reversible process.

At an ionic strength of 3, and an acidity of 0·1–2N, $E_{1/2}$ shifts by -123 mV per pH unit in accordance with the proposed process.

The experimental necessity of the hydrogenation of the electrode for the uranium(VI) reduction process to occur, correlates with the presence of adsorbed hydrogen (H_{ads}) on the platinum surface. Something of the sort has been found for the VO^{2+}/V^{3+} couple.[15]

By analogy, it is reasonable to suppose that the mechanism of UO_2^{2+} reduction implies the intervention of H_{ads}, which acts as a "bridge" in the electron transfer. The electroreduction of UO_2^{2+} to U^{4+} on the DME, in the same experimental conditions,[13,14] at the same potential as on a non-hydrogenated platinum electrode ($W_{1/2} \simeq -0·190$ V, see Fig. 2), may be explained on this basis, since hydrogen is not adsorbed on mercury in the potential range considered.

Because both VO^{2+} and UO_2^{2+} are affected by H_{ads}, we suppose the formation of the hydrogen bridge involves a decrease in the bond energy between the central metal atom and the co-ordinated oxygen atoms, these bonds being broken during the reduction process. It is more difficult to explain the need for a prolonged hydrogenation before reduction of the uranyl ion. Two types of H_{ads} have been observed,[16,17] one very active, the other less so; a surface rearrangement (time-dependent) of the active hydrogen to the less active has also been reported.[17] This may imply that the less active H_{ads} is involved in the uranium(VI) electroreduction. However, unavoidable competitive adsorption of contaminants from the solution poisons the platinum electrode and the subsequent deactivation causes a change in the mechanism of the electroreduction of hydrogen ions[18] and hinders the rapid combination of H_{ads}.

ANALYTICAL APPLICATIONS

Voltammetric determination of uranium(VI)

Uranyl ions, in strongly acidic solutions other than hydrochloric acid, give a well-shaped anodic wave at a hydrogenated platinum electrode. The limiting current is strictly proportional to the uranium(VI) concentration, and thus the voltammetric determination of uranium(VI) is feasible. Sulphuric acid is the most convenient medium.

The proposed method gives reproducible results for uranium(VI) concentrations down to $2 \times 10^{-5}M$ if the DLPRE is used.

As an analytical example we deal with the determination of uranium(VI) in $1M$ sulphuric acid with an electrode prehydrogenated for 120 min as previously indicated ($E_{1/2} = -0·032$ V).

Depending on the nature of the interfering ions the hydrogenation of the electrode can be carried out previously or directly in the test-solution.

The effects of foreign ions on the determination of uranium(VI) are summarized in Table 2. Since the reduction of cadmium(II) occurs at $E_{1/2} \simeq -0·22$ V, it does not interfere if the electrode is previously hydrogenated. When the electrode hydrogenation is performed in the presence of chromium(III) and manganese(II), it is convenient to isolate the platinum counter-electrode from the solution to avoid the formation of dichromate and permanganate ions, which, by oxidizing the H_{ads}, prevent the appearance of the reduction wave of uranium(VI). The reduction of titanium(IV) takes place at about $-0·18$ V and does not interfere. Silver(I) gives a cathodic wave due to reduction to metallic silver ($E_{1/2} \simeq +0·3$ V) and if the electrode hydrogenation is performed in its presence a black deposit of metallic silver forms. Fluoride shifts the cathodic wave of uranium(VI) to more positive potentials, but owing to its corrosive effects, it was not further investigated. The half-wave potentials of copper(II), molybdenum(VI) and bismuth(III) are close to that of uranium(VI) and consequently these species interfere.

Table 2. Effect of diverse ions on the determination of uranium(VI)

Cation	Tolerance limit, *mg*	Anion	Tolerance limit, *mg*
Aluminium	100	Acetate	100
Bismuth	0·2	Arsenate	70
Cadmium	30	Borate	70
Calcium	100	Chloride‡	0·1
Cerium(IV)*	6	Fluoride	20
Chromium(III)	50	Molybdate	0·1
Cobalt(II)	50	Nitrate	100
Copper(II)	0·1	Perchlorate	100
Iron(III)†	3	Phosphate	100
Magnesium	100	Vanadate§	5
Manganese(II)	100		
Nickel	50		
Silver	5		
Titanium(IV)	10		
Thorium	100		
Zirconium	100		

Initial solution: volume 40 ml, UO_2^{2+} 50 μg/ml, $1M$ H_2SO_4.

*$E_{1/2}$ for reduction wave of Ce(IV) $\simeq +1·1$ V.

†$E_{1/2}$ for reduction wave of Fe(III) $\simeq +0·4$ V.

‡ Only on prehydrogenated electrode.

§$E_{1/2}$ for reduction wave of V(V) $\simeq +0·7$ V.

Rotating platinum electrode. The use of the rotating platinum electrode gives the same results as the DLPRE, if previously hydrogenated (Fig. 5). The wave-heights are strictly proportional to the uranium concentrations and the sensitivity of the method is increased by about an order of magnitude, allowing the determination of uranium(VI) down to $3 \times 10^{-6}M$.

Recommended procedure. Perform the determination with nitrogen bubbling through the solution. Pretreat the working electrode as previously indicated, in 40 ml of $1M$ sulphuric acid. Replace 15 ml of the acid with 15 ml of deaerated test-solution. Record the polarogram of the solution over the potential range from $+0·20$ to $-0·30$ V at a scan-rate of 60–120 mV/min. When the rotating platinum electrode is used, it should rotate at about 800 rpm. Determine the uranium(VI) by the standard addition

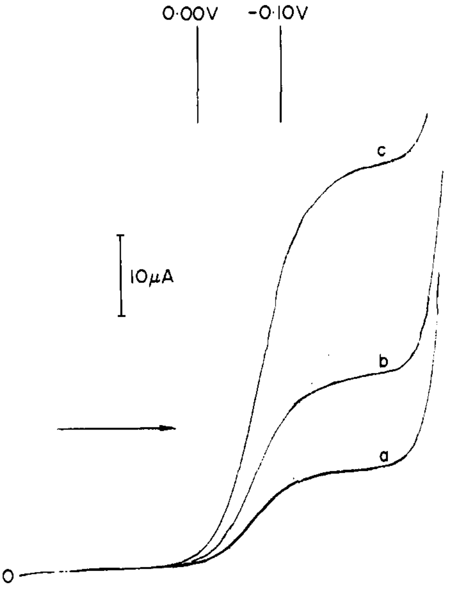

Fig. 5. Voltammograms (hydrogenated RPE) of 5 × $10^{-5}M$ (a), 1 × $10^{-4}M$ (b) and 2 × $10^{-4}M$ UO_2^{2+} in 1M H_2SO_4.

method. Amounts of 0·2–9·5 mg of uranium(VI) were determined with a relative standard deviation of 2·8–0·3% and a relative error of 2·1%.

Simultaneous voltammetric determination of uranium(VI) and uranium(IV)

The electro-oxidation of uranium(IV), at a platinized platinum microelectrode in strongly acidic solutions, has already been reported.[6] A smooth platinum electrode, hydrogenated according to the present paper, enables the oxidation wave of uranium(IV) to be obtained. The two methods differ in the half-wave potential of the oxidation process: in 1M sulphuric acid $E_{1/2}$ = +0·575 V for the platinized electrode, and +0·910 V for the smooth hydrogenated electrode; logarithmic analysis of the ascending part of the wave yields a straight line with slope of 85 mV, compared with 130 mV previously found.

The present method offers the following advantages over the preceding one: (*a*) a simplified procedure because platinizing is unnecessary (appreciable improvement in the analysis of radioactive samples); (*b*) removal of the interference due to vanadium(IV), since it does not take place on the smooth electrode;[19] (*c*) direct determination of uranium(IV) in the presence of small amounts of iron(II) ($E_{1/2}$ = +0·45 V).

From the foregoing it is possible to perform a simultaneous determination of uranium(IV) and (VI) in strongly acidic media, for which no literature references have been found.

In Fig. 6 is shown the voltammogram of 1·30 × 10^{-3} M uranium(VI) and 9·20 × $10^{-4}M$ uranium(IV) in 1M sulphuric acid; it was obtained with a smooth electrode (DLPRE), prehydrogenated for 120 min, the applied potential changing from −0·275 to +1·20 V at 30 mV/min.

Because of the electro-oxidation of H_{ads} at the potential needed for the oxidation of uranium(IV) (> +0·85 V), the determination must be performed by means of calibration curves. The recommended procedure is similar to the preceding one, but as a precaution the potentials are run from negative to positive; the scan-rate can be increased up to 120 mV/min. The rotating platinum electrode gives the same reproducible results.

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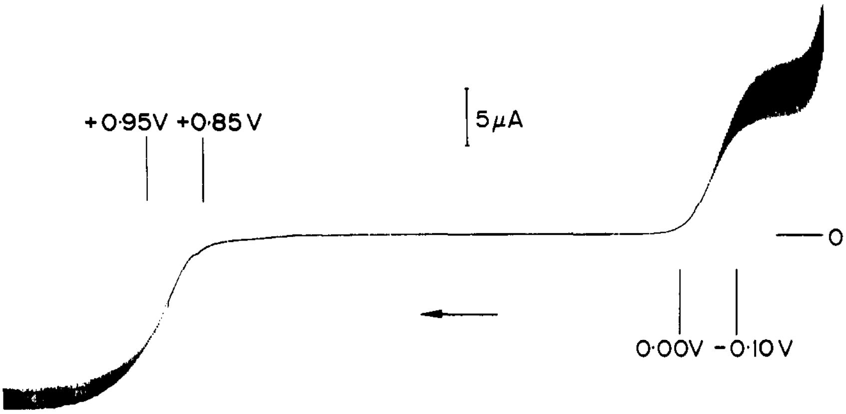

Fig. 6. Voltammogram of 1·30 × $10^{-3}M$ U(VI) and 9·20 × $10^{-4}M$ U(IV).

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TRACE CHARACTERIZATION OF POWDERS BY ATOMIC-ABSORPTION SPECTROMETRY

THE STATE OF THE ART*

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Summary—A review is made of the progress achieved in the last 15 years in the field of trace characterization of powders by direct atomic-absorption spectrometry. The studies covered include the development of novel atomization devices, modification of existing atomic-absorption spectrometers, and the use of closed-cavity vaporizers. A description is given of the capsule-in-flame and circular-cavity furnace type atomizers designed on this principle, of the procedure employed in powder-sample analysis and of some analytical features of the methods used. In conclusion, various modern analytical methods are compared as to the possibilities they offer for the determination of ultratraces in solids, and suggestions are made concerning the possible role of atomic-absorption spectrometry.

Direct trace characterization of various powder materials is undoubtedly one of the most urgent, and at the same time most complicated, problems in atomic-absorption spectrometry and analytical chemistry. This problem has been the subject of continuous study in our laboratory for about 15 years, but only now can we be satisfied that promising ways for its solution finally appear to be seen.

In this work we will consider briefly the most important steps made in this direction in the past, and we will then try to review the progress achieved in some areas of interest, including the most recent achievements. In conclusion we will discuss the role of atomic-absorption spectrometry among other methods of instrumental analysis in the solution of this problem.

METHODS OF ATOMIZATION OF POWDERED SAMPLES

Using the conventional technique of atomic-absorption analysis of liquids[1] for direct trace characterization of powdered samples is impossible primarily because of the inapplicability of the nebulizer-flame type atomizer for these purposes. Although attempts of this kind involving the pulverization of the powder mixed with solid propellant,[2] delivery of the powder to the burner channel by a miniature spiral conveyor[3] or nebulization of a suspension[4] were undertaken, no definite achievements were claimed.

We believe such a technique to be in principle inadequate for a total solution of this problem, on the following grounds. First, the absolute limits of detection of elements in the flame are too high to provide the desirable detection limits for impurities in powders. Indeed, in order to reach a relative detection limit of $10^{-6}\%$ by means of high-temperature flames (for which the average absolute limit of detections of elements is about 10^{-8} g/sec), the powder sample should be introduced into the flame at a rate of about 1 g/sec, which is inconceivable on both technical and economical grounds (the material being frequently quite expensive). Secondly both theoretical[5,6] and experimental[7–9] studies show that sufficiently complete vaporization of aerosol particles of medium- and low-volatility substances in a flame requires thorough grinding of the powder to a size below 1 μm. This operation is complicated and time-consuming and carries the risk of contaminating the sample during the pretreatment. Therefore the only practicable means of vaporization of powder samples remains up to now the use of the graphite furnaces of various types employed widely in the emission analysis of powders.

Another aspect of the problem of developing an atomizer capable of determining as large a number of elements as possible, consists in providing conditions favouring the existence of the sample vapour in the atomized state in the analysis zone (analytical cell). Experiments show that this may be achieved by employing either a hot inert medium inside the furnace or a high-temperature flame. Thus one may conceive at least two different types of atomizer, using

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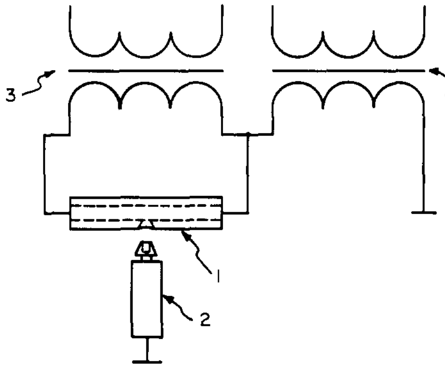

Fig. 1. Graphite cuvette. 1. Graphite tube furnace. 2. Graphite electrode with sample. 3. Step-down transformer (3 kW). 4. Step-down transformer (1 kW).

the graphite vaporizer in combination with either a furnace or a flame.

The first type of atomizer based on an independently heated graphite electrode with the sample, combined with a graphite-tube furnace (the graphite cuvette), was described in 1959.[10,11] Electrode-heating with a d.c. arc, used in the initial version,[10–12] was later replaced by a simpler and more effective a.c. heating with a step-down transformer (Fig. 1).[5,13] The second conceivable type of atomizer, utilizing the combination of a graphite rod with a Mèker burner, was realized in 1969 (Fig. 2).[14] Replacing the air–acetylene flame employed in the first experiments[14] by the nitrous oxide–acetylene flame[15] permitted extension of this method to the determination of elements of low- and medium-volatility.

While the two atomizers are primarily applied in the microanalysis of dry residues from liquid samples, they have also been used in the analysis of powders. Powder samples were placed in the channel of a graphite electrode introduced into a graphite furnace,[5,6,16–20] or in the channel of a graphite rod mounted in the flame.[14,20]

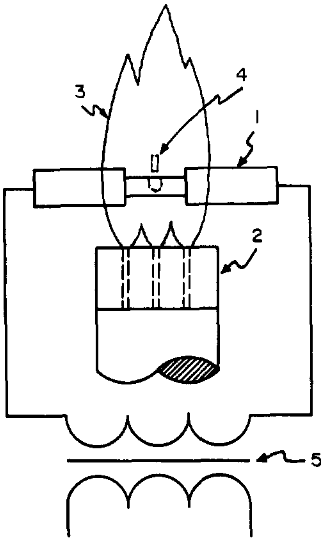

Fig. 2. Furnace-in-flame atomizer. 1. Graphite rod with sample. 2. Mèker burner. 3. Flame. 4. Cross-section of light beam. 5. Step-down transformer (3 kW).

Later, several other powder atomizers, representing modified versions of the cuvette or the furnace-in-flame type were described. The atomizers of the first type are vertical-crucible[21–30] and horizontal-tube furnaces[31–34] heated by a.c.[21–24] or rf[25–30] current, while those of the second type utilize the method of vaporization of powder samples from an iron screw[34,35] into the flame of a slot-burner, and the method of vaporization of solid samples from a graphite microprobe[36] introduced into the flame of the Mèker burner. In contrast to the graphite cuvette and the furnace-in-flame types, in the case of these atomizers[21–36] vaporization of the sample and heating of the analytical zone are performed by a single heater. This not only limits the possibility of separate control of the sample-vaporization regime and of the temperature in the analytical zone in order to ensure optimum conditions for the analysis of particular samples, but also does not provide the temperature required for the atomization of many medium- and low-volatility elements. Therefore despite the successful utilization of these atomizers for the solution of some problems in the area of powder analysis, they are still inferior to the cuvette and the furnace-in-flame in terms of power of detection and range of elements determined.

MODIFICATIONS TO ATOMIC-ABSORPTION SPECTROMETERS

The application of the cuvette and the furnace-in-flame atomizers for the analysis of powder samples entailed considerable changes in the design of other typical units of the atomic-absorption spectrometers used, *viz.* the recording system, optical system and light sources. The reasons for this are as follows.

First, in contrast to affairs in the conventional flame version of the method, the absorption signal resulting from a powder sample vaporized by means of the atomizers described above may represent a pulse of a fairly arbitrary shape with several peaks (Fig. 3). As shown in 1968,[37,38] the only parameter of such a signal which is connected unambiguously with the content of the element in a sample is the pulse area, *i.e.*, the integrated absorbance.

$$Q_A \equiv \int_0^{\tau_1} A\,dt \qquad (1)$$

measured during the total time τ_1 of vaporization of the element in question. This quantity is proportional to the total number of atoms of the element η_0 in the sample and the average time of residence of the atoms τ_2 in the analytical cell:

$$Q_A = A_0\tau_2 \propto \eta_0\tau_2. \qquad (2)$$

The magnitude of A_0 is actually the absorbance for the hypothetical case in which all atoms of the element in question which passed through the analytical

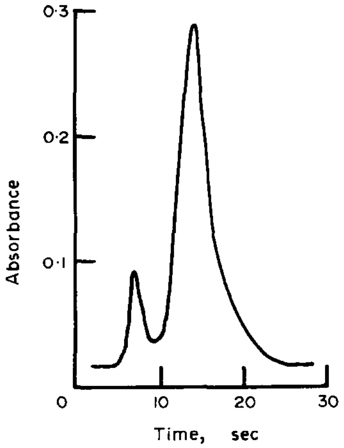

Fig. 3. The recording of an absorption pulse for the Sb 231·1 nm line with antimony vaporized out of graphite powder with a furnace-in-flame atomizer.

cell are considered to be residing in it at the same time.

The pulses can be integrated either by weighing the parts of the chart corresponding to the area of the pulses recorded by a recording potentiometer, or by using electronic integrating devices. The latter method possesses higher precision and speed.

Secondly, the determination of low concentrations of an element in the presence of an excess of the concomitant components in the sample has specific features associated with the appearance of considerable non-selective optical interference resulting from partial scattering and molecular absorption of the light-beam by the vapour of the matrix. The substantial role of this interference in the case of the graphite cuvette was pointed out even in the very first works on the subject.[11,12] The author[5] proposed a method for their automatic correction involving simultaneous recording of absorption from light-sources emitting line and continuum radiation (Fig. 4). This suggestion was based on the work by Koirthyohann and Pickett[39] who employed successive measurement of absorption of light from the same two sources to correct for non-selective interference in the flame. The research carried out by the author and his co-workers[40,41] serves as a basis for the further realization of the method of correcting for non-selective interference in commercial spectrometers.[42]

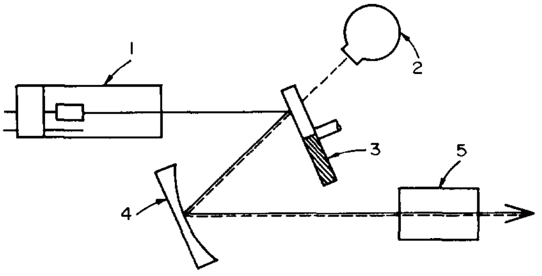

Fig. 4. Deuterium background corrector. 1. Hollow-cathode lamp. 2. D_2-lamp. 3. Rotating chopper. 4. Mirror. 5. Absorption cell.

The third feature which is primarily specific for the cuvette consists in a limited aperture of the traversing light-beam (as compared to the flame) and a strong continuum background from the hot furnace walls. These factors result in a considerable increase of noise in the recording, *i.e.*, in deterioration of the capability of low-level signal detection. The most efficient way to sidestep this limitation lies in the use of brighter light sources.

With this purpose in mind, Kirillova, Levikov and L'vov[5] used spherical radiofrequency lamps (Fig. 5) of the type employed for the optical pumping of lasers.[43] At present, a wide assortment of such lamps suitable for the analysis of more than 30 elements is manufactured in the USSR.[44]

To increase the brightness of conventional hollow-cathode lamps, Bodretsova, L'vov and Mosichev[5,45] proposed to use radiofrequency (60 MHz) rather than d.c. current for the lamp-supply. Later, Dawson and Ellis[46] showed that the same effect can be attained by feeding the lamps with a high-amplitude pulsed current of a few hundred Hz frequency. A comparative study[47] of the characteristics of hollow-cathode lamps supplied with pulsed and continuous currents revealed considerable advantages of the pulsed-power supply when the graphite cuvette was used. Owing to their relative simplicity and versatility, both these techniques turned out to be preferable to using the boosted-output lamps proposed earlier by Sullivan and Walsh.[48]

The brightness of the light-sources chosen as a result of these studies, *viz.* of the spherical radiofrequency and hollow-cathode lamps supplied with rf or pulsed current, exceeds, on the average, by two orders of magnitude that of the d.c. hollow-cathode lamps, and in most cases turns out to be sufficient for practically complete elimination of interference originating from the hot furnace and for compensation for the loss of light in its passage through the cuvette.

LIMITATIONS OF CONVENTIONAL METHODS OF POWDER VAPORIZATION FROM THE CHANNEL

At the beginning of the 70's we not only possessed two essentially different atomizers capable of atomizing powder samples but also had at our disposal quite efficient means of recording absorption signals of arbitary shape against the strong non-selective interference from the matrix and radiation interference

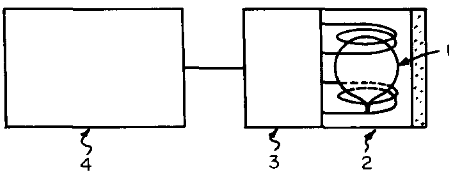

Fig. 5. High-intensity line-source with a spherical electrodeless lamp. 1. Lamp inside an RF-coil. 2. Protective screen. 3. Radio-frequency generator. 4. Power supply.

from the graphite heaters. However, despite the fact that both atomizers were successfully utilized for the analysis of some powder materials,[49] the general state of the art could hardly be considered satisfactory.

Indeed, the application of both atomizers was limited to cases of determining highly-volatile elements in less volatile material where fractional vaporization of impurities could be used. Pulse vaporization of medium-volatility and low-volatility elements from volatile matrices resulted in uncontrollable losses from the sample because of swelling and ejection of the powder from the channel as a result of violent liberation of vapours produced by highly-volatile components present in the sample.

Another serious drawback of both atomizers consisted in their capacity being limited to samples of only a few mg in weight, because of inefficient heating in the vaporizer channel. This produced an adverse effect on the representativeness of sampling and the relative limits of detection.

Both these drawbacks are to a certain extent inherent in all vaporizers used in practical spectral analysis where the vaporized sample is delivered to the analytical zone through a hole provided for this purpose over the cavity with the sample. Therefore they could be eliminated only by designing a vaporizer of a completely new kind which would preclude the possibility of uncontrollable mechanical losses of the sample from the cavity while at the same time providing efficient heating and transport to the analytical zone of much larger amounts (up to a few tens or even hundreds of mg) of the substance being analysed.

As frequently happens, the solution to this problem was quite close. Indeed, every experimenter working on emission spectral analysis is familiar with the phenomenon of partial diffusion of the sample vapour through the walls of graphite electrodes.[50] We also try to overcome this drawback of graphite in atomic-absorption measurements with graphite furnaces. For example, to eliminate vapour losses caused by diffusion through the walls of the graphite cuvette, the walls were lined with tantalum or tungsten foil,[13] and later the walls were coated with pyrolitic carbon impermeable to gas.[5]

The essence of the solution to this problem found and realized by the author together with Katskov and Kruglikova[51,52] consisted of vaporizing powder samples in a closed cavity with graphite walls permeable to gases (Fig. 6). The porosity of the graphite used as material for the heater now changed from a drawback to an advantageous property. It should be noted that using this property of graphite in analytical work is not novel. Indeed, there are reports on the application of graphite capsules for the extraction of gases from metals,[53] and of porous graphite partitions to separate the zones of sample vaporization and excitation in the hot hollow-cathode discharge.[54,55]. Nevertheless, the problems solved in those works appear to be much more modest than the one that faced us.

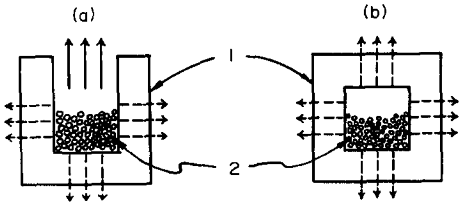

Fig. 6. A simplified representation of the conventional (*a*) and proposed (*b*) methods of powder vaporization. 1. Furnace. 2. Powder sample.

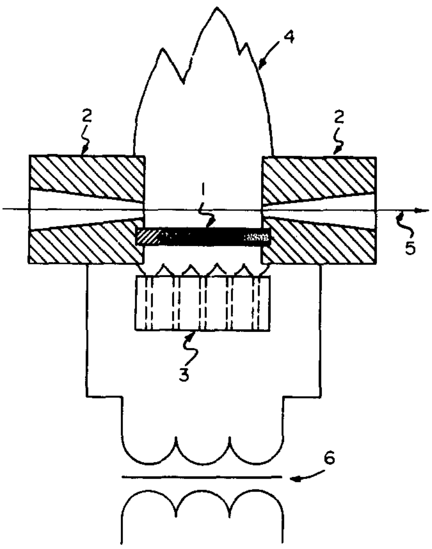

Fig. 7. Capsule-in-flame atomizer. 1. Capsule. 2. Graphite washer. 3. Méker burner. 4. Flame. 5. Light beam. 6. Step-down transformer (3 kW).

THE DESIGN OF ATOMIZERS INVOLVING SAMPLE VAPORIZATION FROM A CLOSED CAVITY

To apply the proposed principle of vaporization in practical work, it was necessary to design heaters for the furnace-in-flame and cuvette atomizers combining the use of large samples, fast and complete vaporization of the element of interest from the sample, and efficient use of the sample vapour for measuring absorption, with simplicity of the analytical procedure and reliability of the equipment. As a result of comparison of various solutions to this problem, the following atomizer designs were chosen.

The furnaces used in the furnace-in-flame atomizers are ordinarily hollow cylinders (capsules) aligned along the spectrometer optical axis (Fig. 7). The effective volume of the cavity can be varied from 45 to 60 mm^3 by changing the diameter. Owing to the large ratio of the heated surface of the sample to its volume, such a shape of capsule ensures fast and uniform heating and vaporization of samples at a maximum rate of vapour diffusion through the furnace walls. The sample vapour emerging from the capsule walls is carried by the laminar flow of the flame gases and enters the analytical zone through which the light-beam passes.

The material chosen for the capsules was fine-grained graphite combining satisfactory gas permeability (0·5–0·9 cm^2/sec) with high mechanical strength and purity.

The capsule with the sample is mounted horizontally between two cylindrical graphite washers with holes for passing the light-beam above the capsule. The washers serve to deliver current from a step-down transformer and preclude the ejection of material during vaporization. The washers are set inside water-cooled holders. To facilitate replacement of capsules and to exclude the possibility of their deformation because of expansion of the graphite, one of the holders is spring-loaded and can be moved along the optical axis.

The burner with the flame can be shifted in the direction perpendicular to the optical axis. The burner has interchangeable nozzles of the Méker type with 60 holes and can be used with the acetylene–air or acetylene–nitrous oxide flame. The actual choice of flame, just as in the case of element-determination in solution, depends on the volatility of the metal and the thermal stability of the compounds forming in the course of vaporization. To prevent oxidation of the capsules, a reducing flame is used. The total gas flow-rate does not exceed 6 l./min. There is no danger of the flame striking back at any combination of the component flow-rates. The general view of an atomizer stand is shown in Fig. 8.

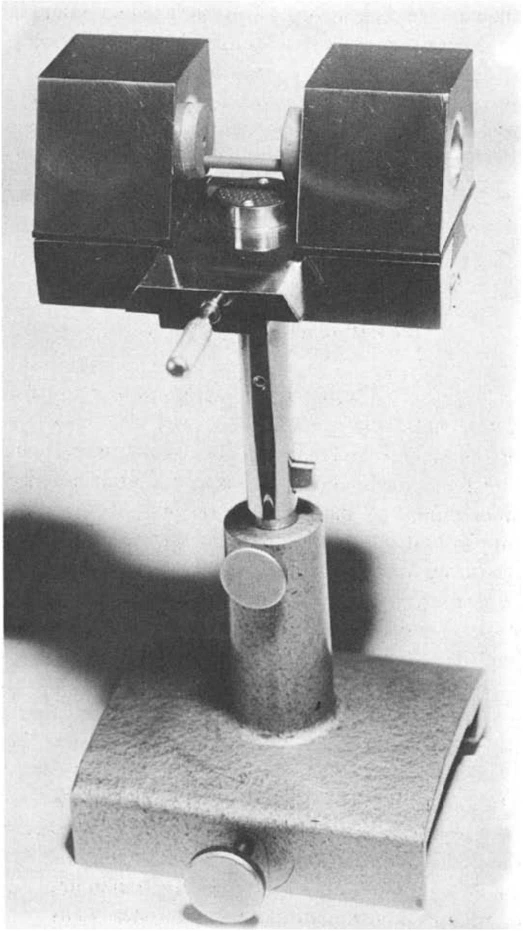

Fig. 8. Stand for the capsule-in-flame atomizer.

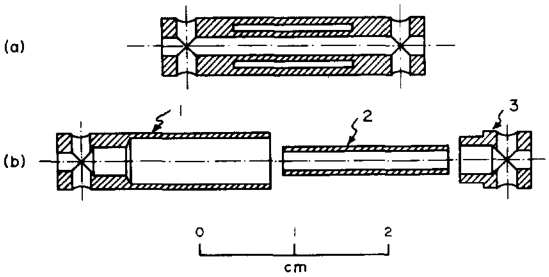

Fig. 9. Circular cavity furnace; (*A*) assembled, (*B*) dismantled. 1. Casing. 2. Inner tube. 3. Stopper.

The furnace with a circular cavity[51] turned out to be the simplest and most efficient combination of the graphite cuvette with a new kind of vaporizer. The furnace consists of a casing, a tube and a stopper (Fig. 9). The sample to be analysed is placed in a circular cavity about 1 mm wide between the casing and the tube. The total volume of the circular cavity is about 150 mm^3. When the furnace is heated, the vapour of the sample passes through the porous walls of the inner tube (made of porous graphite) and enters the analytical zone traversed by the light-beam. Thus the direction of motion of the sample vapour in this case is to some extent opposite to that from the cavity to the analytical zone in the capsule-in-flame atomizer.

To exclude partial loss of vapour through the outer furnace walls, the casing and the stopper are made of uniform pyrolytic carbon impermeable to gases. To preclude the vapour emerging from the furnace from condensing on the graphite washers, transverse holes are cut at the ends of the furnace, through which the vapour is forced by convection to flow in the vertical direction.

The dimensions of the circular-cavity furnace are chosen so as to make it interchangeable with the capsule. To minimize the oxidation of the outer furnace walls, reducing flames can be used, just as in the case of the furnace-in-flame atomizer, or an argon sheath can be used. In the latter case, the furnace can be isolated still more effectively from the atmosphere by shielding the space between the holders with a protective screen.

Note that although the same heater is used here both for sample vaporization and for maintaining the analytical zone at a high temperature, the design of the circular-cavity furnace, because of the different heat capacities and thermal insulation of the inner and outer tubes, provides a possibility of heating the inner zone before the vapour to be analysed starts to enter it, conditions which are optimal for complete dissociation of thermally stable oxides.

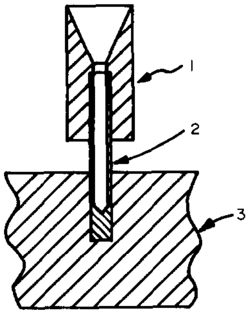

Fig. 10. A device for loading the powder sample into the capsule. 1. "Plexiglass funnel" 2. Capsule. 3. Vibrating stand.

ANALYTICAL PROCEDURE

In most cases where these atomizers are used for analysis of solids it is expedient to mix the sample with graphite powder. By preventing the sample in the cavity from melting or sintering into a bead, the presence of graphite thus provides a faster and more complete vaporization of impurities. In the case of low-melting matrices graphite reduces the possibility of direct leakage of the melt through the vaporizer walls. Besides, in the powder analysis graphite acts as a diluting agent (similar to the solvents used when analysing solutions) thus permitting the sample to be brought to the optimum mass.

Grinding the sample and simultaneously mixing it with graphite can be conveniently performed with a laboratory-type vibrating mill with several containers 100 ml in volume mounted on it. The containers and the grinding balls are made of "Plexiglass" to reduce the contamination hazard. The procedure of grinding and mixing takes about 5–10 min. When determining abundant elements, one should first run a blank analysis on pure graphite to check for possible contamination of the ground sample by impurities present in "Plexiglass" or remaining on the surface of the balls and of the container because of incomplete cleaning after the previous samples.

The samples are loaded into the capsules by means of the device shown in Fig. 10. The capsule (after a preliminary burn-cycle), or the circular-cavity furnace with the stopper removed, is mounted in the holes of a stand fixed onto an electromagnetic vibrator. A preset amount of the ground material is placed with a measuring scoop of about 40 mm^3 capacity into a "Plexiglass" funnel. When the vibrator is turned on, the material will uniformly fill the cavity. The upper part of the capsule cavity (not less than 3–5 mm) is then filled with pure graphite powder, preventing the sample from coming into contact with the graphite washer.

The capsule thus prepared is fixed between the graphite washers on the atomizer stand, and the measurements are begun. The flame is moved under the capsule, and the heating is turned on. The integrated absorbance is measured by means of an electronic integrator. The integration time is chosen in advance in accordance with the volatility of the element of interest and the vaporizer heating power selected. On completion of the absorption pulse integration, the heating is switched off and the flame moved aside. After cooling, the capsule is taken out of the atomizer stand and the next capsule with the sample is put in place. The capsule should be cleaned from the remains of the sample and subsequently ignited, after which it may again be used in the analysis.

This procedure of sample loading and absorbance measurement refers equally to the circular-cavity furnaces, the only difference consisting in the possible use of a weak argon flow as a shielding atmosphere for the furnace.

With the heating power limited to 1 kW for the capsule and 2 kW for the circular-cavity furnace, each is capable of withstanding several tens of measurements.

THE ANALYTICAL CHARACTERISTICS OF THE METHODS

Elements determined

A list of elements determined with the capsule-in-flame atomizer[52] is presented in Table 1. The high efficiency of heating and vaporization of material placed in the capsule enables reliable determination of

Table 1. Absolute sensitivity and relative detection limits of elements with the graphite capsule-in-flame atomizer

Line, *nm*	Heating power, *kW*	Flame*	Characteristic amount of element corresponding to $Q_\lambda = 1\%$ abs × sec, *g*	Relative detection limit† %
Ag 328·1	0·5	A–A	3×10^{-10}	1×10^{-6}
Al 309·3	1·7	N–A	8×10^{-10}	3×10^{-6}
Au 242·8	1·0	A–A	8×10^{-10}	3×10^{-6}
Bi 306·9	0·5	A–A	3×10^{-9}	1×10^{-5}
Be 234·8	1·4	N–A	3×10^{-11}	1×10^{-7}
Ca 422·7	1·2	N–A	3×10^{-11}	1×10^{-7}
Cd 228·8	0·3	A–A	4×10^{-11}	1×10^{-7}
Co 240·7	1·6	A–A	3×10^{-10}	2×10^{-6}
Cr 357·9	2·0	N–A	6×10^{-11}	3×10^{-7}
Cu 324·8	1·0	A–A	3×10^{-10}	2×10^{-6}
Eu 459·4	2·2	N–A	3×10^{-10}	2×10^{-6}
Fe 248·3	1·5	A–A	2×10^{-10}	1×10^{-6}
Ge 265·2	1·4	N–A	1×10^{-8}	4×10^{-5}
In 303·9	0·7	A–A	7×10^{-10}	2×10^{-6}
Mg 285·2	0·4	A–A	3×10^{-11}	1×10^{-7}
Mn 279·5	0·5	A–A	1×10^{-10}	4×10^{-7}
Mo 313·3	2·4	N–A	2×10^{-10}	3×10^{-6}
Ni 232·0	1·8	A–A	2×10^{-10}	1×10^{-6}
Pb 283·3	0·5	A–A	2×10^{-9}	6×10^{-6}
P 213·5	0·8	N–A	6×10^{-7}	2×10^{-3}
Pt 265·9	1·4	A–A	1×10^{-8}	4×10^{-5}
Sb 231·1	0·5	A–A	2×10^{-9}	7×10^{-6}
Si 251·6	2·0	N–A	1×10^{-9}	1×10^{-5}
Sn 286·3	0·5	N–A	6×10^{-9}	2×10^{-5}
Ti 364·3	2·6	N–A	1×10^{-9}	1×10^{-5}
V 318·4	2·5	N–A	1×10^{-9}	1×10^{-5}
Zn 213·8	0·8	A–A	4×10^{-11}	2×10^{-7}

* A–A = air/acetylene; N–A = nitrous oxide/acetylene.

† The detection limit was evaluated by the 2*s*-criterion where *s* is the standard deviation of blank measurements. It corresponds to operation of a "Saturn" spectrometer in the double-beam mode in the absence of non-selective absorption, at 40-mg sample weight.

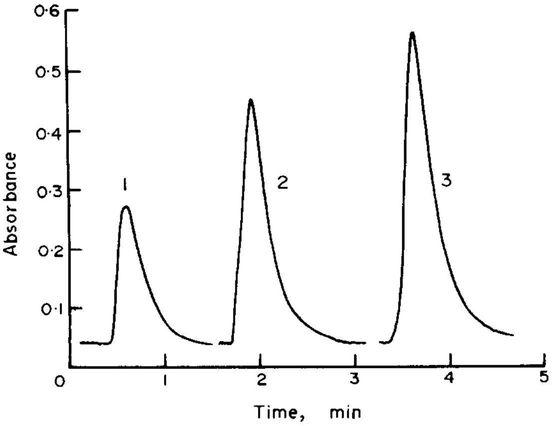

Fig. 11. Recording of absorbance for the Ti 364·3 nm line when determining titanium in standard samples with a capsule-in-flame atomizer. 1. Magnesite brick ($1{\cdot}5 \times 10^{-2}$% Ti). 2. Dolomite ($2{\cdot}8 \times 10^{-2}$% Ti). 3. Manganese ore ($5{\cdot}8 \times 10^{-2}$% Ti).

of such low volatility elements as titanium, vanadium, molybdenum and silicon, which boil at temperatures in excess of 3500° to be carried out. The time needed to extract an impurity, depending on its volatility and heating characteritics, varies from a fraction of a second to a few tens of seconds. As an illustration, Fig. 11 presents recordings for titanium determined in various materials at a maximum allowable power of 2·6 kW. A further increase of capsule heating power in order to determine elements forming the most thermally stable carbides (hafnium, niobium, tungsten and so on) turns out to be impossible because of the fast burn-out of the capsule. From the data available, about 50 elements can be determined in this way.

The range of elements that can be determined with the circular-cavity furnace is more limited (Table 2). This is due to the lower limiting temperature to which the circular cavity can be heated compared with that for the capsule cavity. It may be assumed that 30–40 elements can be determined with this atomizer.

Table 2. Absolute sensitivity and relative detection limits of elements with the circular-cavity furnace atomizer

Line, *nm*	Heating power, *kW*	Pulse duration, *sec*	Characteristic amount of element corresponding to Q_λ = 1% abs × sec, *g*	Relative detection limit %
Ag 328·1	1·0	6	7×10^{-13}	2×10^{-9}
Al 309·3	3·0	10	2×10^{-11}	8×10^{-8}
Ca 422·7	2·2	10	5×10^{-13}	2×10^{-9}
Cd 228·8	1·0	7	7×10^{-14}	2×10^{-10}
Co 240·7	3·6	12	2×10^{-11}	7×10^{-8}
Cr 357·9	3·9	15	5×10^{-11}	2×10^{-7}
Cu 324·7	3·0	9	9×10^{-13}	3×10^{-9}
In 303·9	2·0	10	8×10^{-12}	3×10^{-8}
Mn 279·5	2·0	4	4×10^{-13}	1×10^{-9}
Ni 232·0	3·7	15	9×10^{-13}	4×10^{-9}
Pb 283·3	1·0	6	4×10^{-12}	1×10^{-8}
Sb 231·1	2·0	10	1×10^{-11}	5×10^{-8}
Sn 286·3	2·0	6	4×10^{-11}	1×10^{-7}
Zn 213·9	1·0	4	1×10^{-13}	2×10^{-10}

* The detection limit was evaluated by the 2*s*-criterion where *s* is the standard deviation of blank measurements. It corresponds to operation of a "Saturn" spectrometer in the double-beam mode in the the absence of non-selective absorption, at 100-mg sample weight.

Table 3. Illustrating the analysis of powder samples with the graphite capsule-in-flame atomizer

Material analysed	Elements determined	Non-selective interference	Impurity content, %
MoO_3, Gd_2O_3	Cd, Ca, Cu, Eu, Mg, Zn	No	10^{-3} 10^{-6}
Al_2O_3	Cu, Mg, Fe	No	10^{-3} 10^{-4}
Nb_2O_5	Al, Cu, Fe	No	10^{-3} 10^{-4}
LiOH, I_2O_5, HIO_3, Li_2CO_3	Al, Pb	Yes	10^{-3} 10^{-5}
KH_2PO_4	Al, Fe, Na, Ni	Yes	10^{-2}–10^{-4}
$BaCO_3$, $Sr(NO_3)_2$	Co, Cu, Fe	No	10^{-3}–10^{-5}
Sulphur	Fe	No	10^{-2} 10^{-5}
SiC, Si_3N_4	Fe	No	10^{-1} 10^{-2}
SiO_2	Cu	Yes	10^{-3} 10^{-5}
Ferrite	Co	Yes	10^{-1} 10^{-2}
Carbon & graphite material	See Table 1	No	10^{-1}–10^{-7}

Materials analysed

Tables 3 and 4 give lists of materials which have been analysed with the capsule-in-flame atomizer.[52] It includes chemical reagents, rocks, metals, slags, semiconductors, carbon and graphite materials. Non-selective spectral interference is not an obstacle to analysis provided it is corrected for automatically. Experimental determinations of impurities in substances of organic nature (biological material, tissue, paper, technical oil, etc.) did not reveal any sample loss during the preliminary pyrolysis of organic substances in the capsule cavity, so the method can be extended to these materials.

The circular-cavity furnace has so far been used only to determine impurities in graphite powder[51] and in silica. However, the method can apparently also be employed as successfully in other cases where the volatility of the impurities of interest exceeds by far that of the major components of the matrix. The possibility of extending the method to volatile materials is limited by the extremely strong non-selective absorption of the light-beam after partial vaporization of the matrix. This may result in a practically complete absorption of the light-flux.

Table 4. Trace characterization of powder samples by different methods

Material	Element determined	Result of chemical or spectral determination, %	Result of AA-analysis (capsule-in-flame), %
Open-hearth slag*	V	$4{\cdot}5 \times 10^{-2}$	$4{\cdot}0 \times 10^{-2}$
Open-hearth slag*	P	$4{\cdot}3 \times 10^{-1}$	$4{\cdot}5 \times 10^{-1}$
Manganese ore*	Co	$4{\cdot}0 \times 10^{-3}$	$5{\cdot}0 \times 10^{-3}$
Zirconium dioxide*	Sb	$1{\cdot}2 \times 10^{-4}$	$1{\cdot}4 \times 10^{-4}$
Fusible quartz	Au	$1{\cdot}4 \times 10^{-4}$	$1{\cdot}6 \times 10^{-4}$
Granite gneiss	Co	$1{\cdot}0 \times 10^{-4}$	$0{\cdot}9 \times 10^{-4}$
Tantalum	Fe	$5{\cdot}0 \times 10^{-2}$	$4{\cdot}0 \times 10^{-2}$

* Standard samples

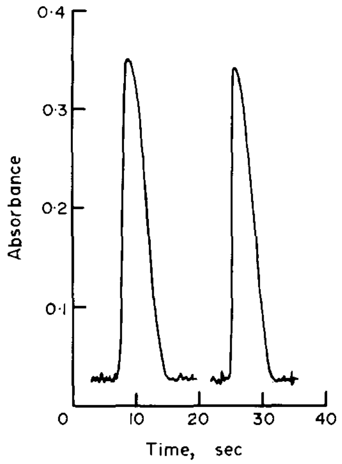

Fig. 12. Recording of absorbance for the Cd 228·8 nm line when determining $7 \times 10^{-8}\%$ Cd in silica, with a circular-cavity furnace.

Sensitivity and detection limits

The absolute amounts of elements corresponding to integral values of 1% absorbance in 1 sec are presented in Tables 1 and 2 for both atomizers. A comparison of these data with the corresponding data[49] available for the furnace-in-flame atomizer and the graphite cuvette shows them to be in good agreement, thus indicating that replacing the conventional vaporizer (the channel with a hole) by a closed-cavity type did not reduce the absolute sensitivity of the two methods. This is equally true for a comparison of the absolute detection limits provided by the modified and original atomizers.

At the same time, the possibility of using 10–100 times larger samples than previously possible[5,14] permits the relative sensitivity and relative power of detection to be raised by this factor. The recording (Fig. 12) of the determination of cadmium in silica at the level of $7 \times 10^{-8}\%$ illustrates the inherent capabilities of the circular-cavity furnace.

Calibration and accuracy

As noted above, measuring the absorbance Q_A permits, in principle, exclusion of the effect of the kinetics of liberation and transport of the analyte to the analytical cell, on the results obtained. The necessary requirements to be met here are the completeness of extraction of the element from the sample, constant time of residence of the atoms in the analytical cell and a linear dependence of absorbance on the atom concentration n over the range of variation of n in the course of vaporization of the element.

If the conditions above are satisfied, the spectrometer readings can be calibrated by means of any substance containing a known amount of the element to be determined, including pure solutions transferred into the capsule or the circular cavity. The calibration method which was found to be most convenient from the practical standpoint involves the use of several standards of graphite containing the elements of interest in the range 10^{-3}–$10^{-7}\%$ (for the circular-cavity furnace additional standards with impurity contents down to $n \times 10^{-9}\%$ were prepared).

The correctness of the analyses performed with this calibration technique was checked many times on samples with known impurity content. As an example, Table 4 presents the results of such a comparison obtained with the capsule-in-flame atomizer.

The most serious sources of systematic error may come from incomplete extraction of the element in question in the course of fractional vaporization of impurities from a sample, and from deviation of the $A = f(n)$ relationship from linearity. The effect of the first of these sources of error can be revealed and eliminated by increasing the vaporizer heating rate, while that of the second can be readily eliminated by reducing the heating power to the level at which the maximum values of A remain within the range of linearity between A and n. It should be noted, however, that the effect of non-linearity on the value of Q_A is always much smaller than in the case of pulse-peak recording.[38]

Precision

The scatter of the measurement data about the mean value, for both methods, is mainly associated with non-homogeneous distribution of the element of interest in the powder sample. For instance the relative standard deviation of determination of 3×10^{-7} g of lead with the capsule-in-flame atomizer was 4% when samples were taken from an aqueous solution of lead nitrate by means of a micropipette (sampling error 2·5%). When lead was determined in standard powder samples prepared by repeated dilution of the original standard ($3 \times 10^{-3}\%$ lead) with pure graphite powder, the relative standard deviation was 8% for a sample with $1 \times 10^{-3}\%$ lead, and 14% for a sample with $3 \times 10^{-4}\%$ lead.[56]

Taking into account the decisive effect of sample inhomogeneity on the precision, sample-weighing can be replaced by the faster and simpler method of taking a fixed volume of powder. The error of volume-sampling is about 4%[56] at a scoop capacity of 40 mm^3. One should, of course, consider possible differences between the apparent density of the mixture to be analysed and that of the standard (pure graphite).

Thus, on the average, at element contents 10–20 times the detection limit, the relative standard deviation is 5–10% for a homogeneous sample. For samples with inhomogeneous impurity distribution the error increases.

The precision reached with the circular-cavity furnace is, on the average, the same.

Speed of analysis

In the determination of elements in several samples, the major part of the time is taken up by the preparation of the substances to be analysed and their

Table 5. A comparison of instrumental methods for direct determination of impurities in powder samples*

Characteristic	Methods compared			
	CF–AAS	DCA–ES	SS–MS	NA
Total number of elements	50	60	75	70
Detection limit (%)	10^{-4}–10^{-7}	10^{-3}–10^{-6}	10^{-5}–10^{-7}	10^{-5}–10^{-8}†
Possibility of multi-elemental analysis	–	+	+	+
Reliability of simplifed calibration techniques	+	–	±	±
Speed of analysis	+	–	–	±
Precision	+	–	–	+
Reprensentativeness of sampling	±	±	–	+
Possibility of non-destructive analysis	–	–	–	+
Simplicity of equipment and analytical procedure	+	+	–	–
Equipment cost	+	+	–	–

* The advantage of the method (or methods) over the others with respect to each feature is specified with the signs (+) or (±) depending on the actual degree of this advantage.

† With a sample of 1–10 g irradiated for 1 hr by a thermal neutron flux of $1{\cdot}8 \times 10^{12}$ n.cm^{-2}.sec^{-1}.

loading into the vaporizer cavity. We have succeeded[52] in cutting down this time by grinding and loading several samples at a time. Thus, determination of 10 elements in 10 samples, with use of an electronic integrator, takes 5 hr, including the time needed to prepare and load the samples, to change hollow-cathode lamps, and to set the chosen analytical lines, so the mean time taken for one determination is 3 min.

THE STATE OF THE ART

The problem of direct trace and ultratrace characterization of powder samples is solved in modern analytical chemistry more or less successfully by several methods of instrumental analysis, among them emission optical spectroscopy, activation analysis and mass spectrometry.[57–63] It is instructive to compare the methods of atomic-absorption analysis described in this work, in particular its more versatile version employing the capsule-in-flame atomizer (CF–AAS) with the methods above. Of the various methods used in activation, optical emission and mass spectrometric analysis we will choose for our comparison the most efficient versions, *i.e.*, neutron activation (NA), emission spectrography with a d.c. carbon arc (DCA-ES) and spark-source mass spectrometry (SS–MS). The most essential characteristics of these methods are compared in Table 5.

The most promising results in the trace characterization of powder samples are undoubtedly obtained in spark-source mass spectrometry and especially in neutron-activation analysis, the latter providing non-destructive analysis of the samples with the maximum representativeness of sampling. The methods of optical emission and absorption spectroscopy are inferior both in the number of the elements covered and in the power of detection. (An exception is the circular-cavity furnace, which has potential detection-limit capabilities which in some cases considerably exceed those of the non-optical methods.)

At the same time, in some respects optical spectroscopy may turn out to be preferable to the non-optical methods. For example, the relative simplicity of the equipment and procedure in spectral analysis makes this easy to learn and operate by personnel of medium and low qualification, and the cost of the equipment is moderate, *i.e.*, $10,000–20,000 for the optical as compared with $50,000–100,000 for the non-optical methods. Note that it is these factors that are responsible for emission spectroscopy being more popular than the non-optical methods of analysis.

As for a comparison of the emission and atomic-absorption methods of analysis, one should bear in mind the following considerations. The most serious limitation of the atomic-absorption method which manifests itself most of all in the analysis of expensive high-purity materials is the impossibility of simultaneously determining a group of impurities of interest. At the same time, in speed and precision, as well as in the reliability of the simplified calibration techniques (*e.g.*, involving synthetic standards based on graphite powder) the atomic-absorption method possesses certain advantages over emission spectroscopy. This is associated with differences in the techniques of recording analytical signals (by photoelectric and photographic means) and with the much greater effect of the matrix on the conditions of atomization and spectral excitation in emission as compared with atomic-absorption spectroscopy.

The considerations above suggest that despite some limitations of the atomic-absorption method it should become no less popular in the trace characterization of powder samples than in other areas of analytical chemistry where the atomic-absorption technique has already gained recognition, *i.e.*, the determination of major components and of traces of elements in solutions, and in microanalysis. It will apparently find widest application in the research groups which are not directly connected with specialized analytical laboratories and which are therefore interested in solving their particular analytical problems without outside help.

Further progress in atomic-absorption spectroscopy depends to a considerable extent on the availability of commercial equipment to perform such analyses and further accumulation of experimental data supporting the capabilities of the method. One may hope that considering the present popularity of atomizers utilizing resistance furnaces in the field of microanalysis, the techniques described in the present paper will be recognized in the very near future.

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SUR LE MICRODOSAGE DU SILICIUM DANS LES COMPOSES ORGANOSILICIES PAR CHLOROCARBOPYROLYSE ET MESURE PAR ABSORPTION ATOMIQUE

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Résumé—La méthode décrite s'applique au microdosage du silicium dans les composés organosiliciés stables (solides ou liquides à faible tension de vapeur). Le composé contenant du silicium est pyrolysé dans une atmosphère d'azote chloré à 1100°, ce qui donne lieu à la formation quantitative de tétrachlorure de silicium qui passe en phase gazeuse. Séparé du chlore en excès par condensation dans un piège froid à $-78°$ suivie d'une évaporation fractionnée, le tétrachlorure de silicium (Eb = 56,8°) est injecté dans la flamme protoxyde d'azote–acétylène d'un spectrophotomètre d'absorption atomique. L'intégration de la variation de transmittance mesurée, en fonction du temps, fournit une valeur numérique qui permet de déterminer la masse de silicium contenue dans le prélèvement analytique. Les résultats obtenus sont satisfaisants.

Le dosage du silicium dans les composés organosiliciés n'a pas fait l'objet de nombreux travaux à l'échelle microanalytique; Reverchon et Legrand les ont brièvement rappelés.[1]

Diverses méthodes de "minéralisation" de ces composés conduisent à l'obtention du silicium à doser, combiné sous forme de silicates; ce sont, par exemple, la combustion dans l'oxygène, suivant la technique de Schöniger, soit en fiole de polyéthylène,[2] soit en fiole de nickel,[1] ou l'attaque par le peroxyde de sodium en bombe de Wurzschmitt.[3] En ce qui concerne le dosage du silicium dans les silicates ainsi formés, il semble qu'à l'échelle microanalytique la méthode la plus appropriée soit le titrage de l'ion silicomolybdique par colorimétrie spectrophotométrique.[1,3]

La spectrophotométrie d'absorption atomique semble également se prêter au titrage du silicium combiné sous forme de silicates, mais, malgré l'emploi de lampes à cathodes creuses alimentées par un courant de haute intensité et de flammes à protoxyde d'azote–acétylène, à hautes températures et fortement réductrices, l'application de cette méthode demeure des plus délicates du fait de sa faible sensibilité, surtout lorsque les solutions à titrer contiennent moins de 10 μg/ml de silicium, comme c'est le cas en microanalyse organique; c'est pourquoi, nous n'avons pu appliquer cette méthode classique, telle quelle, au microdosage du silicium dans les composés organiques.

Une possibilité d'augmenter la sensibilité du dosage du silicium par absorption atomique a été développée par Trudell et Boltz;[4] ces auteurs mettent en oeuvre la formation de complexe silicomolybdique, l'extraction de celui-ci, puis la précipitation du silicomolybdate par un excès de nitrate de plomb; le dosage du silicate se ramène ensuite au dosage, par absorption atomique, de l'excès de plomb restant.

Cette méthode permet de doser des quantités de silicium comprises entre 0,5 et 7 μg, à l'aide de courbes d'étalonnage, tandis que ces valeurs limites s'élèvent à 10 et 200 μg lorsque les solutions aqueuses d'ions silicates sont injectées directement dans la flamme du spectrophotomètre d'absorption atomique; elle oblige, cependant, l'opérateur à effectuer des extractions et des centrifugations successives, augmentant, de ce fait, la durée de la détermination et la rendant plus difficile à appliquer, en raison de la multiplicité des opérations qu'elle comporte.

Toutes les méthodes citées impliquent un traitement du silicate formé, après minéralisation, en vue de sa mesure quantitative, suivant divers principes d'analyse, ce qui conduit à un mode opératoire discontinu.

Afin de pouvoir appliquer directement le principe de l'absorption atomique au dosage spécifique du silicium à l'échelle microanalytique, il nous est apparu intéressant de combiner cet élément, initialement porté par une substance organique siliciée, dans une molécule gazeuse, grâce à une "minéralisation" appropriée. L'injection de ce gaz silicié dans la flamme du spectrophotomètre permet alors d'effectuer la mesure d'absorption sur la totalité des molécules siliciées contenant le silicium du prélèvement analytique alors qu'en solution aqueuse, la mesure n'est effectuée, pratiquement, que sur un dixième de cette quantité.

Nous avons choisi le tétrachlorure de silicium (point de fusion: $-68,3°$; point d'ébullition: $56,8°$) comme molécule gazeuse intermédiaire*.

La minéralisation correspondante est effectuée par pyrolyse des prélèvements des composés organiques siliciés dans une atmosphère chlorée†. Dans les composés oxygénés, le tétrachlorure de silicium peut se former à partir de la silice (qui peut être produite, intermédiairement), en présence de carbone et de chlore, suivant la réaction d'Oerstedt:[5]

$$SiO_2 + 2\,C + 2\,Cl_2 \rightarrow SiCl_4 + 2\,CO$$

Le carbone est, ici, engendré *in situ* par la pyrolyse de la substance organique.

Dans les composés non oxygénés, le tétrachlorure de silicium peut se former directement par chloration du silicium ou des silanes formés lors de la pyrolyse du prélèvement microanalytique.

PRINCIPE

Le prélèvement microanalytique (200–700 μg) est pyrolysé à 1100° dans une atmosphère d'azote chargée en chlore; la chambre de pyrolyse est, ensuite, balayée par un courant d'azote chloré, puis par de l'azote pur. Le tétrachlorure de silicium formé est condensé dans un piège refroidi à $-78°$ rempli de grains d'alumine frittée.

L'excès de chlore retenu dans le piège est séparé du tétrachlorure de silicium par élution dans un courant d'azote annexe; le tétrachlorure de silicium est volatilisé par réchauffage du piège, entraîné par le courant d'azote annexe et introduit dans la flamme protoxyde d'azote–acétylène du spectrophotomètre d'absorption atomique, après avoir traversé une garniture de laine d'argent sur laquelle il est préalablement débarrassé du chlore résiduel.

La transmittance du rayonnement de la lampe à cathode creuse, après absorption dans la flamme du spectrophotomètre d'absorption atomique, varie lors de la présence dans cette dernière, de silicium élémentaire provenant de la dissociation thermique du tétrachlorure de silicium. La variation de cette transmittance en fonction du temps est intégrée, dans l'intervalle de temps correspondant à la présence du silicium dans la flamme. L'expérience montre que le logarithme de la grandeur numérique obtenue par intégration varie linéairement en fonction du logarithme de la quantité de silicium (10 à 60 μg) initialement présent dans le prélèvement analytique.

PARTIE EXPERIMENTALE

Appareillage (Figure 1)

Dispositif de purification de l'azote. Un tube d'azote comprimé pourvu d'un manodétendeur alimente les deux circuits d'azote principal (chlorocarbopyrolyse de la substance) et annexe (injection du tétrachlorure de silicium dans la flamme du spectrophotomètre d'absorption atomique). Chacun des deux circuits est pourvu d'un régulateur de pression constitué par un tube en T plongeant à profondeur réglable dans une éprouvette remplie d'huile de vaseline pure à travers laquelle l'excès de gaz s'échappe dans l'atmosphère.

Afin d'obtenir de l'azote rigoureusement pur, il traverse dans chacun des deux circuits un tube purificateur (25, 8) garni de fragments de fils de cuivre obtenu par réduction d'oxyde de cuivre en "fils" portés à la température de 490° dans un four tubulaire (9, 26), puis un tube absorbeur (10, 24) comportant une garniture d'amiante sodée et de perchlorate de magnésium, assurant la rétention du dioxyde de carbone et de l'eau; le gaz traverse, ensuite dans chacun des circuits, un rotamètre (11, 23) dont l'un (23) est muni d'une vanne à pointeau‡ permettant un réglage fin du débit gazeux, la vanne (13) permettant le réglage du circuit d'azote chargé en chlore, et passe par une vanne à commande électromagnétique (12, 18).

Générateur de chlore. Le chlore est produit par électrolyse d'une solution de chlorure de sodium dans un mélange eau–acide perchlorique (volume à volume) entre deux électrodes de platine (plaques de platine de 200 mm^2 dont l'une est disposée dans un compartiment séparé de la solution par un verre fritté de porosité n° 4 et de surface égale à 10 mm^2).

Le chlore issue de l'électrolyseur (14) traverse un tube dessicateur à perchlorate de magnésium (15), puis est condensé dans un piège constitué par un tube en U de 6 mm de diamètre intérieur refroidi à $-78°$ par le système acétone–carboglace (16). Une heure d'électrolyse sous une intensité de 2 A permet de préparer la quantité de chlore nécessaire à une semaine de travail.

Le chlore, ainsi produit par électrolyse, est purifié par passage d'un courant d'azote pendant 30 mn dans le piège refroidi; l'azote chargé des impuretés du chlore se dégage dans une solution de soude par l'intermédiaire du barboteur (17).

Le courant d'azote passant à travers le piège se charge de 6% de chlore, en volume.

Tube à pyrolyse. Le tube à pyrolyse (3), en carbone vitreux de qualité V25§, a 750 mm de longueur et 15 et 19 mm de diamètres; son extrémité d'amont est ouverte et son extrémité d'aval, initialement fermée, est percée d'un orifice de 0,3 mm de diamètre; il est protégé de l'oxydation par l'air par un tube en silice transparente (4), de qualité étirée, de 26 et 22 mm de diamètres. Ce dernier comprend un évasement garni de polychlorure de vinyle permettant de réaliser, en amont, un joint étanche entre lui-même et le tube de carbone.

A cette fin, on introduit dans l'évasement une solution de polychlorure de vinyle (initialement en poudre) dans le tétrahydrofurane que l'on chauffe ensuite doucement afin d'évaporer le solvant.

Le tube à pyrolyse comporte 3 parties essentielles:

—une partie d'amont refroidie par un réfrigérant (7), de 100 mm de longueur, constitué par un bloc de laiton à double parois où circule un courant d'eau froide,

—une chambre à pyrolyse de 80 mm de longueur portée à une température de 1100° par un four électrique approprié (6),

—une chambre de réaction de 360 mm de longueur, portée par le four (5) à 1100°, contenant, dans sa partie d'aval, un tampon conducteur thermique de 50 mm de longueur constitué par une feuille rectangulaire de carbone "Papiex" (de 50 × 100 mm) enroulée sur elle-même, suivie

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* En fait, il est possible que d'autres chlorures de silicium volatils se forment également au cours de la "chlorocarbopyrolyse" du prélèvement analytique, ci-après décrite, ce dont il sera fait état dans notre exposé. En vue d'en simplifier l'écriture, nous n'y citerons conventionnellement que le tétrachlorure de silicium.

† Nous proposons de dénommer *chlorocarbopyrolyse* le traitement d'un prélèvement analytique, en atmosphère de chlore (avec ou sans addition de charbon), visant à l'obtention du chlorure d'un élément initialement combiné dans la substance inorganique ou organique de ce prélèvement, en vue de son dosage.

‡ Non représentée sur la figure.

§ Carbone Lorraine (France).

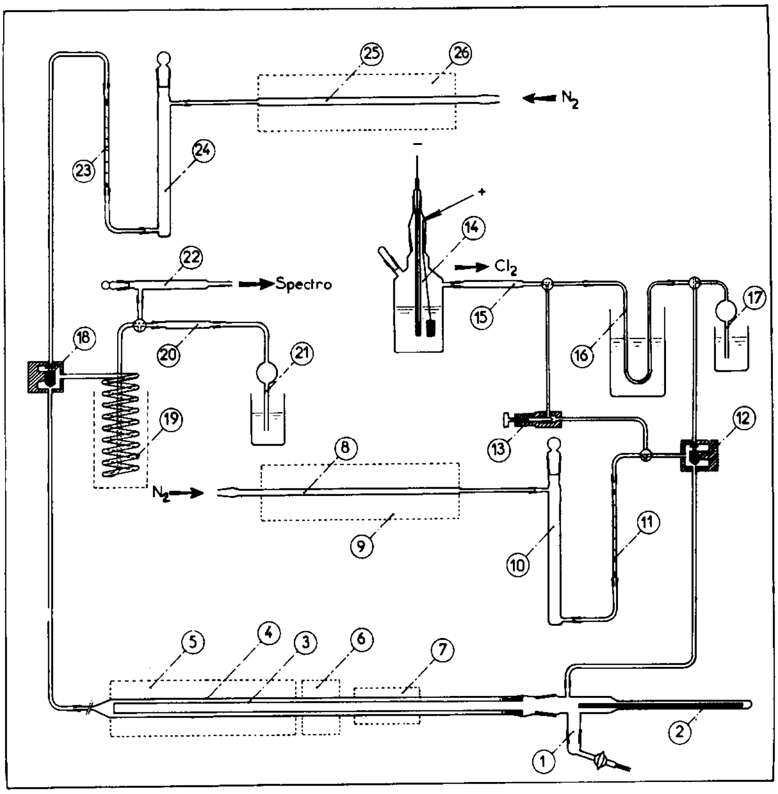

Fig. 1

d'une garniture de feutre de carbone[*] de 150 mm de longueur qui se sature superficiellement de chlore, lors du passage du courant d'azote chloré.

Le tube à pyrolyse est complété par un système à poussoir (2) d'introduction de la nacelle porteuse du prélèvement analytique dans la chambre de pyrolyse; il est constitué par un barreau cylindrique de carbone, de qualité spectrographique de 8 mm de diamètre. A son extrémité d'amont, le barreau est percé et fileté, ce qui permet d'y introduire, de fixer et de protéger par un bouchon de carbone fileté un aimant cylindrique de fer doux; son extrémité d'aval est creusée de façon à constituer une cavité cylindrique coaxiale servant de logement aux nacelles de platine, porteuses des prélèvements analytiques.

Le tube à pyrolyse comporte, en outre, un dispositif de balayage débouchant dans l'atmosphère par un ajutage à robinet s'adaptant par un rodage conique à l'orifice d'introduction de la nacelle (1) et permettant de balayer l'air, introduit en même temps que le prélèvement analytique dans ladite nacelle de platine, à l'aide du courant d'azote principal.

Condensation du tétrachlorure de silicium. A la sortie du tube à pyrolyse, le tétrachlorure de silicium est condensé dans un piège en verre "Pyrex" (19), plongé dans un bain à −78° constitué par le système acétone–glace carbonique. Ce piège est un serpentin, réalisé avec une canne de 150 mm de longueur et de 9 et 6 mm de diamètres, enroulé en hélice autour d'une branche verticale; il est rempli d'alumine frittée (qualité ALCEL[†]) de granulométrie 20–30 mesh, préalablement calcinée à 1000° pendant 2 hr.

Un enroulement chauffant constitué par 8 m de fil de cuivre de 0,35 mm de diamètre bobiné sur le piège parallèlement à son axe vertical et alimenté sous 10 V, permet de réchauffer celui-ci en vue d'évaporer le tétrachlorure de silicium.

Rétention du chlore. Entre le piège et le spectrophotomètre d'absorption atomique est disposé un tube purificateur (22) de 8 et 11 mm de diamètres et de 150 mm de longueur, rempli de laine d'argent,[‡] qui absorbe le chlore résiduel, susceptible de rester mélangé au tétrachlorure de silicium, avant l'injection de ce dernier dans la flamme du spectrophotomètre. Les barboteurs (17 et 21) permettent d'absorber le chlore en excès balayé par l'azote, dans une solution alcaline (soude 6*N*).

Vannes électromagnétiques à commande automatique programmée. Les vannes électromagnétiques (12 et 18) à trois voies sont commandées par des minuteries Crouzet dont les temps sont réglables. La vanne (18) permet de balayer le piège (19) soit par le courant gazeux principal sortant du tube à pyrolyse, soit par le courant d'azote annexe.

Appareillage de mesure

Spectromètre d'absorption atomique (Unicam SP90 série 1) avec une lampe à cathode creuse au silicium (intensité: 6 mA; largeur de fente: 0.08 mm; longueur d'onde 2516 Å); mesure effectuée en transmittance. Enregistreur Kipp et Zonen BC 5 (12 gammes de tension, échelle utilisée: 5 mV). Intégrateur Kipp et Zonen BC 1, couplé à l'enregistreur pour l'intégration des courbes pendant l'enregistrement.

L'introduction des gaz s'effectue dans la chambre de prémélange des gaz par un tube droit en acier inoxydable de 1 mm de diamètre intérieur remplaçant le dispositif de nébulisation. Du fait de la pression qui règne dans la chambre de prémélange, il est nécessaire d'introduire l'azote de balayage du piège sous une pression de 0,8 bar; une vanne réglable intercalée entre la partie amont du circuit d'azote et le régulateur de pression, permet l'utilisation de ce dernier sous une telle pression.

Protoxyde d'azote: qualité industrielle, tube de 6 m^3 livré sous pression de 40 bars; débit 5 l./mn sous pression de 4 bars.

Acétylène: qualité industrielle, tube de 4 m^3, livré sous pression de 15 bars; débit 0,25 l./mn sous pression de 1,5 bar.

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[*] Carbone Lorraine (France).

[†] Desmarquet (France).

[‡] Lyon-Alemand, Paris.

Mode opératoire

L'appareillage de minéralisation étant balayé par le courant d'azote principal, le spectrophotomètre est mis sous tension; une demi-heure est suffisante pour obtenir un rayonnement stable de la cathode creuse.

La flamme protoxyde d'azote–acétylène est, alors, allumée, pendant 20 mn, afin que l'appareil de mesure atteigne sa température de régime; durant ce temps, une "minéralisation" préliminaire d'un prélèvement analytique est effectuée dans l'appareil, ce qui permet la mise en condition nécessaire du dispositif de minéralisation.

Analyse proprement dite

—Commander la vanne (18) (position basse) afin de faire balayer le piège (19) par le courant d'azote annexe; refroidir ce piège.

—Introduire la nacelle porteuse du prélèvement analytique dans le tube à pyrolyse par l'orifice (1) et la poser dans le logement du poussoir (2); boucher l'orifice (1) avec son capuchon à ajutage à robinet et ouvrir ce dernier afin de faire balayer la partie antérieure du tube à pyrolyse par le courant d'azote principal; ce courant s'écoule ainsi directement dans l'atmosphère, la vanne (18), en position basse, ne lui permettant pas de traverser le tube à pyrolyse.

—Fermer le robinet du capuchon à ajutage.

—Etablir le débit de pyrolyse (31 ml/mn) d'azote chloré pendant 2 mn par commande de la vanne (12) et fermeture du courant d'azote annexe par la vanne (18).

—Introduire rapidement la nacelle au centre de la chambre de pyrolyse en déplaçant le poussoir à l'aide d'un aimant extérieur.

—Rétablir le courant d'azote pur (56 ml/mn) au bout de 3 mn par commande de la vanne (12) (position basse); le laisser circuler pendant 5 mn.

—Commander la vanne (18) (position haute) afin de faire balayer le piège par le courant d'azote pur (80 ml/mn) pendant 5 mn, temps nécessaire à l'élimination quasi totale, par vaporisation et élution, du chlore liquéfié dans le piège.

—Extraire le poussoir de la chambre de pyrolyse à l'aide de l'aimant extérieur.

—Refroidir le poussoir à l'extérieur du tube, par soufflage d'air comprimé sur toute sa longueur, au moyen d'une rampe percée de trous.

—Réchauffer le piège, à la fin de ce temps.

—Allumer la flamme protoxyde d'azote–acétylène du brûleur du spectrophotomètre.

—Injecter les gaz de balayage dans le spectromètre par commande du robinet à trois voies situé en aval du piège.

—Remettre le compteur de l'intégrateur à zéro; l'intégrateur fonctionne lors du passage de tétrachlorure de silicium dans la flamme.

—Relever le nombre indiqué par le compteur de l'intégrateur dès le retour du traceur de l'enregistreur à la ligne de base initiale.

L'analyse dure environ 25 mn.

Courbe d'étalonnage. L'appareil est étalonné chaque jour par l'analyse de substances-types organosiliciées dont la teneur en silicium est connue et dont les masses de prélèvements doivent être telles qu'elles correspondent à des masses de silicium comprises entre 1 et 60 μg.

Si N représente le résultat numérique lu sur le compteur de l'intégrateur et si x est la masse de silicium, exprimée en μg, l'expérience montre que la courbe d'étalonnage peut être représentée par une équation bilogarithmique qui est linéaire lorsque la masse de silicium est inférieure à 60 μg et qui s'écrit

$$\log N = a \log x + b$$

dans laquelle a est la pente de la droite d'étalonnage tracée sur papier à coordonnées bilogarithmiques et b son ordonnée à l'origine (valeur de log N correspondant à 1 μg de silicium).

Pour une quantité de silicium supérieure à 60 μg la courbe s'infléchit vers une asymptote horizontale, ce qui correspond à la saturation de la flamme par les espèces siliciées.

La valeur de la pente a de l'équation d'étalonnage a pour ordre de grandeur 0,900, mais peut varier d'environ ± 0,1 principalement en fonction de la qualité des gaz de la flamme.

Essai à blanc. L'essai à blanc de l'appareil en fonctionnement (qui doit toujours être effectué après l'analyse d'un composé silicié) ne doit pas donner lieu à un comptage numérique de plus d'une quinzaine de pas du compteur de l'intégrateur, ce qui correspond à une quantité de silicium de l'ordre de grandeur de 1–1,5 μg.

Dans le cas où le comptage d'essai à blanc est supérieur à une quinzaine de pas, il importe de poursuivre le balayage du tube à pyrolyse, par un courant d'azote chloré, jusqu'à obtention d'un comptage "à blanc admissible".

DISCUSSION

Pesage et ordre de grandeur de la masse des prélèvements analytiques

Le pesage est effectué à l'aide d'une balance électromagnétique Mettler ME 22 qui permet de peser à 0,5 μg près les prélèvements microanalytiques en nacelles de platine. La masse des prélèvements analytiques doit être comprise entre 200 et 700 μg suivant la teneur en silicium, afin que la masse du silicium dosée soit elle-même comprise entre 1 et 60 μg. Il est à remarquer que les nacelles de platine perdent en moyenne de 100–200 μg de leur masse par analyse du fait de l'attaque de platine par le chlore.

L'ordre de grandeur décimilligrammique des prélèvements analytiques permet, d'une part, de combiner quantitativement le silicium sous forme de tétrachlorure de silicium lors de la chloropyrolyse de substances organiques, et, d'autre part, de n'injecter dans la flamme du spectromètre que des quantités de produits siliciés telles que la loi d'étalonnage bilogarithmique reste linéaire.

L'expérience montre, en effet, lorsque la masse des prélèvements analytiques dépasse 1 mg, notamment dans le cas des substances où un atome de silicium est lié à 1 ou 2 atomes d'oxygène (triphénlysilanol, par exemple), que la minéralisation n'est pas quantitative et donne donc lieu à des pertes de silicium; en outre, il apparait alors un phénomène de mémoire perturbant l'analyse suivante.

Essai à blanc

Sous réserve de maintenir les masses des prélèvements entre les limites définies sous la précédente rubrique, aucun phénomène de mémoire ne se manifeste au cours d'une série d'analyses. Le résultat positif d'un essai à blanc ne peut provenir, exclusivement, que de l'appareillage et, particulièrement, du tube à pyrolyse. En effet, il s'avère que le renouvellement de la garniture du tube à pyrolyse (papier et feutre de carbone) donne lieu à un résultat d'essai à blanc qui, exprimé en masse de silicium, peut atteindre 15–20 μg, mais que ce "blanc" peut disparaître si l'on prend la précaution de balayer le tube pendant 24 hr par de l'azote chloré.

Remarquons qu'une légère attaque du tube de silice protecteur du tube de graphite vitreux au voisinage de son extrémité d'aval est également susceptible de donner lieu à l'obtention d'un résultat positif d'essai à blanc.

Pyrolyse de la substance organique

Le prélèvement analytique est introduit dans la chambre de pyrolyse portée à une température d'environ 1100° au sein d'une atmosphère d'azote chloré. Les gaz de pyrolyse siliciés traversent le feutre de carbone où le chlore adsorbé permet d'achever la chloration quantitative du silicium donnant naissance à un composé chloré volatil.

Par contre, les produits solides de la pyrolyse susceptibles de retenir du silicium sous forme de résidus dans la nacelle de platine, ou de dépôts, sur les parois du tube de graphite, ne sont au contact du courant d'azote chloré, sous un débit de 21 ml/mn, qu'en la présence éventuelle de faibles quantités de charbon amorphe produit par la pyrolyse qui, d'ailleurs, à 1100°, se graphitise lentement en perdant sa réactivité.

Il est remarquable que le remplacement du feutre de graphite par une garniture de charbon amorphe du type Degussa (tel que celui qui est employé, par exemple, pour le microdosage de l'oxygène d'après le principe de Schütze-Unterzaucher) conduit à une rétention irréversible de silicium, sous la forme probable de carbure de silicium, du fait de la grande réactivité du charbon employé.

Par ailleurs, il n'a pu être démontré de façon formelle que le produit chloré du silicium formé lors de la chlorocarbopyrolyse soit exclusivement constitué par du tétrachlorure de silicium; cependant, si lors de la pyrolyse primaire, il peut se former des mono, di, ou trichlorosilanes, ceux-ci en passant sur la garniture de feutre de carbone, saturée de chlore à 1100° devraient être transformés en tétrachlorosilane; de même, l'excès de chlore disponible par rapport à la quantité de silicium à combiner rend peu probable la formation de composés tels que l'hexachlorodisilane (Si_2Cl_6) ou l'octochlorotrisilane (Si_3Cl_8) *etc.*

Le balayage du tube à pyrolyse par un courant d'azote, sous débit relativement élevé de 56 ml/mn, permet d'entraîner le chlore en excès ainsi que le tétrachlorure de silicium dans le piège froid où ce dernier se solidifie; l'expérience montre qu'un tel débit est nécessaire afin d'éviter toute rétention des composés chlorés du silicium au sein du dispositif de minéralisation, ce qui donnerait lieu soit à une augmentation de la durée d'analyse, soit à un phénomène de mémoire au sein du dispositif de minéralisation.

Condensation des gaz de pyrolyse et réchauffage du piège

Le piège refroidi à $-78°$ contient une garniture d'alumine frittée qui n'a pratiquement pas de propriétés adsorbantes, mais permet de retenir par filtration l'aérosol de tétrachlorure de silicium susceptible de se former par condensation et d'être entraîné par le courant d'azote sous le débit plus élevé (80 ml/mn) utilisé en vue de chasser du piège la majeure partie du chlore simultanément condensé à l'état liquide.

L'élimination du chlore est effectivement nécessaire afin d'éviter les effets nuisibles de sa présence dans les gaz (dont la vapeur de tétrachlorure de silicium) qui sont introduits dans la flamme du spectromètre d'absorption atomique. Le chlore gazeux serait, en effet, susceptible de réagir sur l'acétylène alimentant cette flamme pour former des composés très explosifs et, en outre, si sa concentration était trop élevée, de favoriser la recombinaison partielle du silicium atomique, produit par dissociation thermique du tétrachlorure de silicium suivant la réaction d'équilibre

$$SiCl_4 \rightleftharpoons Si + 2\,Cl_2$$

Quant au chlore résiduel subsistant dans le piège, il est éliminé, en phase gazeuse, après vaporisation du condensat, par passage dans le tube absorbeur à garniture de laine d'argent (qui n'est renouvelée qu'une fois par semaine), situé avant le spectrophotomètre.

La valeur (20 ml/mn) et la constance du débit du courant d'azote injectant les gaz issus du piège froid dans la flamme du spectrophotomètre conditionne la vitesse de passage du tétrachlorure de silicium dans cette flamme de façon reproductible, en fonction du temps.

Dosage du silicium dans le tétrachlorure de silicium

Le dosage du silicium par absorption atomique est effectué dans une flamme protoxyde d'azote–acétylène. L'obtention de résultats reproductibles est conditionnée par le maintien difficile de la constance absolue des conditions de mesure du signal fourni par le système spectromètre–intégrateur lors des différentes analyses effectuées au cours d'une même journée de travail.

Le réglage électronique de l'appareil d'absorption atomique doit impérativement permettre l'obtention d'une réponse très stable, et en particulier, d'une excellente ligne de base. Cette condition est réalisée grâce à la limitation de l'intensité d'alimentation de la lampe à cathode creuse au silicium à 6 mA, du choix de la tension d'alimentation du photomultiplicateur, telle que son gain ne dépasse pas 6, et du choix de la sensibilité de l'enregistreur correspondant à 5 mV pour la pleine échelle. Une plus grande sensibilité conduirait, en effet, à un comptage par l'intégrateur d'un nombre plus grand, pour une même quantité de silicium à doser, mais donnerait lieu simultanément à une dérive importante de la ligne de base, pendant chaque mesure, incompatible avec la précision requise des résultats.

La plus grande difficulté réside dans la nécessité de maintenir la constance des caractéristiques physiques et chimiques de la flamme protoxyde d'azote–acétylène pendant la durée d'une série d'analyses. On dispose, à cette fin, de débitmètres permettant de mesurer les débits du comburant et du combustible sous des pressions bien déterminées.

Par contre, la qualité du combustible évolue au cours de l'utilisation d'une même bouteille; corrélativement, la teneur en acétylène s'appauvrit pour un même débit et le pouvoir réducteur de la flamme décroit provoquant une perte de sensibilité de l'appareillage de mesure qui se traduit par une variation du coefficient de pente de la droite d'étalonnage. Pour pallier cet inconvénient, les bouteilles d'acétylène ne sont pas utilisées en deçà d'une pression de 6 bars.

RESULTATS

La méthode et l'appareillage décrits permettent essentiellement de doser le silicium dans les composés organiques stables, solides ou pâteux de tension de vapeur suffisamment faible pour que reste négligeable toute perte par vaporisation partielle du prélèvement analytique lors de son introduction dans le tube à pyrolyse sous l'effet du contrebalayage par le courant d'azote.

Dans le Tableau 1 sont rassemblés des résultats du dosage du silicium dans des composés organiques contenant exclusivement, outre le silicium, du carbone, de l'hydrogène et de l'oxygène; le silicium peut y être lié soit à des atomes de carbone, soit, simultanément, à 1 ou 2 atomes d'oxygène, soit à l'hydrogène, soit même à un autre atome de silicium.

Divers produits analysés sont des composés de recherches pour lesquels, à défaut de la structure moléculaire, la formule brute est communiquée.

La précision des résultats (exprimée *a contrario* en erreurs absolues) n'atteint pas toujours celle qui est admise pour le dosage des éléments courants en microanalyse organique élémentaire.

CONCLUSION

Le présent travail est une approche en vue de la mise au point d'une méthode de microdosage automatique rapide du silicium dans les composés organiques, voire inorganiques.

Elle a montré la possibilité de faire entrer le silicium dans un molécule gazeuse, le tétrachlorure de silicium, aisément transférable en phase gazeuse du site de traitement ("minéralisation" dans les cas des composés organiques) du prélèvement microanalytique au site du mesurage effectué sur la molécule de transfert. Elle a, d'ores et déjà, permis d'obtenir des résultats satisfaisants, dans le cas des composés organiques siliciés, en ce qui concerne la durée unitaire d'une détermination du silicium dans une série; la précision absolue des résultats des dosages reste en deçà de celle qu'il eût été souhaitable d'atteindre bien qu'elle puisse être considérée comme déjà satisfaisante, eu égard à la masse atomique du silicium, lorsqu'elle est comparée à la précision classique des microdosages du carbone, de l'hydrogène, de l'oxygène et de l'azote dans les composés organiques.

Par ailleurs, l'accroissement de sensibilité du dosage du silicium que permet d'atteindre l'injection de la totalité du silicium à doser, sous la forme de molécules siliciées gazeuses, dans la flamme d'un spectromètre d'absorption atomique, autorise à penser que cette méthode est susceptible d'être appliquée au dosage de traces de silicium dans des substances organiques ou inorganiques sous réserve d'effectuer préalablement une mise au point appropriée du dispositif de traitement (chlorocarbopyrolyse) du prélèvement analytique.

Tableau 1

Composé	Si % calc.	*m*, *mg*	Si % trouvé	Δ%
Triphénylsilane* $(C_{18}H_{16}Si)$	10,79	0,321	10,72	−0,07
		0,413	10,97	+0,18
		0,468	10,47	−0,32
		0,505	10,69	−0,10
		0,344	10,40	−0,39
		0,479	10,52	−0,27
		0,472	10,49	−0.30
		0,508	10,59	−0,20
Triphénylméthylsilane* $(C_{19}H_{18}Si)$	10,23	0,485	10,41	+0,18
		0,306	10,95	+0,72
		0,337	10,45	+0,22
		0,241	10,46	+0,23
		0,331	9,94	−0,29
		0,453	10,02	−0,21
		0,249	10,12	−0,11
		0,383	10,37	+0,14
		0,279	10,38	+0,15
Triphénylsilanol $(C_{18}H_{16}OSi)$	10,16	0,267	10,50	+0,34
		0,434	9,82	−0,34
		0,259	10,16	0
		0,191	10,31	+0,15
		0,376	10,03	−0,13
		0,291	10,31	+0,15
Composé de recherche* $(C_{18}H_{16}Si)$	6,71	0,234	6,92	+0,21
		0,345	6,71	0
		0,198	6,16	−0,55
		0,184	6,58	−0,13
		0,273	6,56	−0,15
		0,248	6,44	−0,27
		0,388	6,86	+0,15
		0,496	6,60	−0,11
		0,280	6,50	−0,21
		0,282	6,77	+0,06
Composé de recherche† organosilane (teneur nulle en oxygène)	9,33	0,325	9,42	+0,09
		0,371	8,41	−0,92
		0,463	8,98	−0,35
Composé de recherche† organosilanol $(C_{26}H_{36}OSi)$	7,15	0,498	7,33	+0,18
		0,552	7,25	+0,10
		0,731	7,25	+0,10
		0,642	7,37	+0,22
		0,277	8,01	+0,86
		0,427	7,26	+0,11
		0,699	6,82	−0,33
Composé de recherche† organosilanol $(C_{20}H_{32}SiO_2)$	8,45	0,288	9,17	+0,72
		0,228	7,89	−0.56
Composé de recherche† organosilane	8,48	0,540	8,26	−0,22
		0,448	8,33	−0.15
		0,333	8,32	−0,16
		0,301	8,74	+0,26
		0,243	8,44	−0,04
Composé de recherche $(C_{15}H_{19}O_2Si)$	10,87	0,259	10,75	−0,12
		0,188	10,83	−0,04
Composé de recherche† triphénylvinylsilane	7,21	0,362	7,12	−0.09
		0,310	7,32	+0,11
Triméthyltriphényl-disilane	16,89	0,255	17,16	+0,27
		0,381	16,80	−0,09
		0,261	17,24	+0,35
		0,403	16,26	−0,63

Les produits marqués (*) ou (†) ont été respectivement mis à notre disposition par Messieurs les Professeurs Calas et Corriu. Nous les en remercions vivement.

m = masse du prélèvement; Δ% = (Si% trouvé − Si% calculé).

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THE ANALYSIS OF COPPER REFINERY SLIMES

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Summary—Methods are reviewed for the determination of the following constituents of copper refinery slimes: aluminium, antimony, arsenic, barium, bismuth, calcium, cobalt, copper, gold, iron, lead, magnesium, manganese, molybdenum, nickel, platinum metals, selenium, silicon, silver, sulphur, tellurium, tin and zinc.

Twenty-five years ago the writer outlined the analysis of copper refinery slimes.[1] Since then, a large expansion of world copper production has occurred, bringing with it a substantial widening of the range of elements in refinery slimes.[2,3] In the same period, many notable improvements in analytical procedures have been made; even completely new techniques such as atomic absorption have been introduced. A review of current practices in this specialized but important sphere might be useful to analysts who are concerned with complex metallurgical products.

In spite of the availability in recent years of high-speed pulverizing equipment and improved mixing devices, the preparation of a representative slime sample remains a time-consuming operation. Usually a number of sample portions are taken from the wet slime, combined and dried at 105°, lightly pulverized if necessary to break up small lumps, and given a brief mixing. After reduction of the sample bulk to a convenient size by riffling or similar means, the material is pulverized to pass a 100-mesh screen. Occasionally a small portion, largely metallic copper, may not pass through the screen; this fraction, and the main portion, must then be weighed and analysed separately. Finally, the 100-mesh material must be thoroughly mixed, an operation which is usually the weakest link in sample preparation. The frequent presence of metallic substances, and the range of specific gravity of slime constituents, from approximately 1 for the organic matter of electrolyte additives to over 21 for platinum, make imperative a complete mixing of the finely-pulverized sample.

The inherent heterogeneity of slimes, and the high value of this material in most copper refineries, leads many chemists to prefer, for most constituents, dissolution of a 5- or 10-g sample, dilution to standard volume, and withdrawal of a suitable aliquot, rather than a direct weighing of a 0·5–1 g sample.

Table 1 shows the range of constituents of copper refinery slimes. The data for alumina, barium, lime, magnesia, and silica in the anode mud from the electrolysis of blister copper may appear surprising. Usually the content of these constituents is very low, but it can be enhanced by additions from slag inclusions, refractories, fluxes, mould washes, or dust from an adjacent tailings area.

For most constituents of slimes, decomposition is effected by a suitable combination of acids, followed if necessary by fusion of any insoluble residue with carbonate, bisulphate or peroxide. For antimony and arsenic, the sample is heated in a Pyrex flask with a mixture of sodium sulphate, sulphuric acid, and a small piece of filter paper. Selenium and tellurium are brought into solution with nitric acid and potassium chlorate, with heating on a water-bath, followed by several evaporations with hydrochloric acid to eliminate nitric acid. It is often necessary to remove antimony, arsenic, selenium and tin from a slime sample; these may be readily volatilized by several evaporations with a mixture of hydrobromic and either sulphuric or perchloric acid.

Table 1. Range of constituents of copper refinery slimes

	%	oz/ton
Aluminium oxide	tr.–10·1	
Antimony	tr.–8·3	
Arsenic	0·1–5·6	
Barium	tr.–0·1	
Bismuth	tr.–1·2	
Calcium oxide	tr.–0·6	
Cobalt	tr.–0·2	
Copper	11–82	
Gold	0·02–2·5	6–729
Iron	tr.–1·4	
Lead	0·2–23·8	
Magnesium oxide	tr.–0·5	
Manganese	tr.–0·2	
Molybdenum	tr.–0·2	
Nickel	tr.–45·2	
Platinum metals	tr.–1·5	tr.–437
Selenium	1·5–28·4	
Silica	0·2–13·6	
Silver	1·1–38·1	321–11100
Sulphur	1·8–11·8	
Tellurium	0·1–8·0	
Tin	tr.–7·0	
Zinc	tr.–0·8	

tr. = trace

Table 2. AAS data for copper refinery slimes

	Wavelength, *nm*	Sensitivity, *μg/ml*	Flame
Aluminium	309·3, 396·2	1	NOA
Antimony	206·8, 217·6, 231·2	1	AA
Arsenic	193·7	poor	all flames absorb strongly
Barium	553·6	1	NOA
Bismuth	223·1	1	AA
Calcium	422·7	0·1	AA
Cobalt	240·7	0·2	AA
Copper	324·8	0·05	AA
Gold	242·8	0·3	AA
Iron	248·3	0·1	AA
Lead	217·0, 283·3	0·3, 0·5	AA
Magnesium	285·2	0·005	AA
Manganese	279·5	0·05	AA
Molybdenum	313·3	1	AA or NOA
Nickel	232·0	0·1	AA
Palladium	247·6	0·5	AA
Platinum	265·9	3	AA
Selenium	196·0	poor	all flames absorb strongly
Silicon	251·6	2	NOA
Silver	328·1	0·03	AA
Tellurium	214·3	0·5	AA
Tin	286·3	3	AA or NOA
Zinc	213·9	0·02	AA

AA = Air–acetylene flame.
NOA = Nitrous oxide–acetylene flame.

In the presence of a substantial excess of a ferric salt, an ammonia/ammonium salt buffer will precipitate antimony, arsenic, bismuth, lead, selenium, tellurium, and tin. Treatment with sulphur dioxide and hydrazine hydrochloride in 10–20% hydrochloric acid medium will precipitate tellurium and gold.

The technique of atomic-absorption spectrophotometry is used extensively in the analysis of slimes, and Table 2 gives the wavelength, sensitivity and flame for these determinations. The acidity of standards and unknowns should match approximately, and sometimes the metal compositions should be roughly similar.

Aluminium

Interferences are removed by hydrobromic–sulphuric acid evaporation, separation by precipitation with ammonia, and sulphur dioxide treatment; electrolysis with a mercury cathode will then leave aluminium virtually alone in the solution. Final determination can be carried out photometrically with aluminon, at 525 nm,[4] or gravimetrically.[5,6]

Aluminium can be determined by atomic absorption; standards and samples should contain about 0·1% potassium or sodium.[7,8]

Antimony

After volatilization of tervalent arsenic from hydrochloric acid solution at 108°, antimony can be distilled at 165° and determined volumetrically with potassium bromate[5] or photometrically with Rhodamine B at 565 nm.[4,5]

Antimony can be determined by atomic absorption; the acidity and metal composition of standards and unknowns should match approximately if bismuth and zinc are present.[7]

Arsenic

Tervalent arsenic can be distilled from a hydrochloric acid solution at 108° and determined volumetrically with iodine or photometrically by the hydrazine sulphate–ammonium molybdate procedure, at 660 or 840 nm.[4,5]

The element can be determined by atomic absorption, using the line at 193·7 nm, but instrumental sensitivity is poor in this spectral region and little information exists on interferences.

Barium

Treatment of the sample with *aqua regia*, hydrofluoric acid, and evaporation to fumes of sulphuric acid, followed by dissolution in water and filtration, will leave barium sulphate in the precipitate together with lead sulphate, silver chloride, and a certain amount of the gold and platinum metals. Fusion with sodium carbonate, dissolution in water, and filtration will leave as a precipitate the carbonates of barium and lead. Dissolution of this precipitate in hydrochloric acid and treatment with hydrogen sulphide will precipitate lead, silver, gold and the platinum metals; barium in the filtrate can eventually be precipitated as sulphate.

Barium can be determined by atomic absorption, preferably with about 1000 μg/ml of potassium added to sample and standard solutions.

Bismuth

After removal of interferences by addition of hydrobromic and sulphuric acids, evaporation, and sulphur dioxide treatment, a precipitation with ammonia will leave bismuth with iron. Dissolution of this precipitate in hydrochloric acid and treatment with hydrogen sulphide will isolate bismuth; final photometric measurement by the thiourea method is done at 420 nm.[4,5]

Bismuth can be determined by atomic absorption without interference from an excess of antimony, copper, iron, lead, tin, or zinc.[8]

Calcium

This element, together with magnesium, is usually determined in the sample portion taken for aluminium. The filtrate from the final removal of aluminium hydroxide, described earlier, contains the calcium and magnesium. Ammonium salts are eliminated by evaporation with nitric acid, and the residue is dissolved in water containing a few drops of hydrochloric acid. A sodium hydroxide–sodium cyanide buffer is added, and, with Calcon as indicator, calcium is titrated with standard EDTA solution.[5,9,10]

Calcium can also be determined by atomic absorption; addition of lanthanum chloride will overcome the interference of aluminium.

Cobalt

Cobalt can be conveniently determined in the solution remaining after the electrolysis of copper, described later, by the nitroso-R-salt photometric procedure, at 520 nm.[4,5] The only interfering element in slimes which must be considered is nickel, if it occurs in amounts substantially more than 25 times that of cobalt. For such samples, it is preferable to remove nickel by means of dimethylglyoxime and destroy organic matter by evaporating the filtrate with nitric and sulphuric acids before proceeding with the nitroso-R-salt reaction.

Atomic absorption can be employed for cobalt; copper, iron, magnesium, manganese, molybdenum, nickel, and silicon do not interfere.

Copper

This element is nearly always the major constituent of anode slimes, and the electrolytic procedure is the most appropriate. This necessitates the removal of elements which deposit, wholly or partially, on the cathode in a nitric–sulphuric acid solution. Silver is initially removed as chloride, and an evaporation with hydrobromic–sulphuric acid mixture volatilizes antimony, arsenic, selenium and tin. Sulphur dioxide and hydrazine hydrochloride in hydrochloric acid precipitate gold and tellurium, and in the presence of an excess of a ferric salt an ammonia precipitation will remove bismuth.

If platinum metals are present in significant quantities, the preliminary acid treatments will volatilize ruthenium and osmium; iridium is not deposited from a nitric–sulphuric acid electrolyte. Platinum and rhodium can be removed by digesting the sample with hot sodium nitrite solution at pH 1·5, neutralizing with sodium hydroxide to pH 10 to precipitate copper and other base metals, and filtering. A reprecipitation passes the platinum metals except palladium, into the filtrate.[11] The palladium is readily separated from copper by dimethylglyoxime in 3% hydrochloric acid.

The amount of molybdenum in slimes is too low for this element to be deposited to a significant extent on the cathode along with the copper.

For a rapid control determination, atomic absorption can be used; aluminium, calcium, cobalt, iron, lead, magnesium, manganese, nickel, silver, tin and zinc do not interfere.

Gold

In most slimes, gold is best determined, together with silver, by a combined wet and fire assay. Treatment with sulphuric acid and mercuric sulphate dissolves copper and other base metals, silver is precipitated with a chloride solution, and the residue is filtered off. The precipitate is transferred to lead foil in a scorifier, an addition of test lead, borax and silica is made, and the sample is heated in an oxidizing muffle until the basic oxides are slagged. The contents of the scorifier are poured into a mould, then the lead button is placed in a cupel and heated until only the gold–silver bead remains. Gold and silver are parted in a porcelain cup first with 2·5 M (1 + 6) and finally with 8·5 M (1 + 1) nitric acid; the gold residue is dried, ignited and weighed.

When the gold content of the bead is less than ten times the platinum content, much of the latter remains with the gold on parting. For these rare occasions, the bead is dissolved in *aqua regia* and evaporated several times with hydrochloric acid to eliminate all nitric acid. The sample is digested with a hot sodium nitrite solution at pH 2, then the solution is neutralized with sodium hydroxide to pH 8 and boiled; the residue is filtered off, ignited in a porcelain crucible at 900° and weighed as pure gold.[12]

Gold can be determined by atomic absorption; no interferences are normally encountered.

Iron

After elimination of interferences by evaporation with hydrobromic–sulphuric acid and precipitations with hydrogen sulphide and ammonia, iron can be determined titrimetrically with potassium dichromate or photometrically with 1,10-phenanthroline, at 508 nm.[4,5]

Atomic absorption can be used for iron; no interference is caused by aluminium, cobalt, copper, magnesium, or nickel.

Lead

Lead may be conveniently determined by evaporating a sulphuric acid solution of the sample to fumes, filtering off and washing the precipitate, dissolving the lead sulphate in hot concentrated ammonium acetate solution, and discarding the residue of silica, gold, silver chloride *etc.* Evaporation of the lead acetate solution with sulphuric–nitric acid to fumes will give a final precipitate of lead sulphate. Polarography may also be used to determine lead in slimes.[13]

Lead may be determined by atomic absorption; no interference arises from copper, iron, tin or zinc. There is less flame background at 283·3 nm than at 217·0 nm.

Magnesium

This element is usually determined, like calcium, in the sample taken for aluminium. After the latter has been separated as hydroxide and the filtrate containing calcium and magnesium made up to a convenient volume, an aliquot is withdrawn. Ammonia–ammonium chloride buffer and Eriochrome Black T indicator are added, and the solution is titrated with standard EDTA solution. This gives calcium + magnesium; the volume of EDTA used in the titration for calcium alone, described earlier, is deducted to give the amount of EDTA required for magnesium.[9,10]

Atomic absorption may be used advantageously for magnesium; no interference arises from copper, iron, tin or zinc. The sensitivity is high; a value of 0·005 μg/ml is frequently quoted.[8,14]

Manganese

By oxidation with bromine, manganese can be precipitated with an ammonia ammonium salt buffer, cobalt, copper, nickel and zinc passing into the filtrate. After dissolution of the precipitate in acid, treatment of the solution with hydrogen sulphide, and filtration, manganese is obtained in the filtrate, free from any element which will interfere with the potassium periodate photometric procedure.[4,5]

Manganese can be measured by atomic absorption; no interference can normally be expected from the calcium, cobalt, copper, iron, lead, magnesium, molybdenum, nickel or zinc in slimes.

Molybdenum

Interferences are removed by addition and evaporation of hydrobromic–sulphuric acid mixture and precipitation with sulphur dioxide. Addition of α-benzoinoxime to the cold oxidized filtrate to complex molybdenum, followed by a chloroform extraction and destruction of the chloroform with nitric–sulphuric acid mixture will isolate molybdenum for subsequent determination by the thiocyanate–stannous chloride photometric method; an isopropyl ether extraction to concentrate the colour for measurement at 540 nm is usually desirable.[4,5,15]

Atomic absorption offers an alternative technique for molybdenum; negligible interference may be expected from copper, iron, lead, manganese, nickel or tin.

Nickel

Most copper slimes have a nickel content of 0·1–8%; if a chemical method is desired, the gravimetric dimethylglyoxime procedure is preferred, following the determination of copper by electrolysis.

For lower concentrations of nickel, the photometric dimethylglyoxime method with measurement at 530 nm, after copper removal, is thoroughly reliable.

A few slimes contain such a high quantity of nickel that electrolytic deposition on a platinum cathode, from an ammoniacal solution containing ammonium sulphate is preferred.

Atomic absorption may be used to determine nickel; no interference will be encountered from aluminium, calcium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, silver, tin or zinc.

Platinum metals

With a few exceptions, the platinum metals in copper slimes are almost entirely platinum and palladium. They are usually determined by a combined wet and fire assay.[12]

An appropriate sample is dissolved in the manner described earlier for gold. Slimes nearly always contain more than ten times as much silver as gold + platinum metals, but if not, sufficient silver as nitrate or sulphate should be added initially to give this ratio. After the filtration, the filtrate, which contains a good part of the palladium, is retained. The precipitate, which contains all the gold and platinum, is scorified and cupelled as described previously for gold. The gold–silver–platinum bead, containing a small quantity of palladium, is parted in hot concentrated sulphuric acid. The residue contains gold and platinum; silver and palladium are in the filtrate. Silver is determined as chloride, and palladium with dimethylglyoxime in 3% hydrochloric acid. The major part of the palladium, in the original filtrate, is also determined with dimethylglyoxime but with a reprecipitation to remove occluded ions. If the palladium content is low, it may be measured photometrically by a dimethylglyoxime–chloroform method, at 375 nm.[5]

The residue of gold and platinum from the sulphuric parting, after weighing, is dissolved in *aqua regia*. Gold is determined by sodium nitrite, as described earlier. The balance is platinum, possibly with traces of iridium and rhodium. The platinum figure may be confirmed by adding *aqua regia* to the filtrate from the gold separation, evaporating to dryness, and then adding hydrochloric acid and evaporating to dryness again, this last step being repeated several times. The residue is dissolved in 1% hydrochloric acid containing several grams of sodium acetate, and platinum is precipitated by formic acid.[11] If the platinum content is low, it can be measured photometrically with stannous chloride, at 403 nm.[5]

Atomic absorption can also be used to determine the platinum metals; very few elements interfere.

Selenium

This element is almost invariably determined in slimes by precipitation from concentrated hydrochloric acid solution with sulphur dioxide. After prior removal of silver as chloride, and of lead as sulphate if necessary, passage of a stream of sulphur dioxide into a 70–90% hydrochloric acid solution will precipitate only selenium and gold. Treatment of this precipitate with nitric acid will dissolve the selenium, leaving gold as a residue. Repeated evaporations of the selenium-containing solution after additions of hydrochloric acid, followed by a repetition of the previous precipitation by sulphur dioxide from concentrated hydrochloric acid will yield pure selenium.[5,11,16] The filtrate and washings from the precipitation of selenium + gold should be retained for the tellurium determination.

Selenium can be measured by atomic absorption, but the sensitivity for this element is poor. The selenium content of slimes is nearly always above the preferred range for a photometric method, but if the latter is applicable, the 3,3′-diaminobenzidine procedure is thoroughly reliable.[4,5,16]

Silicon

The classic gravimetric method of dehydration with perchloric acid and volatilization of silica with hydrofluoric acid remains the preferred chemical procedure for most slimes.[17]

The element can also be determined by atomic absorption; no interference occurs from aluminium, calcium or iron.

Silver

Silver is usually determined by the wet and fire assay described for gold. The element may also be found by the conventional precipitation and weighing of silver chloride, if the first precipitate is leached with ammonia solution to dissolve silver and leave impurities behind.

Silver may also be determined by atomic absorption; no interference occurs from aluminium, bismuth, calcium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, tin or zinc.

Sulphur

The classic gravimetric procedure, oxidation of sulphur to sulphate followed by precipitation with barium chloride, remains the preferred procedure for this complex material. The sample is treated with potassium bromide and bromine, then nitric acid, the solution is evaporated to dryness, the residue moistened with hydrochloric acid and then heated to dryness again (this step being repeated several times), and finally the residue is treated with hydrochloric acid, the solution is diluted, and the precipitate filtered off and washed. Because the precipitate contains insoluble sulphates in addition to silica, it is digested for 30 min in boiling sodium carbonate solution, filtered off and washed, and the filtrate is added to the original filtrate.

If the slimes contain an appreciable amount of antimony, this should be removed by digesting for an hour in warm 20% hydrochloric acid solution with ingot-iron filings, before adjustment of the acidity to about 1% hydrochloric acid and precipitation of barium sulphate in the usual manner.

Tellurium

Tellurium is nearly always determined by precipitation from dilute hydrochloric acid with sulphur dioxide. After the removal of selenium and gold in concentrated hydrochloric acid medium by sulphur dioxide, dilution to about 10–20% hydrochloric acid and the addition of hydrazine hydrochloride will precipitate tellurium.

Atomic absorption can be used to determine tellurium; no interference is normally encountered from aluminium, antimony, cobalt, copper, iron, lead, magnesium, selenium or zinc.

Tin

After isolation by distillation, tin can be readily determined titrimetrically or photometrically. With slimes, the same sample can usually serve for arsenic, antimony and tin. From hydrochloric acid containing a reducing agent, arsenic is distilled at 108° and antimony at 165°; if hydrobromic acid is then added to give a 3:1 mixture of hydrochloric and hydrobromic acids, tin can be distilled at 145–160°.

In the distillate, tin can be determined titrimetrically with iodine after reduction by metallic nickel. For a small quantity of tin, the photometric dithiol procedure is rapid and reliable; measurement is made at 530 nm. Polarography offers another suitable technique for tin in slimes.[13]

Tin can also be measured by atomic absorption; a large excess of antimony will interfere.

Zinc

If a chemical determination is desired, the classic potassium ferrocyanide titrimetric method may be employed for higher levels of zinc, whereas for traces a photometric procedure using dithizone is satisfactory.[4,5] In both cases the analysis is carried out on the solution remaining after the electro-deposition of copper.

Atomic absorption may be used to determine zinc, conveniently after the electrolysis of copper. The remaining constituents in the sample, aluminium, calcium, cobalt, iron, magnesium, manganese, molybdenum, and nickel, do not interfere.

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DETERMINATION OF TRACES OF CADMIUM IN ALLOY STEELS BY ANODIC STRIPPING VOLTAMMETRY

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Summary—Concentrations of cadmium of the order of 0·1 ppm in alloy steels containing large concentrations of chromium and nickel (*ca.* 17 and 13% respectively), about 0·1% of copper and a number of metals at low concentrations, were determined by anodic stripping voltammetry with a hanging mercury-drop electrode in $1M$ hydrochloric acid. Cadmium was separated on Dowex 50W-X8 cation-exchanger in a medium at pH 1·3 containing excess of EDTA. Mercury-film electrodes cannot be used for this determination, because the peak for cadmium is distorted by evolution of hydrogen on the electrode support. The relative standard deviation of the determination of 0·44 ppm of cadmium in steel is 3·2% and the confidence limits for 95% probability are 0·44 ± 0·02 ppm. The error in the cadmium recovery does not exceed + 8%.

The content of cadmium in special alloy steels employed in nuclear technology is very significant because of its very high neutron-absorption cross-section. The amounts of cadmium typically present in these steels are so low that they cannot be determined by conventional atomic-absorption spectroscopy in this complex matrix. However, this metal is readily determinable by anodic stripping techniques with mercury electrodes.[1,2] The main drawback of stripping techniques is the poorer selectivity compared with atomic absorption spectroscopy. This problem can sometimes be overcome by employing mercury-film electrodes, which yield much sharper stripping peaks. However, in such complicated matrices as steels containing large amounts of alloying metals, preliminary separation of interfering elements is usually necessary. In this study, stripping voltammetry employing mercury-film and hanging mercury-drop electrodes was combined with an ion-exchange separation.

EXPERIMENTAL

Reagents

All chemicals employed were of *p.a.* purity (Lachema, Czechoslovakia), except for hydrochloric and nitric acids which were labelled as chemicals for semiconductors. Solutions were prepared with redistilled water and were found to be free from traces of cadmium determinable by stripping voltammetry; all the chemicals contained trace concentrations of lead and copper, which, however, were low enough not to interfere in the determination of cadmium.

A standard 1-mg/ml cadmium solution was prepared by dissolving 1·0000 g of spectrographically pure metal in 10 ml of concentrated hydrochloric acid with addition of several drops of hydrogen peroxide. Excess of peroxide was expelled by boiling for 10 min and the cooled solution was diluted to 1000 ml with redistilled water. Less concentrated standard solutions were prepared from this stock solution immediately before use.

For the cation-exchange separation procedure, Dowex 50W-X8 resin (50/100 mesh) was employed. The column used was 1 cm in internal diameter and 7 cm high.

The solutions were deaerated before electrolysis, with nitrogen which had been freed from oxygen by passage through a heated column packed with copper filings and through traps containing a solution of a vanadium(II) salt and amalgamated zinc.

Apparatus

The stripping voltammetric determinations were carried out with the LP-60 (Laboratorní přístroje, Czechoslovakia) and PO-4 (Radiometer, Denmark) polarographs with a two-electrode circuit, using a saturated calomel reference electrode. Measurements with the hanging mercury-drop electrode (HMDE) (Metrohm, Switzerland) were carried out on 40 ml of solution in the Metrohm electrolysis cell. The measurements with mercury-film electrodes (MFE's) were carried out in a 10-ml electrolysis cell (Radiometer, Denmark). In all cases, the solutions were stirred during the pre-electrolysis with a glass stirrer, driven by a Radiometer synchronous motor at a speed of *ca.* 600 rpm, and a 1-min rest period followed the pre-electrolysis before the potential scan.

MFE's were prepared in the laboratory by depositing mercury on a graphite or glassy carbon support. Spectral-grade graphite (Kablo, Czechoslovakia) was impregnated with paraffin for 4 hr at 100° *in vacuo*. Then a rod 3 mm in diameter was cemented in glass tubing with silicone-rubber cement and the electroactive disk area was polished with metallographic papers (2/0, 4/0, 6/0; SIA, Switzerland) and with damp velvet. A 3-mm thick rod of glassy carbon (Le Carbone Lorraine, France) was cemented in glass tubing and polished similarly. Mercury was used as a contact

Table 1. Typical composition of alloy steel studied, with the half-wave potentials on mercury and the stability constants of the complexes with EDTA for the individual components

Component	Approx. conc., %	Half-wave potential on Hg, *V vs.* SCE	Stability constant of the EDTA chelate, log β^5
Fe	> 60	Fe(III): ↑ (1*M* HCl)	Fe(III): 25·1
C	0·035–0·040	—	—
Mn	0·9	Mn(II): → (2*M* HCl + 2*M* KCl)	Mn(II): 13·98
Si	0·4	—	—
P	0·015	—	—
S	0·020	—	—
Cr	17·5	Cr(III): − 0·99 (1*M* HCl)[4]	Cr(III): 23·4
Ni	13·5	Ni(II): − 1·1 ($HClO_4$, pH 0–2)[4]	Ni(II): 18·56
Mo	2·4	Mo(VI): − 0·14 −0·53 (1*M* HCl)[4]	Mo(VI): various complexes with log β from 7·5 to 35·1
Cu	0·10	Cu(II): ↑ −0·33 (2*M* HCl + 2*M* KCl)	Cu(II): 18·8
Co	0·010–0·030	Co(II): → (2*M* HCl + 2*M* KCl)	Co(II): 16·3
N	0·030	—	—
Cd	<0·0001	Cd(II): −0·66 (1*M* HCl)[4]	Cd(II): 16·6

↑ reduction wave merges with the current of mercury anodic dissolution; → no reduction within the accessible potential range.

for these electrodes. A mercury film was deposited on the polished support either *in situ*, according to Florence,[3] at the chosen pre-electrolysis potential, with mercuric nitrate added to the sample solution to yield a final concentration of mercury of $2 \times 10^{-5}M$, or beforehand by a 3-min electrolysis at E between − 0·2 and − 1·5 V in a solution 1*M* in nitric acid and 10^{-3}–$10^{-2}M$ in mercuric nitrate.

All measurements were performed at 20 ± 2°. The potentials are referred to the SCE at the experimental temperature. Small volumes of cadmium standard solutions were delivered from Hamilton syringes.

RESULTS AND DISCUSSION

A typical steel composition for the analysis is given in Table 1. Of the components given, the non-metallic elements will obviously not interfere in the electrochemical determination. If stripping of cadmium is carried out in the usual manner[1,2] in an acidic medium, then the half-wave potentials of the metals present (the third column of Table 1) indicate that Mn(II), Cr(III), Ni(II) and Co(II) will also not interfere, provided that the pre-electrolysis potential is made as positive as possible for this determination (about − 0·8 V). Fe(III), which arises from oxidation of Fe(II) formed during the pre-electrolysis, Mo(VI) and Cu(II), which have stripping peaks which lie between − 0·1 and − 0·2 V, must be removed.

Cation-exchange separation

It can be seen from the fourth column of Table 1 that the chelates with EDTA can be utilized for the separation on a cation-exchanger. If the medium is made sufficiently acid for the Cd–EDTA chelate to dissociate, Cd^{2+} ions will be retained on the resin, while the more stable Cu(II) and Fe(III) chelates will pass through the column because of their negative charge. It is obvious that Cr(III), Ni(II) and Mo(VI) will also be separated in this way. We used this principle previously for the separation of indium, cadmium and lead.[6]

The separation of cadmium and copper, which is critical because of the small difference in the stability constants of the corresponding EDTA chelates, was studied in detail. The resin in the H^+-cycle was first

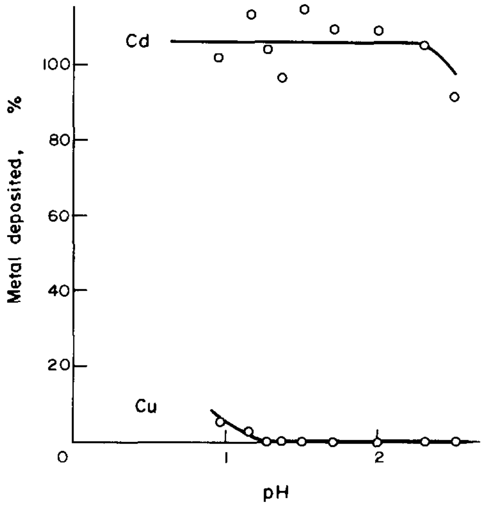

Fig. 1. The separation of 10 μg of Cd and 20 μg of Cu on Dowex 50 W-X8 cation-exchanger as a function of pH. For the conditions see the text.

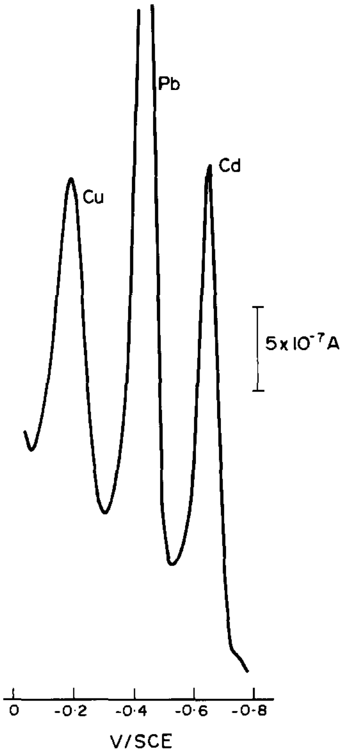

Fig. 2. The separation of 1 μg of Cd from 1000 μg of Cu on Dowex 50 W-X8 cation-exchanger at pH 1·23. $1·25 \times 10^{-3}M$ EDTA; HMDE; 15 min pre-electrolysis at −0·8V; scan-rate, 400 mV/min.

washed with 200 ml of an acetate buffer at the given pH and $1·25 \times 10^{-3}M$ in EDTA. Then 200 ml of a 0·1*M* acetic acid–$1·25 \times 10^{-3}M$ EDTA solution containing known amounts of cadmium and copper, with pH adjusted to the required value with dilute nitric acid, was passed through the column at a rate of 3 ml/min. The column was washed again with 300 ml of the acetate buffer at the required pH (and $1·25 \times 10^{-3}M$ in EDTA) and then cadmium was eluted with 40 ml of 1*M* hydrochloric acid. Cadmium and copper were then determined in the eluate by anodic stripping with the HMDE (pre-electrolysis potential and time, − 0·8 V and 10 or 15 min, respectively, scan-rate, 400 mV/min, the concentration being determined by the standard addition method). The dependence of the separation of 10 μg of Cd and 20 μg of Cu on the pH is given in Fig. 1, and the separation of 1 μg of Cd from 1000 μg of Cu at pH 1·23 is depicted in Fig. 2. Therefore, the separation can be performed over the pH range 1·2–2·0. At these pH values Fe(III), Cr(III), Mo(VI) and possibly Ni(II) will still be firmly complexed and will not be retained on the resin. The concentration of EDTA in practical analyses should be as high as possible, in order to complex all the major components.

Repeated separations of 1 μg of Cd from 1000 μg of Cu showed that the reproducibility of the cadmium recovery is generally better than 7% relative and that the recoveries are on average 7% higher than the theoretical value. There is no difference in the results whether the standard addition is made before or after the ion-exchange separation.

Anodic stripping determinations

The determinations of cadmium in the eluate from the ion-exchanger column, 1*M* in hydrochloric acid, by use of the HMDE, gave good results (see the previous section). However, as the actual amount of cadmium measured in the analyses of the steel samples is less than a twentieth of this, an attempt was made to use MFE's, which are known to have a lower detection limit and yield much sharper peaks.[1,2] Mercury was deposited on polished impregnated graphite and glassy carbon supports both before the determination and *in situ* (see Experimental). However, satisfactory results were not obtained because of a general drawback of MFE's, namely, the interfering effect of the support. It has been shown both for graphite[7] and glassy carbon[8] that, owing to heterogeneity of the support surface, mercury is deposited in the form of tiny droplets rather than as a smooth film. On the uncovered support surface hydrogen is evolved at more positive potentials, especially in acidic solutions, obscuring stripping peaks more negative than about −0·7 V. The cadmium stripping peak appears on the voltammetric curve, but is distorted and the sensitivity is poor. No significant difference was found between the results obtained with impregnated graphite and with glassy carbon. We did not even succeed in reproducing Florence's results[3] in the neutral medium of 0·1*M* potassium nitrate, for which the author reported perfect cadmium peaks. The results are slightly better when the mercury film is deposited before the determination, as the film is thicker and hence the support coverage is higher. However, it must be concluded that mercury-film electrodes are unsuitable for the determination of very low concentrations of cadmium; on the other hand, the determinations of elements yielding more positive stripping peaks (*e.g.*, Pb, Cu, Bi, *etc.*) give excellent results.[9] An example of the determination of 1 μg of Cd and 1 μg of Cu on a mercury-film electrode is given in Fig. 3.

Therefore, the HMDE was used for the measurements on steel samples.

The determination of cadmium in steel samples

The ion-exchange separation and the stripping measurement were carried out on steel samples under the conditions described above. The pH for the cation-exchange separation was adjusted to 1·3 and the EDTA concentration was ten times that in the previous measurements, *i.e.*, $1·25 \times 10^{-2}M$, in order to complex Fe, Cr, Cu and Cd quantitatively (1-g steel samples were used). The solution was boiled briefly before the pH adjustment to enhance the formation of the inert chromium–EDTA chelate. It was again found that there is no difference between the results obtained with the standard addition made

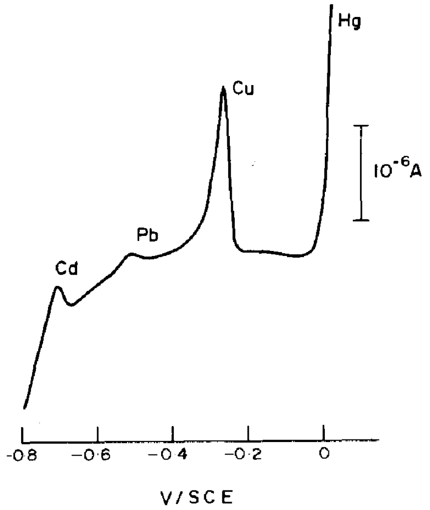

Fig. 3. The stripping voltammogram of 1 μg of Cd and 1 μg of Cu in 10 ml of 1*M* HCl on a mercury-film electrode. Impregnated graphite support, mercury deposited *in situ*; $2 \times 10^{-5}M$ Hg^{2+}; 10 min pre-electrolysis at −0·8V; scan-rate, 400 mV/min.

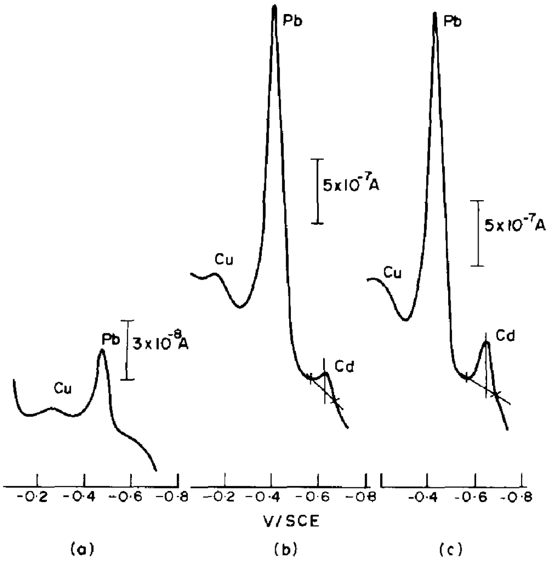

Fig. 4. The stripping voltammetric curves for the determination of cadmium in alloy steel after cation-exchange separation. (*a*) blank; (*b*) the sample; (*c*) the sample with 0·1 μg of Cd added to the electrolysed solution. pH during the cation-exchange, 1·3; EDTA concentration, $1{\cdot}25 \times 10^{-2}M$. Cadmium was eluted with 40 ml of 1*M* HCl; 15-min pre-electrolysis at −0·8 V on the HMDE; scan-rate, 400 mV/min.

before and after the ion-exchange separation. Therefore, a small volume of a standard cadmium solution can be added to the eluate after recording of the voltammetric curve of the sample, and a parallel determination of the sample plus the standard addition can be omitted. Typical voltammetric curves obtained for a steel sample and the blank are given in Fig. 4. It can be seen from Fig. 4 that the steel also contains some lead. However, for the determination of lead, the conditions of the cation-exchange separation would have to be modified, as the retention of lead on the resin is not quantitative (owing to the very similar values of the stability constants of the copper and lead EDTA chelates, $\log \beta_{Cu} = 18{\cdot}8$, $\log \beta_{Pb} = 18{\cdot}3$). The separation from copper and iron is quantitative.

The results of four parallel determinations of cadmium in steel are given in Table 2. The reproducibility of these particular determinations is excellent, better than achieved in separations with pure cadmium and copper solutions. It can thus be expected that the reproducibility will generally not be worse than that described for the separation of pure cadmium and copper, *i.e.*, *ca.* 7%.

Unfortunately, a suitable standard was not available for checking the accuracy of the method. Therefore, the procedure was carried out with several sample solutions containing various amounts of added cadmium. The relative error in the cadmium recovery did not exceed + 8%.

Therefore, the following procedure can be recommended for the determination of traces of cadmium in alloy steels.

Pass 200 ml of a solution containing 40 ml of 0·5*M* acetic acid and 5 ml of 0·05*M* EDTA adjusted to pH 1·3 with dilute nitric acid, through a column 1 cm in diameter, containing the Dowex 50W-X8 cation-exchanger (50–100 mesh) in the H^+-form, at 7 ml/min.

Dissolve 1 g of the steel in a warm mixture of 10 ml of concentrated hydrochloric acid—4 ml of concentrated nitric acid and 10 ml of water. If niobium is present in

Table 2. Results of four parallel determinations of cadmium in steel. For conditions see text

No.	Cd found, *ppm* x_i	$\bar{x}$ *ppm*	$x_i - \bar{x}$ *ppm*	Relative standard deviation, %	Confidence limits (95% probability, *ppm*
1	0·44	0·44	0·00	3·2	0·44 ± 0·02
2	0·43		− 0·01		
3	0·45		+ 0·01		
4	0·46		+0·02		

the sample, add 1–2 ml of concentrated hydrofluoric acid to this solution and heat the mixture again. Transfer the cooled solution to a 100-ml volumetric flask and dilute with water to the mark.

Add to a 10-ml aliquot 50 ml of 0·05*M* EDTA and 40 ml of 0·5*M* acetic acid, dilute with water to *ca.* 200 ml and boil for 10 min. After cooling, adjust the volume to 200 ml, and the pH to 1·3 with dilute nitric acid. Pass the sample solution through the column at 5 ml/min and then wash the resin with 300 ml of a solution containing 5 ml of 0·05*M* EDTA and 60 ml of 0·5*M* acetic acid and adjusted to pH 1·3 with dilute nitric acid, at the same flow-rate. Then elute the cadmium with 40 ml of 1*M* hydrochloric acid. Transfer the eluate, or an aliquot thereof, to the electrolysis cell and deaerate by passing nitrogen for 15 min. Electrolyse at − 0·8 V *vs.* SCE for 15 min with stirring and 1 min further without stirring, at the HMDE. Record the voltammogram from − 0·8 to − 0·2 V at 400 mV/min. During the whole procedure pass nitrogen over the solution.

Add 0·1 or 0·2 μg of cadmium to the solution in the electrolysis cell (use a syringe to add as small a volume as possible) and repeat the stripping determination. Calculate the cadmium content from the difference in the peak-heights before and after the standard addition. The peak-heights are measured as indicated in Fig. 4: the inflexion points on the curve before and after the cadmium peak are connected by a straight line and the vertical distance is measured from this line to the top of the peak.

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STUDIES ON SYNTHETIC INORGANIC ION EXCHANGERS—V

PREPARATION, PROPERTIES AND ION-EXCHANGE BEHAVIOUR OF AMORPHOUS AND CRYSTALLINE THORIUM TUNGSTATE

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Summary—Amorphous and crystalline thorium tungstate have been prepared by mixing $0{\cdot}1M$ thorium nitrate and $0{\cdot}1M$ sodium tungstate under different conditions. The physico-chemical properties, chemical stability, composition, TGA, DTA, X-ray, infrared absorption and ion-exchange behaviour of thorium tungstate are reported and discussed. Distribution coefficients of metal ions on thorium tungstate have been determined at pH 2–3 and 5·5–6·5. Selective ion-exchange separations of bismuth and mercury from other metal ions have been achieved on a column of thorium tungstate.

The importance of synthetic inorganic ion-exchangers has been reviewed.[1] In our earlier papers,[2–5] thorium phosphate was studied as an ion-exchanger. The present report deals with amorphous and crystalline thorium tungstate as an ion-exchanger.

This compound has been examined for ion-exchange properties by Turnov and Kovba[6] and by Qureshi *et al.*[7] The latter prepared non-crystalline thorium tungstate having composition $Th(OH)_2(HWO_4)_2 . nH_2O$. They found that the distribution coefficients were higher for Ga^{3+}, In^{3+}, Zr^{4+}, Pb^{2+} and La^{3+} but they did not investigate the effect of heat treatment on these exchangers. Although crystallization of inorganic ion-exchangers is tedious and difficult, crystalline thorium tungstate offers many advantages. We have prepared and investigated a number of both amorphous and crystalline thorium tungstates of varying compositions, the crystalline variety being the more stable for column operation. The crystalline thorium tungstate prepared by us permits ion-exchange separations much superior to those reported by Qureshi.[7] The crystalline thorium tungstate is stable in water, methanol, ethanol, acetone, dilute mineral acid and dilute alkalis at room temperature and can be used in these media for analytical separations of metal ions.

EXPERIMENTAL

Reagents

All chemicals were of analytical reagent grade.

Apparatus

For separation studies, a glass tube (bore 1·1 cm) was filled with 10 g of thorium tungstate (hydrogen form) on a glass-wool support. The column length was 4·5 cm; the flow-rate was 0·2 ml/min for all separations.

Preparation of thorium tungstate

Thorium tungstate was prepared by adding $0{\cdot}1\ M$ thorium nitrate in $1M$ nitric acid dropwise to $0{\cdot}1M$ sodium tungstate in different volume ratios, with constant stirring. The mixture was kept at room temperature (for crystalline material) or digested on a steam-bath (for the amorphous product) for several hours. Then the product was filtered off and washed with water till the pH of the filtrate was 2·5–3, and dried over phosphorus pentoxide. If the crystalline product was washed until the pH was >3, it became amorphous. Even on digestion for 140 hr on the steam-bath, the product was amorphous, but the crystalline variety was obtained after standing for only 12 hr at room temperature.

Composition

The products were analysed by standard methods,[8–9] and the results are shown in Table 1. Qureshi *et al.*[7] reported compositions varying from 1:1 to 1:1·8 Th:W.

Heat treatment

Thorium tungstate (batch No. 9) was heated in an electric muffle furnace for 1-hr periods at various temperatures up to 1000°. The colour of the sample changed with temperature, from colourless at room temperature, to yellow at 400° and deep green at 900°. Samples of batches 1 and 9 were subjected to thermogravimetric analysis at a heating rate of 8°/min with a MOM (Hungary) thermobalance. Figures 1 and 2 show the TGA and DTA curves. The influence of heat treatment of the ion-exchange capacity was also determined.

pH titration

Topp and Pepper's method was employed,[10] 500 mg of thorium tungstate (batch 9) being shaken with 100 ml of solution containing different amounts of MOH (M = Li, Na and K) for three days at $30 \pm 2°$ with intermittent shaking. After attainment of equilibrium the pH was measured. The experiment was repeated in the presence of sodium chloride, the total sodium concentration being kept at $0{\cdot}1M$. The results (identical for both experiments) are shown in Fig. 3.

Ion-exchange capacity

The exchange capacity was determined by titration of hydrogen ion eluted from the exchanger (1 g) in hydrogen form by sodium chloride solution, with Methyl Orange as indicator. The capacity was also determined by batch operation by shaking 100 ml of $1M$ alkali metal or

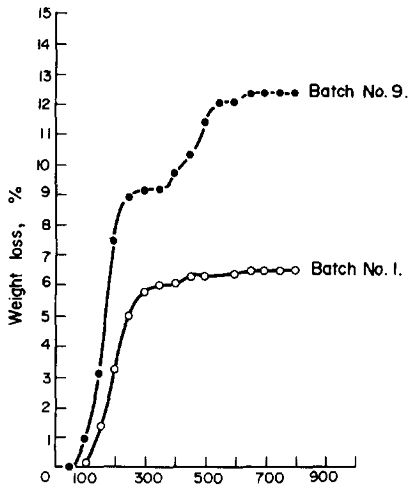

Fig. 1. Thermograms (TGA) of thorium tungstate.

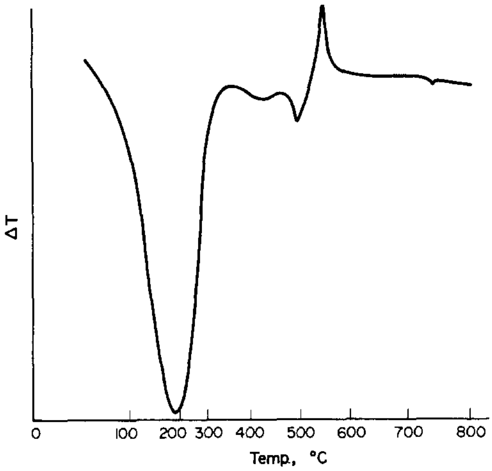

Fig. 2. DTA curve for thorium tungstate (batch 9).

ammonium chloride with 1 g of sample for 4 days with intermittent shaking, and titrating 50 ml of the solution with standard alkali.

Distribution coefficients

The distribution coefficients (K_d) of metal ions were determined by shaking 500 mg of exchanger with 50 ml of $2 \times 10^{-4}M$ metal ion solution ($5 \times 10^{-4}M$ for bismuth, uranium, vanadium and thorium) intermittently during 3 days at 27 ± 2°. The distribution coefficients were determined at pH 2–3 and 5·5–6·5, the pH being adjusted with dilute perchloric acid. The K_d values were calculated from

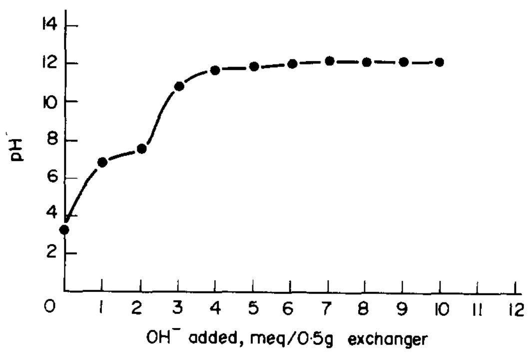

Fig. 3. pH-titration curve for thorium tungstate (batch 9) with 0·1*M* NaOH or NaOH + NaCl.

$$K_d = \frac{\text{Amount of element in exchanger}}{\text{Amount of element in solution}} \times \frac{\text{ml of solution}}{\text{g of exchanger}}$$

Uranyl ions were determined spectrophotometrically with hydrogen peroxide.[11] All other cations were estimated by titration with $2 \times 10^{-3}M$ EDTA.[9–12]

RESULTS AND DISCUSSION

Preparation and composition

The molar ratio of the reagents used in the preparation of the exchanger has little effect on the ion-exchange capacity and the composition of the exchanger (Table 1). A poor yield was obtained of batch 10, which was also difficult to filter.

Properties

The amorphous products are white powders and the crystalline varieties are colourless. X-Ray diffraction data for crystalline thorium tungstate are given in Table 2.

The exchanger (batch 9) remains unaffected after contact for up to 72 hr at room temperature with concentrated ammonia solution, nitric acid, sulphuric acid, perchloric acid (60%) and sodium hydroxide solution. Batch 9 was also stable in ethanol, acetone and acetic acid for up to 60 hr at room temperature.

Table 1. Preparation and composition of thorium tungstate

Batch	0·1*M* Th $(NO_3)_4.4H_2O$ in 1*M* HNO_3:0·1*M* Na_2WO_4 in H_2O, *v/v*	Digestion temperature, °*C*	Digestion time *hr*	pH of the mother liquor	Th:W in the product (by analysis)	Type
1	1:4	80 ± 5	12	1·2	1:4·0	Amorphous
2	1:4	80 ± 5	4	1·3	1:4·5	Amorphous
3	1:4	80 ± 5	48	1·2	1:4·6	Amorphous
4	1:6	80 ± 5	24	1·4	1:4·4	Amorphous
5	1:6	80 ± 5	4	1·4	1:4·4	Amorphous
6	1:6	80 ± 5	48	1·5	1:4·6	Amorphous
7	1:6	80 ± 5	140	1·5	1:5·7	Amorphous
8	1:4	30	12	1·1	1:4·7	Amorphous
9	1:6	30	12	1·5	1:6·2	Crystalline
10	1:8	30	24	2·6	1:4·8	Crystalline

Table 2. X-Ray powder diffraction data for thorium tungstate (batch 9)

θ	d, Å	Intensity
18·90°	2·38	W
20·80°	2·17	W
22·35°	2·02	S
24·10°	1·89	VS
24·75°	1·84	MS
28·03°	1·64	MS
33·30°	1·40	W
34·65°	1·36	W
35·75°	1·32	W

W = weak, S = strong, MS = medium strong, VS = very strong

Table 3. Chemical stability of thorium tungstate (batch 9)

Solvent	Thorium, *mg*/100 *ml*	Tungsten, *mg*/100 *ml*
Demineralized water	0·00	—
Perchloric acid, 3%	0·00	0·82
Perchloric acid, 60%	0·016	0·00
Nitric acid, 0·1 *N*	0·00	0·00
Nitric acid, 1*N*	Decomposed to yellow product	
Hydrochloric acid, 0·1*N*	0·00	0·12
Hydrochloric acid, 1*N*	0·012	—
Sulphuric acid, 0·1*N*	0·006	3·36
Sulphuric acid, 1*N*	Decomposed to yellow product	

The sample became yellow after a few days in concentrated hydrochloric acid at room temperature or after refluxing with 1*N* mineral acid.

The solubility of the exchanger was determined as reported earlier.[2] Thorium was determined spectrophotometrically with thoron at 545 nm[10] and tungsten with thiocyanate at 420 nm.[10] The solubility is shown in Table 3.

Both amorphous and crystalline thorium tungstate, when heated at high temperature (~800°) became green. On heating above 100°, the colour changed from white to grey. The weight loss of thorium tungstate on heating is due to elimination of water and ceases above 650° (Fig. 1). There is an endothermic change at 100–300°, and an exothermic peak at 500–580°, corresponding to formation of oxides (Fig. 2). At 650°, the weight loss is 12·43%. On the assumption that the composition of batch 9 after heating to 650° was $ThO_2.6WO_3$, it was calculated that 13 moles of water were present per mole of exchanger. For batch 1 the result was 4·6 moles of water, on the basis of a composition of $ThO_2.4WO_3$ at 750°.

The infrared spectrum of batch 9 had three well-defined peaks which were similar to those reported by Qureshi.[7] On the basis of the spectra of thorium oxide and sodium tungstate,[13–14] we can postulate that the first and second peaks (at 2820–2990 cm^{-1} and 1500–1700 cm^{-1}) are due to interstitial water molecules. The third peak (at 300–900 cm^{-1}) corresponds to the metal-oxygen bonds, probably in a polymeric compound.

The pH-titration curves of thorium tungstate resemble those of titanium tungstate.[15]

Ion-exchange capacity

The exchange reaction is slow, about 32 hr being required for attainment of equilibrium with 1*M* sodium chloride in batch operation. In column operation the rate of exchange is a function of the salt concentration in the feed stock. The ion-exchange capacity for univalent and bivalent cations is shown in Table 4. The capacity increases as the radius of the hydrated ion decreases, as expected.

The exchange capacity decreases as the temperature of heat treatment of the exchanger increases. The amorphous thorium tungstate (batch 1) is more stable than the crystalline form (batch 9) towards heat, but both lose all ion-exchange character if heated to 500°.

Distribution coefficient studies and ion-exchange separations

Some distribution coefficients are shown in Table 5. Thorium is totally adsorbed from 5 × 10^{-4}*M* solution as was the case with thorium phosphate.[3] Comparison of the selectivity based on the K_d values of metal ions on our thorium tungstate and thorium phosphate[3] ion-exchangers shows that bismuth and lead are more strongly adsorbed than other metal ions in both the exchangers.

The K_d values change with pH of the metal ion solution, as in the case of other inorganic ion-exchangers, especially with strontium and cobalt. The

Table 4. Ion-exchange capacity of thorium tungstate at pH 5·5–6·5

Metal ion	Hydrated ionic radius, Å	Ion-exchange capacity, *meq/g*				
		Batch 1	Batch 4	Batch 6	Batch 8	Batch 9
Li^+	3·4	0·17	0·22	0·20	0·18	0·12
Na^+	2·7	0·27	0·30	0·30	0·29	0·28
K^+	2·3	0·34	0·35	0·35	0·35	0·35
NH_4^+	—	—	—	—	—	0·34
Rb^+	—	—	—	—	—	0·36
Cs^+	—	—	—	—	—	0·37
Mg^{2+}	7·0	0·13	—	—	—	—
Ca^{2+}	6·3	0·26	—	—	—	—
Sr^{2+}	—	0·29	—	—	—	—
Ba^{2+}	5·9	0·38	—	—	—	—

Table 5. Distribution coefficient values of metal ions on thorium tungstate (batch 9) at 27 ± 2°C

Metal ion	Ionic radius, *Å*	K_d (initial pH 2–3)	K_d (initial pH 5·5–6·5)
Zn^{2+}	0·74	37	80
Mg^{2+}	0·65	28	460
Cd^{2+}	0·97	98	98
Pb^{2+}	1·21	310	190
Cu^{2+}	0·92	131	551
Ca^{2+}	0·99	59	170
Sr^{2+}	1·13	3	709
Mn^{2+}	0·80	90	464
Ni^{2+}	0·69	54	325
Co^{2+}	0·72	96	585
Hg^{2+}	1·10	0	7
La^{3+}	1·15	50	—
Al^{3+}	0·50	0	—
Th^{4+}		T.A.	—
VO^{2+}		5	—
UO_2^{2+}		0	—
Bi^{3+}		4000	—
Fe^{3+}		100	—

T.A = Total adsorption.

Table 6. Separation of bismuth or mercury from some other metal ions on a thorium tungstate (batch 9) column at 27 ± 2° (flow-rate 0·2 ml/min)

Mixture separated	Effluent, *ml*	Taken, *mg*	Found, *mg*	Error, %
Co^{2+}	30	0·412	0·424	+3
Bi^{3+}	25	1·21	1·19	−2
Cu^{2+}	30	0·508	0·502	−1
Bi^{3+}	25	1·21	1·21	0
Zn^{2+}	25	0·43	0·42	−2
Bi^{3+}	25	1·21	1·17	−3
Cd^{2+}	25	0·45	0·45	0
Bi^{3+}	25	1·21	1·25	+3
Mg^{2+}	25	0·099	0·094	−5
Bi^{3+}	25	1·21	1·25	+3
Ca^{2+}	30	0·288	0·284	−1
Bi^{3+}	25	1·21	1·25	+3
Mn^{2+}	25	0·368	0·362	−2
Bi^{3+}	25	1·21	1·21	0
Ni^{2+}	25	0·375	0·376	−2
Bi^{3+}	25	1·21	1·25	+3
Pb^{2+}	40	1·53	1·49	−3
Bi^{3+}	25	1·21	1·97	−3
Hg^{2+}	25	0·665	0·661	−1
Cu^{2+}	20	0·228	0·234	+3
Hg^{2+}	25	0·665	0·682	+3
Ni^{2+}	25	0·176	0·170	−3
Hg^{2+}	25	0·665	0·661	−1
Co^{2+}	25	0·260	0·250	−4
Hg^{2+}	25	0·665	0·681	+2
Mn^{2+}	25	0·231	0·236	+2

selectivity of our thorium tungstate is in general quite different from that obtained by Qureshi *et al.*[7] On the basis of the K_d values, some separations of binary mixtures were attempted. Reasonably quantitative separations of bismuth or mercury from some other metals are shown in Table 6. Bismuth was eluted with 1% potassium iodide solution in 0·03*M* sulphuric acid, after the other ion had been eluted with 0·15*M* nitric acid. Mercury was eluted first with $10^{-3}M$ nitric acid, followed by elution of the second ion with 0·15*M* nitric acid.

The K_d values show that crystalline thorium tungstate is a useful ion-exchanger and many interesting separations are possible, especially of bismuth. The method of preparation of inorganic ion-exchangers has a considerable effect on the degree of hydration and the composition of the exchanger since these factors are responsible for the shape and size of the cavities inside the exchanger and for other properties of the exchanger. The exchanger also has good regeneration capacity, so it can be used repeatedly in column operation.

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IRON (III) DERIVATIVES OF 4,7-DIHYDROXY-1,10-PHENANTHROLINE

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Summary—The chemistry of the iron(III) derivatives of 4,7-dihydroxy-1,10-phenanthroline has been studied in detail. Oxidation of the intensely red tris(4,7-dihydroxy-1,10-phenanthroline) iron(II) ion results in a grey compound, tris(4,7-dihydroxy-1,10-phenanthroline)iron(III), which is stable below pH 10. Above pH 10 the grey compound is partially converted into an amber compound in which the ratio of phenanthroline to iron is 2 : 1. The amber compound is the conjugate base of a purple 2 : 1 compound with $pK_a = 9{\cdot}77$. The visible absorption spectra of the three species at various pH values are reported. For 4,7-dihydroxy-1,10-phenanthroline pK_3, as determined by ultraviolet absorptometry, is $12{\cdot}62 \pm 0{\cdot}2$.

The usefulness of 4,7-dihydroxy-1,10-phenanthroline as a reagent for the spectrophotometric determination of iron in highly alkaline solutions was shown by Schilt, Smith and Heimbuch.[1] In recent publications[2,3] we have reported on the use of tris(4,7-dihydroxy-1,10-phenanthroline) iron(II) as a reagent for the spectrophotometric determination of dissolved oxygen, and of the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple as a low-potential oxidation reduction indicator. In the present paper we report on the nature of the iron (III) derivatives of 4,7-dihydroxy-1,10-phenanthroline.

Oxidation of the red tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) ion by air or by potassium ferricyanide results in a grey iron(III) compound which is stable in solution below pH 10 and insoluble below pH 8. The grey compound is slowly converted into an amber compound in solutions of pH greater than 10, the rate of conversion increasing with temperature and concentration of alkali. The iron(III) compound exists solely in the amber form in solutions in which the concentration of sodium hydroxide is 2*M* or greater. Addition of acid to solutions of the amber compound results in the reversible formation of a purple compound, the transition range being pH 8·0—11·5. The purple compound is insoluble below pH 6·5. Solutions of the purple compound slowly decompose over a period of about one day to yield the grey compound. A graphical representation of the inter-relationships of the iron derivatives is shown in Fig. 1.

EXPERIMENTAL

Reagents and solutions

4,7-Dihydroxy-1,10-phenanthroline. Prepared by the method of Snyder and Freier[4] with improvements by Poe.[5] The final product, recrystallized from 6*M* hydrochloric acid, contained 95% w/w 4,7-dihydroxy-1,10-phenanthroline and 5% w/w hydrogen chloride, as determined by titration. Reagent solutions were prepared by adding a minimum amount of ammonia or sodium hydroxide to the recrystallized material in demineralized water.

Ferricperchlorate solutions. Prepared by dissolving electrolytic iron in hot, concentrated perchloric acid and diluting to a known volume with demineralized water.

Other chemicals were from commercial sources.

Buffer solutions. Prepared according to Bates.[6] Buffers at pH 10 and 11 contained sodium carbonate and sodium bicarbonate; those at pH 12 and 13 contained sodium hydroxide and potassium chloride.

Apparatus

A Corning No. 476022 triple-purpose glass electrode and a saturated calomel electrode were used in conjunction with a Beckman Zeromatic SS-3 pH-meter. The pH-meter was calibrated against NBS buffers of pH 6·86, 9·18 and 12·45, prepared as described by Diehl[7] and corrected for temperature as described by Bates.[8]

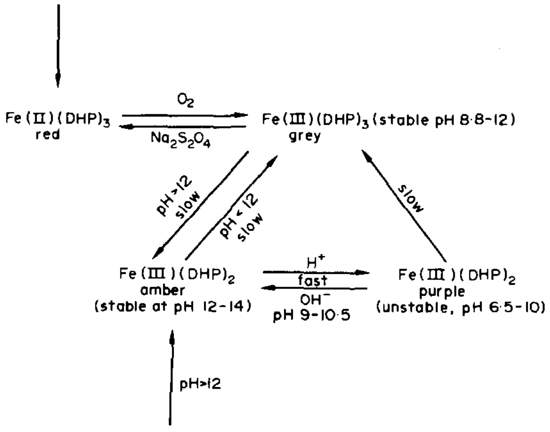

Fig. 1. Summary of the inter-relations of the iron compounds of 4,7-dihydroxy-1,10-phenanthroline.

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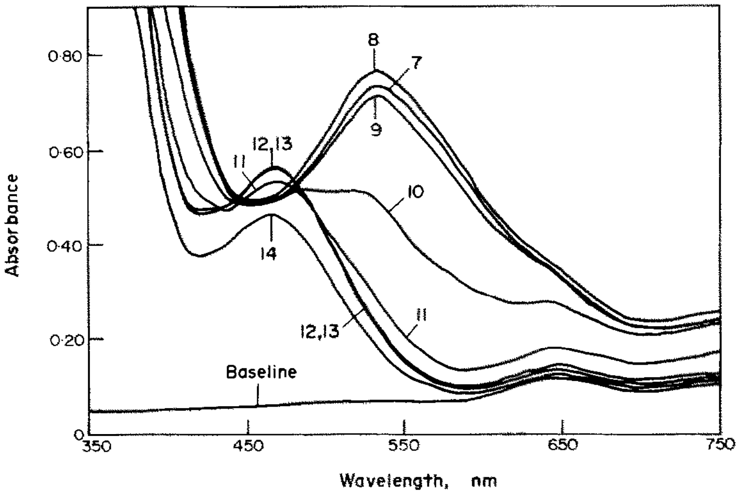


Fig. 2. Absorption spectra of the amber and purple iron(III) derivatives of 4,7-dihydroxy-1,10-phenanthroline. See text for preparation of solutions.

Curve	pH	Colour of solution
7	7·25	purple
8	7·76	purple
9	8·93	purple
10	9·90	—
11	10·67	amber
12	11·90	amber
13	12·90	amber
14	13·80	amber

Beckman DU and Cary 14 spectrophotometers were used. Spectrosil cuvettes with 1·00-cm path-lengths were used throughout.

Visible absorption spectra and composition of the grey, purple and amber iron(III) derivatives of 4,7-dihydroxy-1,10-phenanthroline

Spectra at pH 6–14. To 0·0227 g of 4,7-dihydroxy-1,10-phenanthroline dissolved in 10 ml of 3·16M sodium hydroxide were added 10·5 ml of 1·00 × $10^{-2}M$ ferric perchlorate. The excess of iron, precipitated as ferric hydroxide, was filtered off and the solution diluted to 50·00 ml. A series of 5·00-ml aliquots of this solution was taken and the pH adjusted over the range 6–14 with hydrochloric acid or sodium hydroxide; the resulting solutions were diluted to 25·00 ml with demineralized water. The visible absorption spectra were recorded and the pH of each solution remeasured, Fig. 2. After 14 days the absorption spectrum and pH of each solution were recorded again, Fig. 3.

Spectra in highly alkaline solutions. Aliquots of 1·0 or 10·0M sodium hydroxide, 10·00 ml of 3·37 × $10^{-3}M$ 4,7-dihydroxy-1,10-phenanthroline and 1·00 ml of 3·363 × $10^{-3}M$ ferric perchlorate were placed in 25-ml volumetric flasks, diluted to volume and the visible absorption spectra recorded after 1 hr and 1 day, and again after heating at 80° for 2 hr. The spectra obtained after 1 day are shown in Fig. 4.

Continuous variations studies. Volumes of 3·37 × $10^{-3}M$ 4,7-dihydroxy-1,10-phenanthroline and 3·363 × $10^{-3}M$ ferric perchlorate, such that the sum of the two was constant, were delivered into 25-ml volumetric flasks, each flask containing the same buffer, chosen appropriately for the grey, amber and purple compounds respectively (see next few paragraphs), and diluted to volume. Any precipitate which formed was removed by centrifuging. The absorbance was then measured and the measurements interpreted in the usual way.[9] The results, together with information on the absorption in the visible region, are given in Table 1.

Purple compound. The solutions produced on mixing 4,7-dihydroxy-1,10-phenanthroline and iron(III) perchlorate

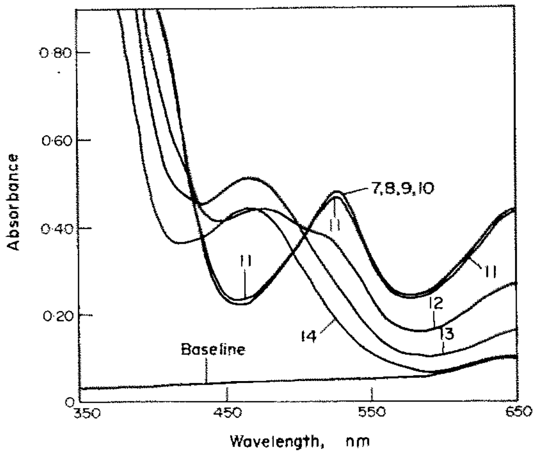


Fig. 3. Absorption spectra of the amber and grey iron(III) derivatives of 4,7-dihydroxy-1,10-phenanthroline. See text for preparation of solutions.

Curve	pH	Colour of solution
7	7·91	grey
8	7·88	grey
9	8·02	grey
10	8·87	grey
11	10·38	grey
12	11·83	—
13	12·90	amber
14	13·80	amber

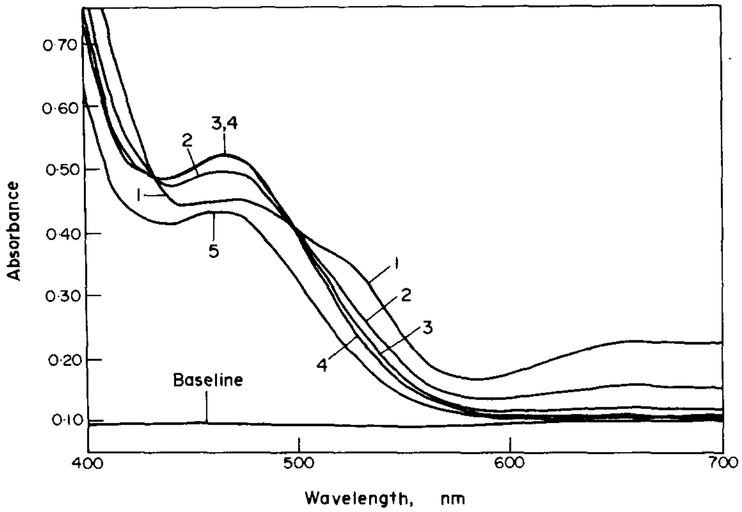


Fig. 4. Absorption spectra of the iron(III)-4,7-dihydroxy-1,10-phenanthroline compound in solutions of sodium hydroxide. Spectra obtained on day following preparation of solutions. Concentration of iron: 1·35 × $10^{-4}M$; concentration of 4,7-diOH-phen: 1·35 × $10^{-3}M$. Concentration of sodium hydroxide, *M*: 1, 0·2; 2, 0·5; 3, 1·0; 4, 2·0; 5, 4·0.

are purple at pH 7–9·5, or amber at pH > 10·5. The absorption spectra at various pH values are shown in Fig. 2.

The solutions for the continuous variations study of the purple compound were prepared by adding phenanthroline and iron(III) to 5 ml of 5·0*M* sodium hydroxide, heating in a hot water-bath to promote formation of the iron compound and coagulation of the small amount of ferric hydroxide formed, and then adding just enough 10*M* hydrochloric acid to cause precipitation of the purple compound, immediately neutralizing with dilute sodium hydroxide solution to yield a purple solution, and adding 5·0 ml of borate buffer (38 g of sodium tetraborate decahydrate per litre, pH 8·65). The solutions were finally diluted to 25·00 ml with demineralized water and the absorbances at 533 nm measured. The purple compound is 1 : 2 metal : ligand, Table 1.

Amber compound. Spectra obtained immediately after mixing 4,7-dihydroxy-1,10-phenanthroline and iron(III) in 0·2–2·0*M* sodium hydroxide were identical, Fig. 4, curve 4. After 1 day the composition of the solutions in 0·2–1·0*M* sodium hydroxide had changed to yield mixtures of the grey and amber compounds, Fig. 4, curves 1, 2, and 3, while the spectrum of the solution in 2·0*M* sodium hydroxide remained unchanged. Heating the solutions produced no further changes in the spectra. From these spectra and other observations, it is apparent that on mixing the phenanthroline and iron(III) in highly alkaline solutions the amber compound is formed first. If the concentration of sodium hydroxide is less than 2*M*, some conversion of the amber compound into the grey compound occurs. The ratio of amber to grey compound at equilibrium depends on the relative amounts of iron, phenanthroline and alkali present, the last of these having the greatest effect.

In the continuous variations study, the solutions were prepared in 0·2*M* sodium hydroxide. Absorbance measurements at 470 nm were made immediately following preparation, before appreciable conversion into the grey compound could occur. The amber compound is also 1 : 2 metal : ligand (Table 1).

Grey compound. The spectra are shown in Figs. 3 and 4. The spectra of the grey compound obtained from the purple compound on standing for two weeks at pH 8–10 were identical with the spectra of the grey compound obtained by oxidation of tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) with oxygen.

In the continuous variations study, the pH used was 9·4, obtained by mixing equal volumes of 2*M* ammonia solution and 2*M* ammonium chloride. After preparation, the solutions were heated at 75° for 2 hr to ensure complete conversion of the iron compound into the grey form, and then cooled. The absorbance of each solution was then measured against a water blank at 526 nm. The grey compound is 1 : 3 metal : ligand (Table 1).

Acid dissociation constant of the purple compound. The rapid and reversible interconversion of the purple and amber compounds is governed by the hydrogen-ion concentration. The acid dissociation constant was determined spectrophotometrically.

A stock solution of the amber compound was prepared by dissolving 0·0456 g (2·04 × 10^{-4} mole) of 4,7-dihydroxy-1,10-phenanthroline in dilute sodium hydroxide solu-

Table 1. Composition, and absorptivity in the visible region, of the iron derivatives of 4,7-dihydroxy-1,10-phenanthroline

Metal ion	Colour	Mole ratio Phen : Fe	λ_{max} *nm*	Absorptivity,* *l. mole.*$^{-1}$ *cm*$^{-1}$
Fe(II)	Red	3 : 1†	520†	1·48 × 10^4†
Fe(III)	Grey	3 : 1	527	3·27 × 10^3
Fe(III)	Purple	2 : 1	533	3·15–3·40 × 10^3
Fe(III)	Amber	2 : 1	465	3·10 × 10^3

* At λ_{max} calculated on the basis of iron concentration without consideration of dimerization through hydroxy bridges.

† From reference 1.

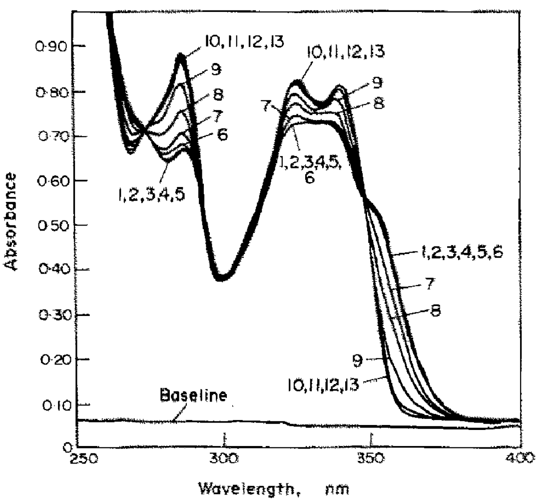


Fig. 5. Effect of pH on the ultraviolet absorption spectrum of 4,7-dihydroxy-1,10-phenanthroline. Concentration of 4,7-dihydroxy-1,10-phenanthroline: 5·00 × $10^{-5}M$. Ionic strength: 1·0. pH: 1, 9·10; 2, 9·59; 3, 10·12; 4, 10·62; 5, 11·08; 6, 11·30; 7, 12·02; 8, 12·55; 9, 13·05; 10, 13·66. NaOH, M 11, 1·0; 12, 2·0; 13, 5·0.

tion and adding 20 ml of 1·00 × $10^{-2}M$ ferric perchlorate (2·0 × 10^{-4} mole). The solution was heated almost to boiling to promote formation of the iron compound and the excess of iron was filtered off as ferric hydroxide. The filtrate was diluted to exactly 100 ml with 10M sodium hydroxide and water so that the final concentration of sodium hydroxide was 2M. Solutions for absorbance measurements were prepared by adjusting 5·00-ml aliquots of the stock solution to the approximate desired pH, adding 2 ml of the appropriate buffer (ammonia–ammonium chloride) to cover the pH range 6·5–12·0, and diluting to 25·00 ml with demineralized water. This gave an ionic strength of approximately 0·4 in each solution. The absorbance of each solution at 533 nm was measured within 30 min after preparation. The pH of each solution was then checked.

To evaluate the dissociation constant, K_A, from the absorbance *vs.* pH data, use was made of the equation

$$\text{pH} = (1/b)\text{p}K_A + (1/b)\log[(A_{HA} - A_{mix})/(A_{mix} - A_A)]$$

which is derived from the mathematical equation defining the overall acid dissociation constant of a multiprotic acid, $K_A = K_1K_2 \ldots K_b$, where b is the number of protons involved, A_{HA} is the absorbance when the compound is 100% protonated (*i.e.*, in this case, all in the purple form), A_A is the absorbance when the compound is 100% dissociated (all in the amber form), and A_{mix} is the absorbance when both the acid (HA) and anion (A^-) are present. The plot of $\log[(A_{HA} - A_{mix})/(A_{mix} - A_A)]$ *vs.* pH is linear with a slope of 0·88 (b = 1·1), and the intercept occurs at pH 9·77. Thus only one proton is involved and pK_A = 9·77 at 23° and an ionic strength equal to 0·4.

Ultraviolet absorption spectrum of 4,7-dihydroxy-1,10-phenanthroline and estimation of pK_3. Ultraviolet absorption spectra of 4,7-dihydroxy-1,10-phenanthroline were obtained over the range from pH 9·1 to 5·0M sodium hydroxide. The third acid dissociation constant, K_3, was estimated from the spectrophotometric data.

To each of thirteen 50-ml volumetric flasks were added 5·00 ml of 5·00 × $10^{-4}M$ 4,7-dihydroxy-1,10-phenanthroline, 10 ml of ammonia/ammonium chloride buffer solution or the amount of sodium hydroxide necessary to adjust the pH to the desired value, and 1·0M potassium chloride to a volume of 50·00 ml to maintain the ionic strength at 1. The ultraviolet absorption spectrum of each solution was obtained between 250 and 400 nm against a blank of distilled water. The pH of each solution was measured after the spectra were recorded.

The spectra are shown in Fig. 5. Two isosbestic points are present, at 274 and 347 nm. Absorbance data at 286 and 360 nm were subjected to the logarithmic treatment described in the preceding section. The values of pK_3 (and b, number of protons involved) obtained were 12·68 (b = 0·95) and 12·57 (b = 1·04), respectively. The average value of pK_3 = 12·62 is believed to be accurate to ±0·2 and applies to aqueous solutions of 4,7-dihydroxy-1,10-phenanthroline having an ionic strength of 1 and a temperature of approximately 25°. The conclusion that only one proton is involved is supported by alkalimetric titration in a mixture of propan-2-ol and dimethylsulphoxide.[10]

The ultraviolet absorption spectrum of 4,7-dihydroxy-1,10-phenanthroline in the presence of iron(III) was also obtained as a function of pH. Two sets of six solutions each 5·00 × $10^{-5}M$ in 4,7-dihydroxy-1,10-phenanthroline and 1·67 × $10^{-5}M$ in ferric perchlorate were prepared at integral pH values from 9 to 14. To one set was added 2·0 ml of sodium hydrosulphite solution (200 mg/ml) per 50 ml. The spectra of the reduced form were not obtained, owing to absorption by hydrosulphite at wavelengths shorter than 380 nm. The spectra of the solutions containing no hydrosulphite were similar to the spectra of uncombined 4,7-dihydroxy-1,10-phenanthroline at corresponding values of pH, Fig. 5. A logarithmic treatment of the absorbance data at 287 and 360 nm gave an average value of pK_3 = 11·9. This value is considerably lower than that for the uncombined phenanthroline, and is reasonable from the standpoint that the iron(III) ion should exert a considerable electron-withdrawing effect. The exact values of pK_3 and b under these conditions were not obtained, owing to incomplete formation of the iron(III) compound and equilibration of the iron(III) compound between the grey and amber forms.

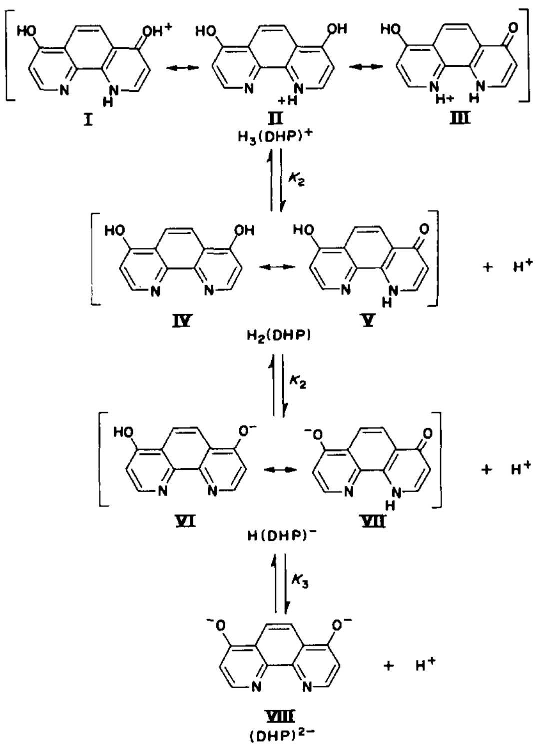
DISCUSSION

We adopt for the protonated, neutral and dissociated forms of 4,7-dihydroxy-1,10-phenanthroline the designations $H_3(DHP)^+$, $H_2(DHP)$, $H(DHP)^-$, and $(DHP)^{2-}$, and for the constants associated with the successive dissociation steps the symbols K_1, K_2 and K_3. Values for K_1, K_2 and K_3 in 1:1 dioxan–water solution were reported by James and Williams[11] (pK_1 = 2·55 ± 0·05, pK_2 = 7·28 ± 0·03, pK_3 = 11·5 ± 0·1). The value of pK_3 in aqueous solution is 12·6, according to the work reported in the preceding section.

Possible structures for the protonated, neutral, and singly-charged anionic forms are shown on the next page. Of the structures **I**, **II**, **III**, the last two appear most likely inasmuch as the positive charge on a ring nitrogen atom allows for better dissipation of the charge in the resonating electron system. Further, structure **II** is preferred over structure **III** because of the electrostatic repulsion developed by protonating both nitrogen atoms simultaneously.

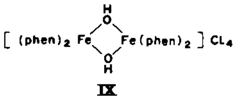
Structure **V** has been shown to be the actual structure of the neutral compound by interpretation of infrared spectra.[12,13]

We believe structure **VI** to be correct for the singly charged anionic form. This belief is based on the

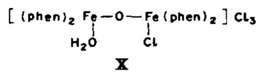


observations that the ultraviolet spectrum of 4,7-dihydroxy-1,10-phenanthroline is hardly affected by the presence of iron, and that the third acid function K_3 is still present in the iron(III) compound, although the value is somewhat altered (see preceding section). Thus the compound exists in the same form in both the uncombined and combined states. The presence of structure **VII** in the iron derivative is highly unlikely, leaving only structure **VI** as the logical choice.

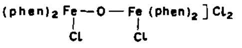
The amber iron(III) derivative of 4,7-dihydroxy-1,10-phenanthroline is analagous to the brown iron(III) derivative of 1,10-phenanthroline. Both compounds are formed by direct addition of salts of iron(III) to solutions of the phenanthroline, and the ratio of phenanthroline to iron in each is two to one. Gaines, Hammett and Walden[14] isolated the brown derivative of 1,10-phenanthroline and reported a composition corresponding to the binuclear hydroxy-bridged species **IX**. Later investigators suggested structures **X** and **XI** on the basis of magnetic data and infrared spectra. Reduction-potential and pH measurements of aqueous solutions favour structure **IX**.[15] In the arguments which follow we have assumed no structures for the purple and amber derivatives of 4,7-dihydroxy-1,10-phenanthroline. The ratio of phenanthroline to iron in both is definitely two to one, however, and they are interconverted by the loss or gain of a single proton.


$[(phen)_2Fe(\mu\text{-}OH)_2Fe(phen)_2]Cl_4$

IX


$[(phen)_2Fe(H_2O)\text{—}O\text{—}Fe(Cl)(phen)_2]Cl_3$

X


$[(phen)_2Fe(Cl)\text{—}O\text{—}Fe(Cl)(phen)_2]Cl_2$

XI

The dissociation constant, $pK_A = 9{\cdot}77$, for the proton involved in this interconversion is associated with a hydroxy group bound directly to the iron atoms. The evidence for this is: (1) the second acid function, K_2, operates in the precipitation of both the combined and uncombined phenanthroline at about pH 8; (2) the third acid function, K_3, is still present in the iron(III) compound although the value for K_3 is somewhat altered [$pK_3 = 12{\cdot}6$ (no iron present); $pK_3 = 11{\cdot}9$ (iron(III) present)]; (3) no change in the visible absorption spectrum of the iron derivatives of 4,7-dihydroxy-1,10-phenanthroline is produced by the dissociation of the hydroxy proton on the phenanthroline ring (K_3); (4) no change in the ultraviolet spectrum of the iron(III) derivatives at wavelengths shorter than 400 nm accompanies the conversion of the purple into the amber compound.

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SHORT COMMUNICATIONS

TRIS(4,7-DIHYDROXY-1,10-PHENANTHROLINE)IRON(II) AS A LOW-POTENTIAL OXIDATION–REDUCTION INDICATOR

DETERMINATION OF HYDROSULPHITE

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In recent papers[1,2] we have reported on the use of the iron(II) derivative and on the nature and inter-relations of the three iron(III) compounds (grey, amber, purple) of 4,7-dihydroxy-1,10-phenanthroline. In the present paper we report on the character of the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple and an application of it as a visual oxidation–reduction indicator for titrations in alkaline solutions with standard ferricyanide.

EXPERIMENTAL

Reagents

Buffer solutions were prepared according to Bates.[3] Those at pH 10 and 11 contained sodium carbonate and sodium bicarbonate; those at pH 12 and 13 contained sodium hydroxide and potassium chloride.

Solutions of potassium ferricyanide were prepared by dissolving 3·3–3·4 g of the anhydrous reagent—grade material in approximately 180 ml of buffer. The pH of the resulting solutions was adjusted to the desired values by the addition of hydrochloric acid or sodium hydroxide, if necessary. After the pH was adjusted, the solutions were diluted to 200 ml with water.

Measurement of formal reduction potential

The reduction potential of the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple in the alkalinity range from pH 10 to 3·2M sodium hydroxide was measured by following the potential of a bright platinum foil electrode in the titration of sodium hydrosulphite in appropriately buffered solutions containing enough of the phenanthroline–iron compound to give a separate feature on the titration curve. The standard oxidizing agent, potassium ferricyanide, was prepared for each titration in a solution identical in pH or alkali concentration with the solutions being titrated. The titrations were performed under an atmosphere of nitrogen.

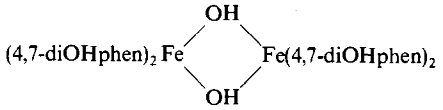
A representative titration curve is shown in Fig. 1. Values for the formal reduction potential at various pH values are given in Table 1.

Formal reduction potentials in solutions outside the pH range reported could not be determined; at lower pH, the oxidation of sodium hydrosulphite with potassium ferricyanide proceeded too slowly near the equivalence-point; in higher concentrations of alkali, the potential drifted considerably.

RESULTS AND DISCUSSION

The formal reduction potential does not change appreciably over the pH range 10–13. The more negative values obtained in 1–3·2M sodium hydroxide cannot be explained simply on the basis of the dissociation of an acid, and the drift observed indicates that the conversion

$(4,7\text{-diOHphen})_3\,\text{Fe(III)} \rightarrow$



$$(4,7\text{-diOHphen})_2\text{Fe}\overset{\text{OH}}{\underset{\text{OH}}{\lt\!\!\gt}}\text{Fe}(4,7\text{-diOHphen})_2$$

is involved. The rate of this reaction increases with increasing alkalinity. Under the conditions of the titrations, some 5–10 min elapsed from the time that the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III) was first formed until the mid-point of the titration was reached. Thus, the condition that the concentrations of the oxidized and reduced forms of the couple be equal at the mid-point was not met. The values obtained in solutions in which the concentration of sodium hydroxide was 1M or greater therefore do not represent the formal reduction potential of the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple. Because the conversion is slow at pH 13, and slower at pH 12, and occurs hardly at all at pH 10–11, the values reported in Table 1 closely reflect the true formal reduction potential.

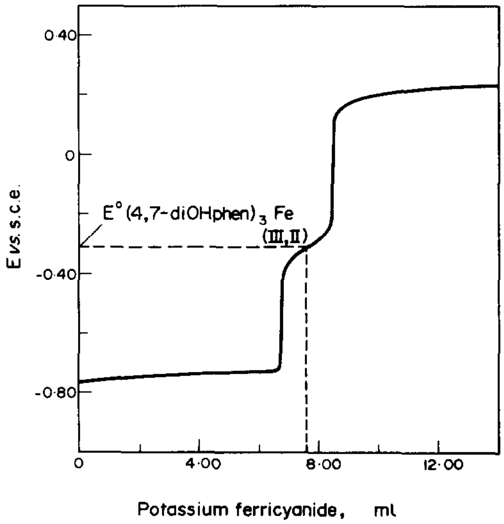


Fig. 1. Titration of sodium hydrosulphite plus tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) with potassium ferricyanide at pH 11. Potassium ferricyanide, 0·0514M; sodium hydrosulphite, 0·0423 g; 4,7-dihydroxy-1,10-phenanthroline, 0·0621 g (0·278 mmole); ferrous ammonium sulphate hexahydrate, 0·0346 g (0·088 mmole).

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Table 1. Formal reduction potential of the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple as a function of pH

Conditions	Formal reduction potential, *V vs. N.H.E.*	Temperature, *°C*
pH 10	−0·064	28
pH 11	−0·063	27
pH 12	−0·053	27
pH 13	−0·070	28
1·0*M* NaOH	(−0·105, −0·115, −0·199)*	25
2·0*M* NaOH	(−0·33)*	
3·2*M* NaOH	(−0·260)*	25

* Serious drift owing to the slow conversion of the iron(III) form of the couple into another species.

Because of the errors inherent in these measurements, it seems best simply to average the values obtained at pH 10–13. We report therefore the value of the formal reduction potential over the pH range 10–13 to be −0·06 V *vs.* the normal hydrogen electrode (N.H.E.). The value we reported earlier, −0·11 V in 1*M* sodium hydroxide,[1] was obtained before the significance of the drift was appreciated, and is wrong. A value of −0·13 V *vs.* N.H.E, was reported earlier by George, Hanania and Eaton,[4] incidentally to a discussion of the reduction potentials of haemes and haemoproteins; no details were given other than that the pH was > 10.

This reduction potential is astonishingly low. The formal reduction potentials of almost all the iron–phenanthroline couples previously reported fall in the range from +0·85 to +1·26 V *vs.* N.H.E. Although those values were determined in acid solution, the phenanthroline–iron(III,II) couples do not involve hydrogen ions and the formal reduction potentials are independent of pH, *e.g.*, for the simplest member of the series, the ferriin–ferroin couple:

$$Fe(1,10\text{-phen})_3^{3+} + e^- = Fe(1,10\text{-phen})_3^{2+};\ E^\circ = +1{\cdot}06\ V$$

The lowest value previously reported is that of the iron(III,II) couple of 3-carbethoxy-4-hydroxy-1,10-phenanthroline, $E^\circ = +0{\cdot}71$ V *vs.* N.H.E.[5]

Use in the determination of hydrosulphite

The tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple serves well as a visual indicator in the titration of sodium hydrosulphite with potassium ferricyanide in 0·1–3·2*M* sodium hydroxide media. The colour change at the end-point is very sharp, one drop or less of 0·05*M* potassium ferricyanide being required to change 70 ml of solution from a distinct pink to practically colourless.

Preparation of indicator solutions. A 2% solution of tris(4,7-dihydroxy-1,10-phenanthroline)iron(III) was prepared by dissolving 0·125 g of 4,7-dihydroxy-1,10-phenanthroline and 0·0669 g of ferric nitrate enneahydrate in 10 ml of a solution containing 1 ml of 16*M* sodium hydroxide.

Results. Variable results were obtained when solid samples of sodium hydrosulphite were titrated, indicating that the samples had undergone various degrees of oxidation before titration. Reproducible results were obtained when aliquots of a solution of sodium hydrosulphite in 2*M* sodium hydroxide, protected from air in, and delivered from, a Machlett burette, were titrated. The amount of indicator used had no effect on the position of the end-point, Table 2. The stoichiometry presumably corresponded[6,7] to the reaction

$$S_2O_4^{2-} + Fe(CN)_6^{3-} + 4OH^- = 2SO_3^{2-} + Fe(CN)_6^{4-} + 2H_2O \quad (1)$$

The indicator also functioned well in the titration of ferricyanide with hydrosulphite, the latter being delivered from a Machlett burette, but the results were not reproducible. The amount of sodium hydrosulphite required to reach the end-point varied inversely with the time taken to complete the titration, probably because of the slow oxidizing action of potassium ferricyanide on the sulphite produced in the oxidation. The reduction potential of the sulphate–sulphite couple in 1*M* sodium hydroxide is given as −0·93 V by Latimer, and that for the ferricyanide–ferrocyanide couple as 0·36 V.[8] The oxidation of sulphite in alkaline solution is therefore thermodynamically favoured. By direct test it was found that sodium sulphite in 2*M* sodium hydroxide is indeed slowly oxidized by potassium ferricyanide.

Neither sodium thiosulphate nor sodium sulphite interferes in the direct titration with potassium ferricyanide. Under the conditions specified, sodium thiosulphate is not oxidized at all by potassium ferricyanide, a very surprising finding inasmuch as the reduction potential of the sulphite–thiosulphate couple in alkaline solution is very low

Table 2. Titration of sodium hydrosulphite with potassium ferricyanide, visual end-point

Sodium hydrosulphite				
Form	Taken	Volume of indicator, *drops*	0·0520*M* potassium ferricyanide required, *ml*	Recovery, %
solid	0·1487 g	3	29·58	90·1
solid	0·1698 g	2	31·70	84·6
solid	0·1707 g	2	32·08	85·1
solution	40·00 ml	1	29·90	$74{\cdot}7_5$
solution	40·00 ml	1	29·91	$74{\cdot}7_8$
solution	40·00 ml	1	29·90	$74{\cdot}7_5$
solution	40·00 ml	10	29·93	$74{\cdot}8_3$
solution	40·00 ml	10	29·89	$74{\cdot}7_3$
solution	40·00 ml	0*	29·95	$74{\cdot}8_8$

* Potentiometric end-point.

($-0{\cdot}58$ V) and that of the tetrathionate–thiosulphate couple is 0·08 V.[8] Although sulphite is produced by oxidation of hydrosulphite with ferricyanide, it does not interfere in the determination because the rate of oxidation of hydrosulphite is much greater than that of sulphite under the conditions specified. However, it is imperative that the solution of hydrosulphite be stirred efficiently while titrant is being added. Inefficient stirring leads to high results, owing to the slow oxidizing action of ferricyanide on sulphite. If the solution is continuously or fairly regularly stirred, the error is less than 0·3%, but if stirring is virtually omitted, errors of up to almost +5% occur.

Tris(4,7-dihydroxy-1-10-phenanthroline)iron(II) failed to function as an indicator in titrations of cobalt(II) sulphate, ascorbic acid, and sodium hypophosphite with potassium ferricyanide, and functioned very poorly as an indicator in the titration of sodium hydrosulphite with potassium octacyanomolybdate(VI). Addition of octacyanomolybdate(VI) to a solution containing the indicator gave an amber colour, and the end-point, from amber to yellow, was so gradual that it was almost impossible to detect. It is suspected that formation of a mixed complex, possibly dicyano-bis(4,7-dihydroxy-1,10-phenanthroline)iron(II), is involved.

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Summary—The formal reduction potential of the tris(4,7-dihydroxy-1,10-phenanthroline)iron(III,II) couple is $-0{\cdot}06$ V in the pH range 10–13, not $-0{\cdot}11$ V as reported earlier. The couple forms an excellent visual oxidation–reduction indicator for the titration of sodium hydrosulphite with potassium ferricyanide in alkaline solution.

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CALCULATION OF ALL EQUILIBRIUM CONCENTRATIONS IN A SYSTEM OF COMPETING COMPLEXATION

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(*Received* 22 *February* 1975. *Accepted* 8 *April* 1975)

It is often necessary to calculate the equilibrium concentration of each species in a multicomponent system of metal ions and ligands. As a rule, the starting data are the total (analytical) concentration of each reactant, the stability constant of each complex and the pH of the final solution. Some programs have been described for solving this problem.[1,2]

The following iterative method is used in the computer program COMICS:[1] the equilibrium concentration of each species is found at the kth approximation ($[A_i^k]$); from these, the total concentration of each of the reactants is calculated (A_i^{calc}); then the $(k+1)$th approximate equilibrium concentrations are determined by the equation:

$$[A_i^{k+1}] = [A_i^k]\left[\frac{A_i^{\text{tot}}}{A_i^{\text{calc}}}\right]^{1/2} \tag{1}$$

where A_i^{tot} is the total concentration of the ith reactant. With this program it turns out that the iterations do not always converge. Therefore it is of interest to examine the criteria for convergence in a more general case.

The present work will consider a somewhat modified program which gives improved intermediate results. Let us write the jth complex formation reaction in the following way:

$$\sum_{i=1}^{M} m_{ij}A_i = [(A_1)_{m_1}(A_2)_{m_2}\cdots(A_M)_{m_M}] \quad (i = 1,\ldots,N) \tag{2}$$

The concentration of this complex is given by:

$$c_j = \beta_j \prod_{i=1}^{M} [A_i]^{m_{ij}} \quad (j = 1,\ldots,N) \tag{3}$$

where A_i are the M different reactants, which may be metal ions, complexing agents, H^+ and OH^- ions; m_{ij} are the stoichiometric coefficients of the ith reactants in the jth complex; β_j is the cumulative stability constant and c_j the equilibrium concentration of the jth complex. For the system described by equations (2) and (3) it is possible to set up M equations for the material balance:

$$\text{ATOT}_i = [A_i] + \sum_{j=1}^{N} m_{ij}c_j \quad (i = 1,\ldots,M) \tag{4}$$

where ATOT_i is the total concentration of the ith reactant. Following COMICS,[1] the approximation to ATOT_i given by the kth iterative step will be denoted by ACALC_i^k. Using equations (3) and (4), it will be shown that

$$\text{ACALC}_i^k = [A_i^k] + \sum_{j=1}^{N} m_{ij}\beta_j \cdot \prod_{i=1}^{M} [A_i^k]^{m_{ij}} \tag{5}$$

$$(i = 1,\ldots M)$$

The $(k+1)$th iteration is obtained by modifying the method employed in COMICS,[1] from which the following general-

($-0{\cdot}58$ V) and that of the tetrathionate–thiosulphate couple is 0·08 V.[8] Although sulphite is produced by oxidation of hydrosulphite with ferricyanide, it does not interfere in the determination because the rate of oxidation of hydrosulphite is much greater than that of sulphite under the conditions specified. However, it is imperative that the solution of hydrosulphite be stirred efficiently while titrant is being added. Inefficient stirring leads to high results, owing to the slow oxidizing action of ferricyanide on sulphite. If the solution is continuously or fairly regularly stirred, the error is less than 0·3%, but if stirring is virtually omitted, errors of up to almost +5% occur.

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$$\text{ACALC}_i^k = [A_i^k] + \sum_{j=1}^{N} m_{ij}\beta_j \cdot \prod_{i=1}^{M} [A_i^k]^{m_{ij}} \qquad (5)$$

$$(i = 1,\ldots M)$$

The $(k+1)$th iteration is obtained by modifying the method employed in COMICS,[1] from which the following general-

Table 1. Calculation of the equilibrium concentrations in a multicomponent system. The total concentration of each reactant is equal to $5 \times 10^{-3} M$. pH = 8·0. The stability constants were taken from refs. 4 and 5.

Equilibrium concentrations below $10^{-7} M$ were not included. NTA is the tertiary anion of nitrilotriacetic acid

	Equilibrium concentration, $10^{-6} M$	Logarithm of stability constant	Composition of species H	 OH	 Cd	 Cu	 Zn	 NTA	 NH_3
1	919·6	2·65	—	—	1	—	—	—	1
2	65·1	4·75	—	—	1	—	—	—	2
3	1·0	6·19	—	—	1	—	—	—	3
4	—	7·12	—	—	1	—	—	—	4
5	—	6·8	—	—	1	—	—	—	5
6	—	5·14	—	—	1	—	—	—	6
7	393·8	4·15	—	—	—	1	—	—	1
8	700	7·65	—	—	—	1	—	—	2
9	305	10·54	—	—	—	1	—	—	3
10	23·1	12·67	—	—	—	1	—	—	4
11	416	2·37	—	—	—	—	1	—	1
12	64·4	4·81	—	—	—	—	1	—	2
13	11·5	7·31	—	—	—	—	1	—	3
14	0·91	9·46	—	—	—	—	1	—	4
15	—	16·12	—	4	—	1	—	—	—
16	146	6·47	—	1	—	1	—	—	—
17	0·73	2·3	—	1	1	—	—	—	—
18	79·4	4·4	—	1	—	—	1	—	—
19	0·74	14·37	—	3	—	—	1	—	—
20	—	15·44	—	4	—	—	1	—	—
21	329	9·80	—	—	1	—	—	1	—
22	—	15·3	—	—	1	—	—	2	—
23	3380	12·68	—	—	—	1	—	1	—
24	1270	10·45	—	—	—	—	1	1	—
25	20·8	14·6	—	1	1	—	—	1	—
26	—	9·73	1	—	—	—	—	1	—
27	—	5·0	1	—	—	—	—	—	1
28	3660	—	—	—	1	—	—	—	—
29	49·6	—	—	—	—	1	—	—	—
30	3160	—	—	—	—	—	1	—	—
31	$1·42 \times 10^{-5}$	—	—	—	—	—	—	1	—
32	562	—	—	—	—	—	—	—	1

ization of equation (1) is obtained:

$$[A_i^{k+1}] = [A_i^k] \cdot \left[\frac{ATOT_i}{ACALC_i^k} \right]^{1/p} \tag{6}$$

where $[A_i^k]$ and $[A_i^{k+1}]$ are consecutive approximations to the equilibrium concentration of the ith reactant. Let us write $[A_i^k]$ as

$$[A_i^k] = A_i + \epsilon_i^k \tag{7}$$

It follows from equations (5), (6) and (7) that

$$\epsilon_i^{k+1} = \left(\frac{ATOT_i}{[A_i] + \epsilon_i^k + \sum_{j=1}^{N} m_{ij} . \beta_j . \prod_{i=1}^{M} ([A_i] + \epsilon_i^k)^{m_{ij}}} \right)^{1/p} \times ([A_i] + \epsilon_i^k) - [A_i] \tag{8}$$

Dividing the numerator and the denominator of the first bracketed expression in equation (8) by $ATOT_i$, one obtains for the first iteration:

$$\epsilon_i^1 = \left[\frac{1}{L_i^0} \right]^{1/p} . ([A_i] + \epsilon_i^0) - [A_i] \tag{9}$$

where

$$L_i^0 = \frac{[A_i] + \epsilon_i^0 + \sum_{j=1}^{N} m_{ij} . \beta_j . \prod_{i=1}^{M} ([A_i] + \epsilon_i^0)^{m_{ij}}}{ATOT_i} > 0 \tag{10}$$

It is known[3] that for $L > 0$:

$$(L)^{-q} = 1 - h \quad \text{where} \quad \lim_{q \to \infty} h = 0 \tag{11}$$

In conformity with condition (11), equation (9) for the first iterative cycle may be rewritten:

$$\epsilon_i^1 = (1 - h)([A_i] + \epsilon_i^0) - [A_i] = \epsilon_i^0 - h([A_i] + \epsilon_i^0) \tag{12}$$

Owing to condition (11), a value of p may be selected such that:

$$|h([A_i] + \epsilon_i^0)| < |\epsilon_i^0| \quad \text{or} \quad |\epsilon_i^1| < |\epsilon_i^0| \tag{13}$$

If $[A_i^k]$ and ϵ_i^k were already chosen, these values in the $(k + 1)$th iteration would be determined by equation (8). Furthermore:

$$|\epsilon_i^0| > |\epsilon_i^1| > \ldots > |\epsilon_i^k|$$

$$\begin{aligned} |L_i^k| &= \frac{\left| [A_i] + \epsilon_i^k + \sum_{j=1}^{N} m_{ij} \beta_j \prod_{i=1}^{M} ([A_i] + \epsilon_i^k)^{m_{ij}} \right|}{ATOT_i} \\ &\leqq \frac{|[A_i]| + |\epsilon_i^k| + \left| \sum_{j=1}^{N} m_{ij} \beta_j \prod_{i=1}^{M} ([A_i] + \epsilon_i^k)^{m_{ij}} \right|}{ATOT_i} \\ &\leqq \frac{|[A_i]| + |\epsilon_i^0| + \left| \sum_{j=1}^{N} m_{ij} \beta_j \prod_{i=1}^{M} ([A_i] + \epsilon_i^0)^{m_{ij}} \right|}{ATOT_i} \\ &\leqq L_i^0 \end{aligned} \tag{14}$$

It follows from equation (14) that the value of p may be fixed for all iterations and depends only on the value of L. It also follows from equations (14) and (8) that p generally increases as m_{ij} increases.

Table 2. Dependence of pX on the quantity of Cu^{2+} added to a "buffer" system of ZnX^-/Zn^{2+} ($c_{Zn^{2+}} = 0{\cdot}3M$; $c_{NTA} = 0{\cdot}2M$)

		Total $[Cu^{2+}]$, *M*				
		0	2×10^{-4}	5×10^{-4}	1×10^{-3}	2×10^{-3}
pH = 6·00	pX =	10·10	10·10	10·10	10·11	10·11
pH = 10·00	pX =	7·79	7·79	7·79	7·80	7·80

An iterative computer program was developed to calculate the equilibrium concentrations of all species in a system of many competing complexation reactions in a single phase; this program is based on equations (5) and (6). The total analytical concentration of each reactant was used as a first approximation of its equilibrium concentration.

The use of generalized forms for the equations of complexation reactions [equation (2)] and a series of other transformations made it possible to reduce the number of commands to 55 from the 140 used in COMICS. It decreases the number of iterations and the computer time. The usefulness of this program has been proved on a series of multicomponent systems. As an example the results of one of these calculations is given in Table 1.

For the parameter $p(i)$ it is enough, as a rule, to employ the largest stoichiometric coefficient of the ith reactant in equation (2). The rate of convergence slows up slightly as $p(i)$ increases. For the system given in Table 1, for example, the parameters $p(i)$ were chosen in accordance with the above; then the parameter for each reactant of the same system was arbitrarily assigned the value $p = 5$. The number of iterations increased in the latter case from 151 to 476.

It is frequently necessary to fix the concentration of one reactant (either metal or ligand) of a system in such a way that it does not change during the course of a reaction. Traditionally, a large excess is introduced, so that its concentration is not altered substantially by the reaction.

A new procedure[6] using an auxiliary "buffering" system eliminates this necessity. For example, let $[X^{3-}]$ be fixed throughout the course of the reaction

$$Cu^{2+} + X^{3-} \rightleftharpoons CuX^- \qquad (15)$$

where X^{3-} is the tertiary nitrilotriacetate anion, $N(CH_2COO)_3^{3-}$. The auxiliary reaction

$$Zn^{2+} + X^{3-} \rightleftharpoons ZnX^- \qquad (16)$$

for which the stability constant β is expressed by

$$\beta_{ZnX} = \frac{[ZnX]}{[Zn^{2+}][X^{3-}]} \qquad (17)$$

may be used to fix the concentration of X^- in the system. From (17) is obtained

$$\log \beta_{ZnX} = pX + \log \frac{[ZnX]}{[Zn^{2+}]} \qquad (18)$$

Equation (18) shows that it is possible to fix various low concentrations of X^{3-} by use of relatively large concentrations of ZnX^- and Zn^{2+}. Copper(II) ions may be added to this "buffer" solution as long as $C_{Cu^{2+}} \ll [Zn^{2+}], [ZnX^-]$ and reaction (15) will proceed with $[X^{3-}]$ constant.

The program COMPLEX was used to calculate the equilibrium concentrations in the system described by equations (15) and (16), taking into account the possible hydrolysis of all reactants. The results, as presented in Table 2, demonstrate that a wide range of total Cu^{2+} concentrations cause no change in $[X^{3-}]$.

Acknowledgement—The author thanks A. Lichtman and Ch. Tobias for their valuable assistance.

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APPENDIX

The computer program COMPLEX is used to read data, to make consecutive approximations for adjusting the equilibrium concentrations of reactants and complexes and to print the results after a satisfactory degree of convergence. The listing of the program includes a description of the input data. In this program the following variables were used:

NE	Number of separate experiments.
M	Number of reactants (up to 18).
TITLE(I)	Array used to print headings.
ATOT(I)	Analytical concentration of each reactant.
AK(I), A(I)	Equilibrium concentration of I-th reactant, as used by iteration, and as calculated.
ACALC(I)	Calculated total concentration of I-th reactant.
N	Number of complex species in system under study (including protonated and hydrolysed forms).
MA(I,J)	Number of units of reactant (I) in complex (J).
MOH(J), MH(J)	Number of hydroxyls and protons in complex species (J).
C(J)	Equilibrium concentration of J-th complex.
E(J)	Log of cumulative stability constant of J-th complex.
SUM(J)	Conditional stability constant of species (J) at a given pH in the log form.
TERM(J)	The same, but in the exponential form.
Y1(I)	Degree of convergence of the I-th reactant.
Y2(I)	Absolute difference between real and calculated total concentration of I-th reactant.
BK(I)	Parameter p (see text) for I-th reactant.
INDEX	Index = 0 for all cards bearing pH values, up to last card when index = 1.

```
      Computer program COMPLEX
C     INPUT DATA
C 1   NUMBER OF SETS OF EXPERIMENTS TO
      BE RUN (I2)
C 2   NUMBER OF REACTANTS AND OF COM-
      PLEX SPECIES FORMED (INCLUDING PRO-
      TONATED AND HYDROLYSED FORMS), (2I2)
C 3   A SERIES OF CARDS WITH THE TITLE OF
      REACTANT, ITS TOTAL CONCENTRATION
      AND PARAMETER P (A5,E15.3,F10.5)
```

C 4 A CARD FOR EACH COMPLEX SPECIES LISTING THE LOGARITHM OF THE CUMULATIVE ASSOCIATION CONSTANT OF THE SPECIES. THE NUMBER OF MOLECULES OF REACTANT (1), (2) ETC. UP TO (18), THE NUMBER OF HYDROXYL IONS, THE NUMBER OF PROTONS (F10.3,20I2)

C 5 A SERIES OF CARDS BEARING PH AND INDEX. INDEX = 0 FOR ALL BUT LAST CARD OF EXPERIMENT WHEN INDEX = 1 (F10.4,I1)

```
      PROGRAM  COMPLEX (INPUT,OUTPUT)
      DIMENSION TITLE(20),ATOT(18),Y1(18),MA(18,50),Y2(18),E(50),
     1A(18),AK(18),MOH(50),MH(50),TERM(50),C(50),ACALC(18),BK(18)
  100 FORMAT(40I2)
  101 FORMAT(A5,E15.3,F10.5)
  103 FORMAT(F10.3,5X,22I2)
  104 FORMAT(F10.4,I1)
      READ 100,NE
      DO 1 IK=1,NE
      READ 100,M,N
      DO 2 I=1,M
      READ 101,TITLE(I),ATOT(I),BK(I)
      Y1(I)=ATOT(I)*.0001
    2 A(I)=ATOT(I)
      DO 3 J=1,N
    3 READ 103,E(J),(MA(I,J),I=1,M),MOH(J),MH(J)
   13 READ 104,PH,INDEX
      NIT=0
      DO 4 J=1,N
      SUM=E(J)-MH(J)*PH+MOH(J)*(PH-14.)
    4 TERM(J)=10.**SUM
   93 CONTINUE
      DO 25 J=1,N
   25 C(J) = TERM(J)
      DO 5 J = 1,N
      DO 5 I = 1,M
    5 C(J) = C(J)*A(I)**MA(I,J)
      NIT=NIT+1
      DO 6 I=1,M
      ACALC(I) = A(I)
      DO 36 J = 1,N
   36 ACALC (I) = ACALC(I) + MA(I,J)*C(J)
      AK(I)=A(I)*(ATOT(I)/ACALC(I))**(1./BK(I))
    6 Y2(I)=ABS(ACALC(I)-ATOT(I))
      IF(NIT-1999)16,16,7
    7 PRINT 205,PH
      GO TO 11
   16 DO 9 I=1,M
      IF(Y1(I)-Y2(I))14,9,9
   14 DO 17 IN=1,M
   17 A(IN)=AK(IN)
      GO TO 93
    9 CONTINUE
      PRINT 209,PH,NIT
   11 PRINT 206,(I,BK(I),TITLE(I),ATOT(I),A(I),I=1,M)
      PRINT 207,(TITLE(I),I=1,M)
      DO 12 J=1,N
   12 PRINT 208, C(J),E(J),MH(J),MOH(J),(MA(I,J),I=1,M)
      IF(INDEX.NE.1)GO TO 13
    1 CONTINUE
  205 FORMAT(//* PH=*,F7.3,40X,* ITERATION DID NOT CONVERGE*/)
  206 FORMAT(I10,F10.5,A10,2E15.3)
  207 FORMAT(/6X,*C*,5X,* LOG BETA*,3X,* H*,4X,*OH *, 180A5/)
  208 FORMAT(2E11.3,12I5)
  209 FORMAT(//* PH=*,F7.3,40X,*NUMBER OF ITERATION=*,I4/)
      STOP
      END
```

Summary—An iterative method and a computer program are presented for calculating equilibrium concentrations of all species in a multicomponent system of many competing complexation reactions. The initial data required are: pH, total concentration of each reactant, stability constant of each complex, and pK_a values. Convergence of the iterations is proved. As an example a system of 7 reactants and 27 complexes is given. A second example for the use of this program, including so-called "ligand buffering", is also shown.

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THE SIGNIFICANCE OF THE $CrO_4^{2-} \rightleftharpoons HCrO_4^-$ EQUILIBRIUM IN THE DETERMINATION OF CHROMIUM(VI) BY FLAME SPECTROMETRY

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It is widely known[1,2] that the sensitivity (1% absorption) for Cr(III) may be significantly different from that for Cr(VI) when chromium is determined by atomic-absorption spectrometry in an air–acetylene flame. However, it is not often realized that the atomic-absorption of Cr(VI) is pH-dependent. This fact has been mentioned briefly by Angino and Billings,[3] quoting a private communication as source, but the extent of, or reason for, the pH effect has not been investigated in detail. The purpose of this communication is to establish that the chromate–dichromate equilibrium is responsible for the pH-effect and to investigate the extent of possible interference in some of the flames which are used for the determination of chromium by flame spectrometry.

EXPERIMENTAL

Reagents

Chromium (VI) and (III) stock solutions, 1000 μg/ml. Prepared from analytical-reagent grade potassium chromate and chromic potassium sulphate respectively.

Buffer solutions. A series of buffer solutions was prepared from sodium acetate or ammonium acetate with acetic acid, ammonia or sodium hydroxide added as appropriate to adjust the pH, so that after 100-fold dilution, the final solutions covered the pH range 3–9.

Apparatus

Atomic-absorption spectrophotometer. An EEL model 240 with normal flat-top 100-mm air-acetylene and 50-mm nitrous oxide–acetylene burners, and a chromium hollow-cathode lamp (357·9 nm).

The flame conditions used were as follows:

Air–acetylene. Air flow, 6·0 l./min; acetylene flow, 1·1 l./min; height of measurement (above burner), 5 mm.

Air–hydrogen. Air flow, 6·6 l./min; hydrogen flow, 9·7 l./min; height of measurement, 3 mm.

Nitrous oxide–acetylene. Nitrous oxide flow, 7·0 l./min; acetylene flow, 3·3 l./min; height of measurement, 4 mm.

Procedure

A series of solutions was prepared containing 4 μg/ml of Cr(III) or Cr(VI), and covering the pH range 3–9. Each solution also contained 4 μg/ml of lithium, to act as an internal standard. The pH of each solution was measured immediately before the nebulization.

RESULTS AND DISCUSSION

The effect of pH on chromium atomic absorption at 357·9 nm at optimum heights and fuel flows when solutions of Cr(III) and Cr(VI) were nebulized into air–hydrogen and air–acetylene flames is shown in Fig. 1. The absorbance of Cr(VI) solutions changes quite significantly over the pH range 5–8 in the air–acetylene flame, and the effect is even more pronounced in the air–hydrogen flame. The extent of the effect can be reduced, but not eliminated, by decreasing the fuel-to-oxidant ratio, or by increasing the fuel and oxidant flow-rates.

If the solutions had stood for more than 1 hr, the absorbance of the Cr(III) solutions at pH above 6 could be increased by shaking them immediately before nebulization. This is a clear indication that the shape of the Cr(III) curves is attributable to precipitation.

With the nitrous oxide–acetylene flame, there was no detectable pH-effect when the Cr(VI) solutions were nebulized. Provided the Cr(III) solutions were shaken vigorously immediately before nebulization, even the effect of precipitation on the absorbance of these solutions could be virtually eliminated by use of the hotter flame. Cr(III) and Cr(VI) also gave similar sensitivities in this flame.

Over the pH range 3–9, when the total level of Cr(VI) is low (as is normally the case when the element is determined by atomic-absorption spectrometry), the equilibrium

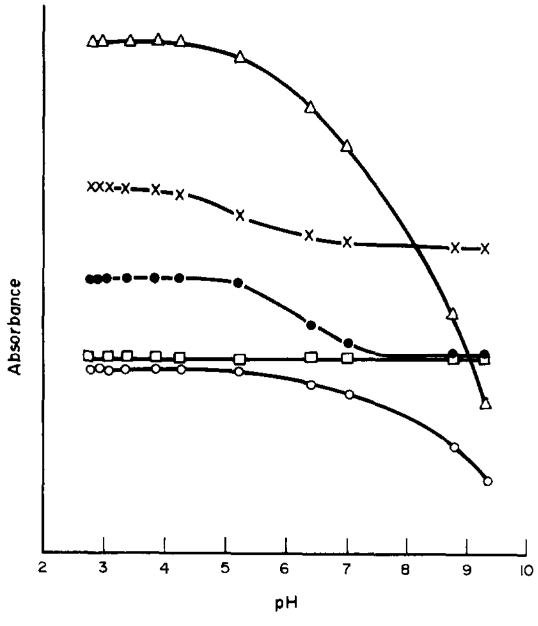

Fig. 1. Effect of pH on chromium atomic absorption; △, Cr(III), air–acetylene; ×, Cr(VI), air–acetylene; ●, Cr(VI), air–hydrogen; Cr(III), air–hydrogen; □, Cr(VI), nitrous oxide–acetylene.

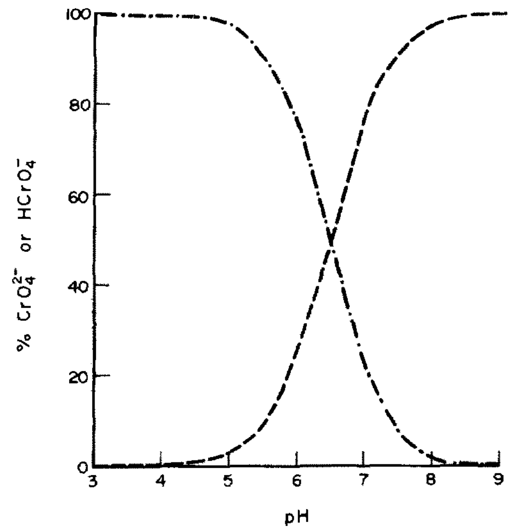

Fig. 2. Distribution diagram for CrO_4^{2-} (---) and $HCrO_4^-$ (-·-·-) as a function of pH for 4 μg/ml Cr(VI).

constants quoted by Perrin[4] show that the equilibria governing the anionic forms present at significant levels are:

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$$
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-$$

The equilibrium constants for these two equilibria are $3{\cdot}24 \times 10^{-7}$ and $3{\cdot}03$ and 10^{-2} respectively at 25°. Combining the dissociation constant expressions with the mass-balance for Cr(VI) species leads to a quadratic equation for $[HCrO_4^-]$.[5] This may be solved provided the total Cr(VI) concentration and the pH are specified. The theoretical effect of pH on the concentrations of $HCrO_4^-$ and CrO_4^{2-}, calculated by this method for a 4-μg/ml Cr(VI) solution, is shown in Fig. 2. At this concentration the $Cr_2O_7^{2-}$ concentration is not significant. The results indicate that unless the sensitivities for Cr as $HCrO_4^-$ and CrO_4^{2-} are identical, a change in absorbance might be expected as the pH as increased from 5 to 8, which is in close agreement with the results reported above. Assuming that all of the chromium is present as $HCrO_4^-$ at pH 3 and below and as CrO_4^{2-} at pH 9 and above, it is possible to calculate the sensitivities for chromium in the two forms. Summation of the absorbances of the two forms calculated from these sensitivity values and the data in Fig. 2, gives theoretical curves which are indistinguishable from the empirical curves shown in Fig. 1, thus confirming the hypothesis that the $CrO_4^{2-} \rightleftharpoons HCrO_4^-$ equilibrium is responsible for the effect.

To confirm that the results were not attributable to interference from the ions used in the preparation of the buffer solutions, the effects of sodium and ammonium ions and acetic acid on the absorbance of chromium(VI) solutions were studied. The pH of the solutions used lay in (or was adjusted to) the range 2·5–4·2. No effect was found at levels up to twice those employed in any of the diluted buffer solutions used. Moreover, plots of absorbance *vs.* pH over the range 4–7 were found to be the same for the air-hydrogen flame, whether the pH was adjusted with sodium acetate/acetic acid or with ammonium acetate/acetic acid, again confirming that the effect is indeed due to variation in pH. The lithium internal standard gave results which showed that no solvent–matrix interaction caused any interference.

Conclusion

Variation in pH can cause a small but significant interference when Cr(VI) is determined by flame spectrometry in an air–acetylene flame. The interference due to the $HCrO_4^- \rightleftharpoons CrO_4^{2-}$ equilibrium is much more severe when the air–hydrogen flame is used, and in this instance accurate pH buffering of sample and standard solutions is essential unless strongly acidic or strongly basic solutions are being nebulized. This flame is often used to determine chromium by atomic-fluorescence spectrometry, where the problem should be equally as severe as that encountered in atomic-absorption spectrometry.

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Summary—Chromium atomic absorption for Cr(VI) solutions in the air–acetylene and air–hydrogen flames is pH-dependent, but not in the nitrous oxide–acetylene flame. The effect is shown to occur as a result of the $HCrO_4^- \rightleftharpoons CrO_4^{2-}$ equilibrium, and may cause significant errors in the determination of chromium by atomic-absorption spectrometry unless the pH of sample and standard solutions is controlled.

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EFFECTS OF AUXILIARY COMPLEX-FORMING AGENTS ON THE RATE OF METALLOCHROMIC INDICATOR COLOUR-CHANGE—III*

MECHANISM OF THE COLOUR CHANGE OF TAC IN NICKEL–EDTA TITRATIONS

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In chelatometric titrations of nickel, the indicator colour-change at the equivalence point being usually slow, the titration should be done at about 80° or higher. In our previous work,[1] it was found that the addition of a small amount of 1,10-phenanthroline improves the rate of indicator colour-change of TAC [2-(2-thiazolylazo)-4-methylphenol] or Xylenol Orange.

In the work described in this paper the rate of the substitution reaction of Ni–TAC with EDTA or 1,10-phenanthroline was studied, and the mechanism of the indicator colour-change is discussed.

EXPERIMENTAL

Reagents

TAC was purified by vacuum sublimation.

A nickel(II) solution was prepared from reagent-grade nickel nitrate.

EDTA was recrystallized from water.

1,10-Phenanthroline was dissolved in dioxan purified as described earlier.[2]

2-(*N*-Morpholino)ethanesulphonic acid (MES) mixed with potassium hydroxide solution was used as buffer.

All other reagents used were of reagent grade.

Procedures

The rate of the substitution reaction was measured under the following conditions: pH 5·7–6·3 (0·01 *M* MES buffer); ionic strength 0·1 (KNO_3); dioxan = 20% v/v; 25 ± 1°.

Substitution reaction of nickel–TAC chelate with EDTA. A solution (100 ml) that was $5{\cdot}25 \times 10^{-6}$ *M* in nickel and $1{\cdot}5$–$3{\cdot}0 \times 10^{-4}$ *M* in TAC was placed in a 50-mm photometric cell, and 1 ml of $1{\cdot}0$–$2{\cdot}0 \times 10^{-2}$ *M* EDTA solution was added rapidly by syringe with stirring. The absorbance of the solution at 590 nm (the absorption maximum of the Ni–TAC chelate) was measured as a function of the reaction time.

Substitution reaction of nickel-TAC chelate with 1,10-*phenanthroline.* The following solutions *A* and *B* were mixed, and the absorbance at 590 nm was recorded as a function of the reaction time by the stopped-flow method. The dead-time of mixing was about 20 msec.

Solution *A*: Ni = $1{\cdot}05 \times 10^{-5}M$, $TAC = 3{\cdot}0$–$4{\cdot}5 \times 10^{-4}M$.
Solution *B*: 1,10-phenanthroline = $2{\cdot}0$–$200 \times 10^{-5}M$.

RESULTS AND DISCUSSION

Substitution reaction with EDTA

In the presence of a large excess of TAC, nickel forms a 1:2 chelate quantitatively over the pH range from 5·7 to 6·3. When a large excess of EDTA relative to nickel is added, the following substitution reaction proceeds to completion.

$$\mathrm{Ni(TAC)_2 + EDTA \rightleftharpoons Ni(EDTA) + 2TAC} \qquad (1)$$

The rate law is expressed as

$$-\frac{d[\mathrm{NiR_2}]}{dt} = k_{0(\mathrm{R,Y,H})}[\mathrm{NiR_2}] \qquad (2)$$

where R is the fully dissociated form of TAC and $k_{0(\mathrm{R,Y,H})}$ is the conditional rate-constant involving the concentrations of TAC, EDTA and hydrogen ion. By representing the absorbances at the reaction times 0, t and ∞ by A_0, A_t and A_∞, we obtain equation (3) from equation (2):

$$\log(A_t - A_\infty) = -\frac{k_{0(\mathrm{R,Y,H})}}{2{\cdot}303}t + \log(A_0 - A_\infty) \qquad (3)$$

The plots of log $(A_t - A_\infty)$ *vs.* the reaction time (t) yielded straight lines for at least 90% of the total reaction at the various concentrations of TAC, EDTA and hydrogen ion used, thus the reaction was pseudo first-order with respect to NiR_2. The conditional rate-constants $k_{0(\mathrm{R,Y,H})}$ were obtained from the slopes. The data summarized in Table 1 indicate that the values of $k_{0(\mathrm{R,Y,H})}$ are proportional to the concentration of EDTA and the reciprocal of the concentration of TAC. The plots of $k_{0(\mathrm{H})}$ *vs.* $[H^+]$ gave a straight line with an intercept on the *y*-axis. Hence

$$-\frac{d[\mathrm{NiR_2}]}{dt} = (k'_1[\mathrm{H^+}] + k'_2)\frac{[\mathrm{NiR_2}][\mathrm{Y'}]}{[\mathrm{HR}]} \qquad (4)$$

where [Y′] is the total concentration of EDTA not combined with nickel ion, and we propose the following reaction mechanism.

$$\left(\begin{array}{ll} \mathrm{NiR_2 + H^+ \rightleftharpoons NiR^+ + HR} & (5) \\ \mathrm{NiR^+ + Y' \xrightarrow{k_1} NiY^{2-} + HR} & (6) \end{array}\right.$$

$$\left(\begin{array}{ll} \mathrm{NiR_2 + H_2O \rightleftharpoons NiR(OH) + HR} & (7) \\ \mathrm{NiR(OH) + Y' \xrightarrow{k_2} NiY^{2-} + HR + OH^-} & (8) \end{array}\right.$$

The equilibria (5) and (7) precede the reactions (6) and (8), and the reaction of NiR^+ or NiR(OH) with EDTA

---

* Parts I and II: see references 1 and 2.

Table 1. First-order conditional rate-constants $k_{0(R,X,H)}$ (25°C, μ = 0·1, dioxan 20% v/v, Ni 5·25 × 10^{-6} *M*)

$10^4 \times C_{EDTA}$, *M*	$10^4 \times C_{TAC}$, *M*	pH	$10^2 \times k_{0(R,Y,H)}$, *sec*$^{-1}$
1·00	1·50	5·81	3·64
		5·87	3·13
		5·94	2·99
		6·03	2·43
		6·16	2·21
	2·00	5·84	2·55
		5·94	2·10
		6·31	1·30
	2·25	5·80	2·43
	3·00	5·94	1·42
1·50	1·50	5·78	5·67
		5·84	5·42
		5·88	4·82
		5·94	4·10
		5·98	4·19
		6·07	3·62
		6·20	2·96
2·00	1·50	5·76	8·24
		5·83	6·91
		5·94	5·94
		6·01	5·60
		6·14	4·42
		6·24	3·76

might be the rate-determining steps. This mechanism is similar to that of the substitution reaction of the mercury(II)–PAR chelate with DCTA.[3] Equation (4) can be rewritten as

$$-\frac{d[\mathrm{NiR_2}]}{dt} = k_1[\mathrm{NiR^+}][\mathrm{Y'}] + k_2[\mathrm{NiR(OH)}][\mathrm{Y'}] \qquad (9)$$

where

$$k_1 = k_1' \frac{K^{R}_{NiR_2}}{K^{H}_{HR}} \qquad (10)$$

$$k_2 = k_2' \frac{K^{R}_{NiR_2}}{K^{H}_{HR}\, K^{OH}_{NiR(OH)}\, K_W} \qquad (11)$$

With k_1' and k_2' obtained from the slope and *y*-intercept of the plot, the values 2·1 × 10^3 and 7·9 × 10^6 l. mole^{-1} sec^{-1} for k_1 and k_2 were obtained by the use of equations (10) and (11) and $K^{R}_{NiR_2} = 10^{7\cdot2}$,[4] $K^{H}_{HR} = 10^{8\cdot3}$,[4] $K^{OH}_{NiR(OH)} = 10^{4\cdot5}$,* $K_W = 10^{-14\cdot4}$.*

Substitution reaction with 1,10-*phenanthroline*

The rate of this substitution reaction was determined under the same experimental conditions as in the case of EDTA.

$$\mathrm{Ni(TAC)_2 + 3phen \rightleftharpoons Ni(phen)_3 + 2TAC} \qquad (12)$$

The rate of decrease of $[\mathrm{NiR_2}]$ with reaction time was linear for over 90% of the reaction. The rate law is expressed as

$$-\frac{d[\mathrm{NiR_2}]}{dt} = k_{0(R,X,H)}[\mathrm{NiR_2}] \qquad (13)$$

where X is 1,10-phenanthroline.

The conditional rate-constants $K_{0(R,X,H)}$ for various experimental conditions are summarized in Table 2. Plots of

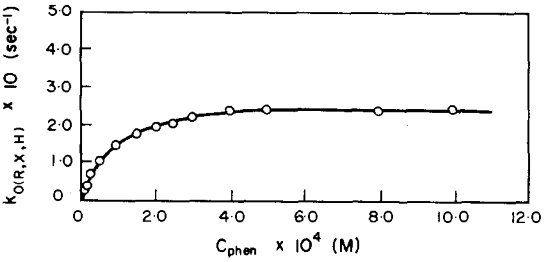

Fig. 1. Plots of $k_{0(R,X,H)}$ *vs.* C_{phen}. C_{Ni}: 5·25 × 10^{-6} *M*; C_{TAC}: 1·50 × 10^{-4} *M*. pH 6·00, μ = 0·1 (KNO_3), 20% v/v dioxan, 25°C.

$k_{0(R,X,H)}$ *vs.* $[H^+]$ gave straight lines with zero intercept, and $k_{0(R,X,H)}$ was independent of TAC concentration. As shown in Fig. 1, $k_{0(R,X,H)}$ shows first-order dependence on the concentration of 1,10-phenanthroline, but becomes independent of it when more than a large enough excess of 1,10-phenanthroline is present. From these results, the following mechanism may be proposed.

$$\mathrm{NiR_2 + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiR^+ + HR} \qquad (14)$$

$$\mathrm{NiR^+ + X \rightleftharpoons NiRX^+} \qquad (15)$$

$$\mathrm{NiRX^+ + X \xrightarrow{k_4} NiX_2^{2+} + R^-} \qquad (16)$$

The reaction (15) is much more faster than reactions (14) and (16) because one molecule of 1,10-phenanthroline may easily co-ordinate with the Ni–TAC complex to form a stable octahedral configuration. Also it is reasonable to assume that the formation constant K^{X}_{NiRX} may be of the same order as K^{X}_{NiX} and so equilibrium (15) lies far to the right, *i.e.*, $[\mathrm{NiR^+}] = [\mathrm{NiRX^+}]$.

When a sufficient excess of 1,10-phenanthroline is present, reaction (16) may proceed much faster than equation

Table 2. First-order conditional rate-constants $K_{0(R,X,H)}$ (25°C, μ = 0·1, dioxan 20% v/v, Ni 5·25 × 10^{-6} *M*)

$10^4 \times C_{phen}$, *M*	$10^4 \times C_{TAC}$, *M*	pH	$10 \times k_{0(R,X,H)}$, *sec*$^{-1}$
0·50	1·50	5·90	1·40
	1·50	6·13	0·91
1·00	1·50	5·89	2·03
	1·50	5·98	1·74
	1·50	6·13	1·25
10·0	1·50	5·88	3·12
	1·50	5·96	2·63
	1·50	6·13	1·84
1·00	1·50	6·00	1·45
	1·65	6·00	1·53
	1·95	6·00	1·53
10·0	1·65	6·00	2·36
	1·95	6·00	2·34
	2·25	6·00	2·34
0·10	1·50	6·00	0·25
0·20	1·50	6·00	0·35
0·30	1·50	6·00	0·68
0·50	1·50	6·00	1·06
1·00	1·50	6·00	1·45
1·50	1·50	6·00	1·81
2·00	1·50	6·00	1·95
2·50	1·50	6·00	1·98
3·00	1·50	6·00	2·21
4·00	1·50	6·00	2·38
5·00	1·50	6·00	2·42
8·00	1·50	6·00	2·38
10·0	1·50	6·00	2·38

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* $K^{OH}_{NiR(OH)}$ was estimated spectrophotometrically and K_W was determined by pH-titration under the experimental conditions.

(14) and the release of TAC from NiR_2 may be the rate-determining step. The value of k_3 was calculated to be $2{\cdot}4 \times 10^5$ $1.mole^{-1}.sec^{-1}$.

When 1,10-phenanthroline is in smaller excess, $k_{0(R,X,H)}$ depends on both $[H^+]$ and [1,10-phenanthroline]. The steady-state approximation for $NiRX^+$ was applied, *i.e.*,

$$-\frac{d[NiR_2]}{dt} = \frac{d[NiX_2^{2+}]}{dt} \tag{17}$$

where

$$-\frac{d[NiR_2]}{dt} = k_3[NiR_2][H^+] - k_{-3}[NiR^+][HR] \tag{18}$$

$$\frac{d[NiX_2^{2+}]}{dt} = k_4[NiRX^+][X] \tag{19}$$

and

$$[NiR^+] = [NiRX^+] \tag{20}$$

From equations (13) and (17)–(20) we obtain

$$\frac{[H^+]}{k_{0(R,X,H)}} = \frac{k_{-3}}{k_3 k_4}\frac{[HR]}{[X]} + \frac{1}{k_3} \tag{21}$$

Since $k_3/k_{-3} = K^{H}_{HR}/K^{R}_{NiR_2} = 10^{1{\cdot}1}$, the values of k_3 and k_4 can be calculated. The value of k_3 is in good agreement with that obtained from $k_{0(R,X,H)}$ when 1,10-phenanthroline is present in sufficient excess, and $k_4 = 5{\cdot}1 \times 10^4$ $1.mole^{-1}.sec^{-1}$.

The rate-constant k_3 compares reasonably with the rate-constant $k = 1 \times 10^6$ $1.mole^{-1}.sec^{-1}$ for the reaction[5]

$$Ni(dien)_2^{2+} + H^+ \overset{k}{\rightleftharpoons} Ni(dien)^{2+} + Hdien^+ \tag{22}$$

The rate of the substitution reaction of Ni–TAC with 1,10-phenanthroline is much faster than that with EDTA and the Ni–phen complex formed by reactions (14)–(16) may undergo fast substitution with EDTA. In the titration of nickel with TAC as indicator a very sharp colour-change could be obtained at 50° by the addition of a small amount of 1,10-phenanthroline ([phen]/[Ni] = 1/200).

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Summary—The rate of the ligand-substitution reaction of nickel(II)–TAC chelate (NiR_2) with EDTA (Y) and 1,10-phenanthroline (X) has been determined spectrophotometrically in 20% v/v dioxan over the pH range 5·7–6·3 at $\mu = 0{\cdot}1$ (KNO_3) and 25 ± 1°. The substitution reaction with EDTA proceeds through the following two pathways:

$$NiR_2 + H^+ \rightleftharpoons NiR^+ + HR,$$

$$NiR^+ + Y' \xrightarrow{k_1} NiY^{2-} + HR,$$

and

$$NiR_2 + H_2O \rightleftharpoons NiR(OH) + HR,$$

$$NiR(OH) + Y' \xrightarrow{k_2} NiY^{2-} + HR + OH^-.$$

The reaction of NiR^+ or NiR(OH) with EDTA is the rate-determining step, and $k_1 = 2{\cdot}1 \times 10^3$ $1.mole^{-1}.sec^{-1}$ and $k_2 = 7{\cdot}9 \times 10^6$ $1.mole^{-1}.sec^{-1}$. The substitution reaction with 1,10-phenanthroline proceeds as follows:

$$NiR_2 + H^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiR^+ + HR,$$

$$NiR^+ + X \rightleftharpoons NiRX^+,$$

$$NiRX^+ + X \xrightarrow{k_4} NiX_2^{2+} + R^-.$$

At higher concentrations of 1,10-phenanthroline the release of TAC from NiR_2 by hydrogen ion is the rate-determining step, and $k_3 = 2{\cdot}4 \times 10^5$ $1.mole^{-1}.sec^{-1}$. At lower concentrations of 1,10-phenanthroline $-d[NiR_2]/dt$ is proportional both to $[H^+]$ and [X]. The value $k_4 = 5{\cdot}1 \times 10^4$ $1.mole^{-1}.sec^{-1}$ was calculated by the use of the steady-state approximation for $[NiRX^+]$. The substitution with 1,10-phenanthroline proceeds much faster than that with EDTA. By the addition of a small amount of 1,10-phenanthroline, Ni can be titrated with EDTA at 50°, with TAC as an indicator.

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MINIATURE POTASSIUM-SENSITIVE ELECTRODES WITH NEUTRAL CARRIERS IN A POLY(VINYL CHLORIDE) MATRIX

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The bulky nature of commercial potassium ion-selective electrodes[1] restricts their use in microanalytical applications and in certain biological and clinical measurements. However, use of the neutral carrier sensor in softened poly(vinyl chloride) membranes[2] allows more scope in the preparation of ion-selective electrodes. This is illustrated by the coated wire electrode,[2–4] although the thermodynamically poorly defined potential at the platinum-PVC interface is reflected in the long-term drift and the unequal potentials of different electrodes.

Electrodes can also be miniaturized by reduction in the membrane area, and in this paper we describe the preparation and properties of potassium ion-selective electrodes made with valinomycin or dimethyldibenzo-30-crown-10 in a thin PVC membrane[2,5,6] less than 0·2 mm^2 in area.

EXPERIMENTAL

Electrode preparation

Valinomycin or dimethyldibenzo-30-crown-10 (1 mg) is dissolved in 0·1 ml of dipentylphthalate and mixed with 1 ml of 5% high-molecular weight PVC in cyclohexanone. The solution is poured onto a microscope slide on an area of 1 cm^2. Free evaporation of cyclohexanone at room temperature yields a membrane approximately 0·15 mm thick. The electrode body (Fig. 1) consists of a glass tube 4 mm in diameter, drawn out at the end to a capillary about 3 cm long, inner diameter 0·5 mm. A membrane, 2 × 2 mm in size, is placed on the capillary tip and fixed by slipping over it a polythene sleeve, about 8 mm long. The electrode is completed by filling it with $10^{-3}M$ potassium chloride and inserting a silver–silver chloride wire reference electrode. If flexibility of the whole electrode body is required, it may be constructed from polythene.

Apparatus

All measurements of potentials were made at 25° against a saturated calomel electrode (Radelkis OP 815) connected with the measured solutions by a salt bridge of 0·1*M* ammonium nitrate with an asbestos-fibre junction. A Radiometer PHM 64 pH-meter and a Metrohm E 336 potentiograph connected through a Keithley electrometer 610 C were used. The measuring techniques have been described earlier.[4]

RESULTS AND DISCUSSION

Electrodes with a miniature membrane exhibited surprisingly good properties, resembling those of the electrodes with an 8-mm effective diameter studied earlier.[2,5] The electrode response in solutions of potassium ions over a concentration range of 10^{-1}–$10^{-6}M$ potassium chloride was examined. The calibration curves for electrodes with both neutral carriers were linear for the range 10^{-1}–$10^{-5}M$ potassium chloride and near to Nernstian in this region. The values of the constant E_0 in the Nernst equation, referred to the double-junction SCE, and the slopes calculated by means of regression analysis for the linear parts of calibration curves, are given together with the standard error estimates S_{yx} in Table 1. The correlation coefficient was in all cases better than 0·99997, which proves the outstanding linearity of response over the concentration range under investigation. The constant E_0 has the same value both for valinomycin and the crown-compound if the same experimental conditions are maintained in electrode preparation.

The potassium/sodium selectivity of the electrodes was studied by the mixed-solutions method at a constant level of 0·1*M* sodium chloride and a varied concentration of potassium ion. The selectivity coefficient $k_{K,Na}$ obtained by graphical evaluation for the valinomycin electrode was $2{\cdot}30 \times 10^{-4}$, that for the electrode with dimethyldibenzo-30-crown-10 was $2{\cdot}38 \times 10^{-3}$. Both values are in accordance with the selectivity of standard-size electrodes.[2,5]

The speed of response of both electrodes was followed by the dynamic method for a tenfold increase in the potassium ion concentration from initial levels of 10^{-5}, 10^{-4} and $10^{-3}M$ and for a thousandfold increase in concentration from $10^{-5}M$ in vigorously stirred solutions. The

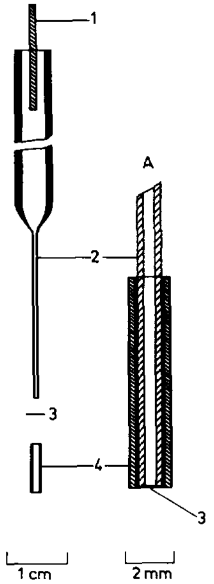

Fig. 1. Miniature potassium electrode. (1) Ag/AgCl reference electrode, (2) glass tube, (3) PVC membrane, (4) polythene sleeve. (A) Detail of assembled electrode tip.

Table 1. Calibration parameters of miniature potassium electrodes

Electrode	E_0, mV vs. SCE	Slope mV/$-\log a_{K^+}$	S_{yx}, mV
Valinomycin—initial	324·6	58·8	0·61
Crown—initial	325·5	58·5	0·43
—150 hr use	324·4	58·1	0·44
—200 hr use	324·5	57·9	0·53
—350 hr use	324·2	58·3	0·54
—500 hr use	322·0	58·4	0·36

time needed for attaining the final value of the potentials was 15 sec for the electrode with valinomycin and 5 sec for the electrode with the crown-compound. For the electrode with dimethyldibenzo-30-crown-10 the response-time was also examined. A newly prepared electrode reaches stable potentials after preconditioning for 30 min. The standard deviations calculated from 60 readings of the potentials at concentration levels of 10^{-2}, 10^{-3} and $10^{-4}M$ potassium chloride, taken during a period of 1 hr, were 0·07, 0·10, and 0·46 mV respectively. The long-term stability of the continuously used electrode was followed by recalibrating it regularly over a period of three weeks. The parameters obtained by linear regression analysis of the calibration plots are given in Table 1. They show that the maximum long-term drift of the potential amounts to 2 mV per week, the slope remaining practically without change. These results with the miniature electrode fully agree with our earlier findings,[4] while being in contrast with the recently published results of Semler and Adametzová.[7] These authors have observed for the electrode with dimethyldibenzo-30-crown-10 in a PVC matrix (without further details as to the membrane composition and electrode construction) linearity of the response over a narrower concentration range, a considerable drift of the potential, and a low selectivity. In our opinion, these results are open to question.

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Summary—A miniature version of the potassium ion-selective electrode with valinomycin or dimethyldibenzo-30-crown-10 in a poly(vinyl chloride) matrix is described. Electrodes having an effective membrane area of <0·2 mm^2 exhibit Nernstian behaviour within a range of activities of the potassium ion of 10^{-1}–$10^{-5}M$, a rapid response and good long-term potential stability.

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ANALYTICAL DATA

THE THERMODYNAMICS OF ETHYLENE-DIAMINE COMPLEXES OF SILVER

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In its complexes with amino-groups as donors, Ag(I) has a characteristic co-ordination number of two. These complexes are assumed to be linear. When the ligand is bidentate there is some tendency to form chelates, but the formation of polynuclear complexes with a chain or even a ring structure is more likely, and mononuclear complexes are always possible. Moreover one of the two donor groups can be protonated.

The system ethylenediamine–Ag(I) has been investigated by Schwarzenbach *et al.*,[1] who reported the formation of $AgHL^{2+}$, Ag_2L^{2+}, AgL^+, AgL_2^+ and $Ag_2L_2^{2+}$. The reason for a new investigation of this system was to search for the presence of the complexes $Ag(HL)_2^{3+}$ and $AgHL_2^{2+}$. The likelihood of these complexes can be argued from the fact that for such Ag(I) complexes the stability constant of AgL_2 is usually greater than the constant of AgL. This has been confirmed for Ag(I) complexes with positively charged ligands.[2] A second aim was determination of the thermodynamics of formation of these complexes, in particular to obtain information about the structure of these complexes.

EXPERIMENTAL

Ethylenediamine was converted into the dinitrate and purified by repeated crystallization.

To all solutions enough potassium nitrate was added to give a nitrate concentration of 0·5*M*.

Potentiometric measurements were performed with a Radiometer pHM52, using an Ingold HA 201 glass electrode for pH measurements and a solid state Coleman Ag/AgS electrode for pAg. As a reference a double-junction Ingold electrode was used, with 3*M* potassium chloride in the inner compartment. Standardization was done with solutions having an ionic strength of 0·5. All measurements were performed in vessels kept at a temperature of 25 ± 0·1° in a room at 25 ± 1°.

Calorimetric measurements were made with an LKB 8700–2 titration calorimeter.

Calculations were done on a Siemens 4004/15 computer.

RESULTS

Since polynuclear and protonated complexes were expected, a relatively large amount of experimental data with a wide range of values for C_{Ag} and C_L, the total concentrations of silver and ligand, was needed. C_{Ag} was varied from 10^{-4} to $10^{-2}M$ and C_L from 10^{-3} to $10^{-1}M$.

In addition to the indifferent electrolyte, each solution contained a certain amount of the ligand in the acid form, silver nitrate and potassium hydroxide. The pH and pAg values of each solution were determined experimentally. The experimental data for about 200 solutions were analysed by a computer program very similar to that described by Sillén.[3]

Table 1. The stability constants of the complexes

Complex	$\log \beta_{pqy}$
$AgHL^{2+}$	2·34
$AgH_2L_2^{3+}$	4·90
$AgHL_2^{2+}$	6·47
AgL_2^+	7·64
$Ag_2L_2^{2+}$	13·15

The following complexes were proved to be present in reasonable amount over at least part of the concentration range studied: $AgHL^{2+}$, $AgH_2L_2^{3+}$, $AgHL_2^{2+}$, AgL_2^+ and $Ag_2L_2^{2+}$. There was no evidence for the complexes Ag_2L^{2+} and AgL^+.

The stability constants β_{pqy} are defined by the reaction

$$p'L + yHL^+ + qAg^+ \rightleftharpoons Ag_qH_yL_p{}^{(y+q)+} \qquad (1)$$

with $p = p' + y$. β_{pqy} (in Table 1) is given in concentration units:

$$\beta_{pqy} = \frac{[Ag_qH_yL_p^{(q+y)+}]}{[Ag^+]^q\,[L]^{p'}\,[HL^+]^y}$$

The standard deviation of these stability constants is estimated to be 0·02.

The enthalpy change $\Delta H^\circ{}_{pqy}$, for the reaction in equation (1), was calculated from calorimetric data. The reaction vessel was filled with a solution containing silver nitrate, diprotonated ethylenediamine and enough potassium nitrate to ensure a final nitrate concentration of 0·5*M*. A certain amount of potassium hydroxide was added and the evolved heat *Q* was measured. Several such experiments were performed. A least-squares procedure using equation (2) gives the value for $\Delta H^\circ{}_{pqy}$.

$$\begin{aligned} -Q = {} & \Delta H_1^0 K_1 [H^+][L] + (\Delta H_1^0 + \Delta H_2^0)[L] \\ & + \sum_p \sum_q \sum_y \{[\Delta H_{pqy}^0 + y\Delta H_1^0 + (p-y)(\Delta H_1^0 \\ & + \Delta H_2^0)]\,K_1\,\beta_{pqy}\,[Ag^+]^q [L]^p [H^+]^y\} \qquad (2) \end{aligned}$$

Table 2. Free-energy, enthalpy and entropy changes

Complex	ΔG°_{pqy}, *kJ/mole*	ΔH°_{pqy}, *kJ/mole*	ΔS°_{pqy}, *J.mole^{-1} deg^{-1}*
$AgHL^{2+}$	−13·35	−25·4	−41
$AgH_2L_2^{3+}$	−27·99	−50·8	−77
$AgHL_2^{2+}$	−36·94	−56·9	−66
AgL_2^+	−43·60	−52·5	−30
$Ag_2L_2^{2+}$	−75·02	−97·1	−74

A preliminary interpretation of these results seems to indicate that the $Ag_2L_2^{2+}$ complex mainly exists as a closed ring.

K_1 is the protonation constant of HL^+, ΔH_1° is the enthalpy change of the reaction $H_2L^{2+} + OH^- \rightleftharpoons HL^+ + H_2O$ and ΔH_2° that of the reaction $HL^+ + OH^- \rightleftharpoons L + H_2O$. The values for ΔH_1° and ΔH_2° were reported earlier.[4] The values for $[Ag^+]$, $[L]$ and $[H^+]$ were calculated by using the computer program BDTV.[5]

The results are summarized in Table 2 together with the corresponding values for $\Delta G^\circ_{pqy} = -RT\ln\beta_{pqy}$ and $\Delta S^\circ = (\Delta H^\circ_{pqy} - \Delta G^\circ_{pqy})/T$.

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Summary—The silver(I)-ethylenediamine system has been investigated and the existence of $AgHL^{2+}$, $AgH_2L_2^{3+}$, $AgHL_2^{2+}$, AgL_2^+ and $Ag_2L_2^{2+}$, with stability constants $10^{2.33}$, $10^{4.88}$, $10^{6.47}$, $10^{7.64}$, $10^{13.13}$ has been demonstrated.

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AN EVALUATION OF FOUR TITRIMETRIC METHODS FOR THE DETERMINATION OF LEAD IN ORES

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Summary—Four titrimetric methods for the determination of lead in ores were evaluated. In the absence of bismuth and indium, a method based on EDTA titration of lead, after chloroform extraction of lead diethyldithiocarbamate, yields accurate and more precise results than the other methods evaluated. Interference from indium can be avoided by di-isopropyl ether extraction of its bromide from 6*M* hydrobromic acid. Interference from bismuth can be eliminated by separating it from lead by chloroform extraction of its xanthate from 2*M* hydrochloric acid–tartaric acid media.

The preparation and characterization of ores for use as certified reference materials is a continuing project [Canadian Certified Reference Materials Project (CCRMP)] sponsored by the Canada Centre for Mineral and Energy Technology. As part of this project, a zinc–tin–copper–lead ore, MP-1, and a zinc–lead–tin–silver ore, KC-1, have been issued with recommended values for lead.[1,2] As shown in Tables 1 and 2, the ranges of lead values obtained in the interlaboratory certification programme for MP-1, and especially KC-1, were unexpectedly large. In a number of cases the participating laboratories were requested to repeat their analyses because their results were not in accord with the tentative consensus values, but even after corrected results were submitted, the spread of the lead results was twice that of the zinc results in the same materials.[1–3] It was therefore considered imperative to evaluate the titrimetric methods used and to delineate their inherent errors.

The methods are: the molybdate method using tannic acid as an external indicator;[4,5] the chromate method in which iodine, liberated after dissolution of lead chromate and reduction of chromium(VI) with potassium iodide, is titrated with sodium thiosulphate solution;[6] the ASTM EDTA method;[7] and another EDTA method in which lead is separated from the matrix elements by chloroform extraction of its diethyldithiocarbamate complex.[8,9]

EXPERIMENTAL EVALUATION OF METHODS

Reagents

Sodium thiosulphate solution, 0·05*M*.

Lead solution (~4 *mg/ml*). Approximately 8 g (accurately weighed) of high-purity lead pellets were dissolved in 200 ml of concentrated nitric acid, with precautions to avoid loss by spray, and the solution was diluted to 2 litres with water.

Potassium dichromate solution (5 *mg/ml*). Pure potassium dichromate (0·5000 g) was dissolved in water and the solution was diluted to 100 ml.

Iodine indicator, 5% *w/v solution*. Approximately 5 g each of iodine indicator and potassium iodide were dissolved in water and the solution was diluted to 100 ml.

Sodium acetate–acetic acid solution. Approximately 25 ml of concentrated acetic acid and 325 ml of saturated sodium acetate solution were diluted to 1 litre with water.

Hydrochloric acid–sodium chloride solution. Approximately 150 ml each of water and concentrated hydrochloric acid were mixed with 1000 ml of saturated sodium chloride solution.

Sodium acetate wash solution. Approximately 50 ml of saturated sodium acetate solution were mixed with 1000 ml of water.

Ammonium molybdate solution, 0·007*M*. Ammonium paramolybdate tetrahydrate (8·8 g) was dissolved in water and the solution was diluted to 1 litre.

Ammonium acetate–acetic acid solution. Approximately 250 ml of concentrated ammonia solution were added, slowly with stirring, to 300 ml of concentrated acetic acid.

EDTA solution, 0·01*M*.

Acetate buffer solution, *pH* 6. Approximately 27 g of sodium acetate trihydrate were dissolved in 1 litre of water and the pH of the solution was adjusted to 6·0 ± 0·1 (pH-meter) with 5% v/v acetic acid.

Sodium diethyldithiocarbamate (*NaDDTC*), 5% *w/v solution*. Prepared fresh as required, stabilized by adding several drops of concentrated ammonia solution and filtered before use.

Tartaric acid–potassium cyanide wash solution. Approximately 25 ml of water were mixed with 20 ml of 20% tartaric acid solution, the pH of the solution was adjusted to 10·0 ± 0·1 (pH-meter) with concentrated ammonia solution, then 10 ml were added in excess followed by 30 ml each of water and freshly prepared 20% potassium cyanide solution.

Pre-equilibrated di-isopropyl ether

Analytical-reagent grade chemicals were used for all other solutions.

Choice of reference materials

KC-1 and MP-1 were chosen for use in the evaluation tests because of their accurately known lead contents (6·98 and 1·93%, respectively) and because other reference lead

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Table 1. Correlation of lead results for KC-1, with the analytical method employed. Recommended value 6·98% Pb; 95% confidence interval 6·94–7·02%

	Analytical method, mean value and range, % Pb							
Laboratory	Atomic-absorption spectrophotometry	Gravimetric	Polarographic	X-ray fluorescence	Titrimetric molybdate	Titrimetric chromate	Titrimetric EDTA	Titrimetric Na DDTC EDTA
1	6·960 (6·87–7·06)	7·161 (6·92–7·33)						
2	6·869 (6·85–6·88)							
3					7·12[b] 7·068 (7·05–7·10)[a]		7·20[b] 6·995 (6·86–7·07)[a+]	
4							7·23[b] 7·001 (6·96–7·04)[ax]	
5				6·954 (6·88–7·11)				
7	6·73[b] 6·748 (6·57–6·90)[a]				6·76[b] 6·698 (6·54–6·79)[a]			
8	6·986 (6·94–7·01)						6·630 (6·55–6·68)[•]	
9	7·02 (7·0–7·1)				6·955 (6·92–6·99)			
10	6·996 (6·96–7·04)		6·978 (6·96–7·02)			6·989 (6·96–7·04)		
11							6·955 (6·92–6·98)[x]	
12								6·967 (6·90–7·01)
13	7·21[b] 7·053 (6·98$_2$–7·10$_9$)[a]							
14	7·37[b] 6·880 (6·85–6·90)[a]		7·33[b]		6·843 (6·80$_7$–6·88$_3$)			
15							7·041 (6·99–7·07)[+]	
17	7·17[b] 6·960 (6·91–7·02)[a]				7·17[b]			
18					7·003 (6·98–7·04)			
20	6·77[b] 6·955 (6·85–7·04)[a]							
22	7·178 (7·15–7·20)				7·183 (7·15–7·20)			
23		6·833 (6·77–6·92)			6·975 (6·93–7·03)			
24	7·043 (6·98–7·12)					6·971 (6·93–7·01)		
25	7·292 (7·26–7·34)				7·254 (7·12–7·35)			
Mean	6·995	6·997	6·978	6·954	6·972	6·980	6·924	6·967

[+] ASTM method E-16.
[x] Similar to ASTM method E-16.
[•] Lead separated by electrolysis.
[a] Analysis repeated by contributing laboratory.
[b] Results not employed for certification of lead.

Table 2. Correlation of lead results for MP-1 with the analytical method employed. Recommended value 1·93% Pb; 95% confidence interval 1·90–1·96%

	Analytical method, mean value and range, % Pb					
Laboratory	Atomic-absorption spectrophotometry	Polarographic	X-ray fluorescence	Titrimetric molybdate	Titrimetric chromate	Titrimetric Na DDTC–EDTA
1	1·971 (1·96–1·98)					
2	1·972 (1·92–2·00)			1·981 (1·95–2·01)		
3	1·79 (1·79–1·79)					
4	2·022 (1·97–2·08)					
5		1·759 (1·73–1·78)				
6	1·892 (1·88–1·90)			1·916 (1·90–1·94)		
7				1·939 (1·90–1·98)		
8	1·942 (1·88–1·96)					
9	1·974 (1·95–2·00)					
10	1·892 (1·88–1·90)	1·887 (1·88$_6$–1·88$_8$)				
11		1·843 (1·83–1·87)				
12	1·889 (1·84$_5$–1·92$_5$)				1·910 (1·83–1·98)	1·875 (1·85–1·90)
13					1·993 (1·98$_1$–2·00$_8$)*	
14	1·904 (1·87$_1$–1·95$_3$)					
15	1·893 (1·85–1·92)					
16		1·950 (1·94–1·98)				
17	1·928 (1·85–2·06)					
18						2·082 (2·05–2·11)
19			1·921 (1·85–2·01)			
Mean	1·922	1·860	1·921	1·945	1·952	1·979

* Listed as gravimetric in the report on MP-1.[1]

ores were not available. The approximate chemical composition of these ores is shown in Table 3. In all the evaluation tests to be described, five replicate samples of KC-1 (1 g) and MP-1 (2 g) were used.

Procedure for the decomposition of KC-1 and MP-1

The samples were heated with 15 ml of concentrated hydrochloric acid for 5–10 min in a covered 400-ml Teflon beaker, then 10 ml each of water and concentrated nitric acid and 5 ml of concentrated hydrofluoric acid were added and the solution was heated for ~30 min. After the addition of 10 ml more of concentrated nitric acid and 3 ml of concentrated hydrofluoric acid, the solution was heated for 20–30 min, the cover was removed, 15 ml of 50% v/v sulphuric acid were added and the solution was evaporated to fumes of sulphur trioxide. After cooling, 10 ml each of concentrated hydrochloric and hydrobromic acids were added and the solution was evaporated to fumes of sulphur trioxide to remove arsenic and tin. After heating with 10 ml more of concentrated hydrobromic acid to ensure the complete removal of arsenic and tin, the solution was evaporated to fumes of sulphur trioxide twice, after washing down the sides of the beaker with water each time, to ensure the complete removal of nitric, hydrochloric, hydrobromic and hydrofluoric acids, and finally until 3–5 ml of sulphuric acid remained.

Table 3. Approximate chemical composition of MP-1 and KC-1[1,2]

	% Present			% Present	
Element	KC-1	MP-1	Element	KC-1	MP-1
O	14	26·8	Pb	6·98*	1·93*
Si	11	19·4	Sn	0·68*	2·50*
Al	0·8	3·63	Cu	0·114*	2·15*
Fe	16	5·68	Ag	0·114*	59·5 (ppm)*
Ca	0·3	3·36	Ti	—	0·07
Mg	0·05	0·04	F	—	4·04
Na	0·2	0·01	As	—	0·79*
K	0·1	0·10	Cd	—	0·07
Mn	0·05	0·05	In	—	0·071*
S	28	11·8	Bi	—	0·025*
C	0·2	0·10	W	—	0·02
Zn	20·37*	16·33*	Mo	—	0·014*

* Certified values.

Chromate Method

Standardization of sodium thiosulphate solution

Three 10-ml aliquots of standard potassium dichromate solution were diluted to ~150 ml with water. After addition of 6 ml of concentrated hydrochloric acid and 10 ml of freshly prepared 20% potassium iodide solution, each solution was titrated with sodium thiosulphate solution until the brown colour of the liberated iodine had almost disappeared and the solution was yellowish-green. After addition of 5 ml of freshly prepared 5% iodine indicator solution, the titration was continued until the solution was clear green. The normality and the "true" lead equivalent (mg/ml) of the sodium thiosulphate solution were calculated from the mean.

The sodium thiosulphate solution was also standardized with four aliquots of standard lead solution containing approximately the same amount of lead as would be derived from samples of the certified reference ore to be analysed. These solutions, except for the additions of nitric, hydrochloric, hydrofluoric and hydrobromic acids described in the decomposition procedure, were evaporated to fumes of sulphur trioxide three times, the sides of the beaker being washed down with water each time, to remove nitric acid, and carried through the procedure described. The "apparent" lead equivalent of the solution was calculated from the mean.

Procedure

Fifty ml of water were added to the solution obtained as described under "decomposition", the solution was heated to dissolve the soluble salts, then diluted to about 100 ml with water and cooled in an ice-bath for 45 min. The lead sulphate (and insoluble material) was filtered off on Whatman No. 42 paper. The beaker was washed 3 times with cold 1% v/v sulphuric acid, the paper and precipitate were washed once with the same solution, then the beaker and precipitate were each washed once with cold water.

The precipitate was transferred to the original beaker with a jet of water, and a small piece of moistened filter paper was used to clean the lip of the funnel. After addition of 25 ml of hot sodium acetate–acetic acid solution, the solution was boiled for at least 20 min to ensure complete dissolution of the lead sulphate. The hot solution was filtered through the original filter paper and the beaker, and paper plus residue, were each washed twice with ~ 10-ml portions of hot sodium acetate–acetic acid solution, and again twice with hot water. The filtrate and washings were collected in a 400-ml beaker, diluted to ~ 150 ml with water, if necessary, heated to boiling and then treated with 10 ml of saturated potassium dichromate solution added slowly by pipette. The solution was boiled gently for 15–20 min until the precipitate became orange-red. The precipitate was allowed to settle until the supernatant solution was clear, then filtered off by suction on a fine-porosity porcelain crucible containing a $\frac{1}{4}$-in. layer of paper pulp. The beaker and crucible plus precipitate were each washed 5 times with 10–15-ml portions of sodium acetate wash solution. The sides of the beaker were washed down with 25 ml of hydrochloric acid–sodium chloride solution and the solution was added to the crucible containing the bulk of the precipitate. After about 5 min (for the precipitate to dissolve) suction was applied and the solution collected in a clean 500-ml suction flask. The beaker was washed twice with ~ 10-ml portions of the hydrochloric acid–sodium chloride solution (from a wash-bottle) and the crucible once with 10–15 ml of the same solution. The beaker and crucible were then each washed twice with water, the walls of the flask were washed down with a little water, 10 ml of freshly prepared 20% potassium iodide solution were added and the solution was titrated as described above.

Recovery of lead from the lead sulphate filtrate. The combined filtrate and washings from the separation of lead sulphate were evaporated to dryness to remove sulphuric acid, then 10 ml of concentrated nitric acid and 25 ml of water were added and the solution was heated to dissolve the salts. The solution was diluted to ~ 150 ml with water and sufficient concentrated ammonia solution was added to precipitate hydrous ferric oxide, then several drops were added in excess followed by 20 ml of freshly prepared saturated ammonium carbonate solution. The solution was boiled for several minutes to coagulate the hydrous ferric oxide–lead carbonate precipitate, which was then filtered off on Whatman No. 541 paper, and the beaker, and paper plus precipitate, were washed 3 and 4 times, respectively, with hot water. The filtrate and washings were discarded. The bulk of the precipitate was transferred to the original beaker with a jet of water, and 10 ml of concentrated nitric acid were added to dissolve it. The solution was filtered through the original filter paper into a 200-ml volumetric flask, the beaker and the paper were each washed twice with small portions of hot 10% v/v nitric acid and then once with water. The paper was discarded, the solution was diluted to volume with water, and the lead was determined by atomic-absorption spectrophotometry (AAS).

Recovery of lead from the filter paper after separation and dissolution of lead sulphate. The filter paper containing the acid-insoluble material remaining after the dissolution of lead sulphate was transferred to a covered 250-ml beaker, 10 ml each of concentrated nitric and perchloric acids were added, the mixture was heated to decompose the paper, and the solution was evaporated to dryness. Five ml of concentrated nitric acid and 25 ml of water were added, then the solution was heated to dissolve the soluble salts and diluted to ~ 100 ml with water. After the addition of 1 ml of 20% ferric nitrate (9-hydrate) solution as a collector for lead, hydrous ferric oxide and residual lead were precipitated and the lead determined (100-ml final volume) by AAS as described above.

Recovery of lead from the lead chromate filtrate. The combined filtrate and washings obtained after the separation of lead chromate were allowed to stand for 24 hr, then filtered through Whatman No. 42 paper and the beaker washed once with a small portion of water. The sides of the beaker were washed down with ~ 20 ml of 25% v/v nitric acid to dissolve any residual lead chromate, and the solution was poured into the filter paper and collected in a 50-ml volumetric flask. The beaker and paper were each washed with small portions of water, the solution was diluted to volume with water and lead determined by AAS.

Molybdate Method

Standardization of ammonium molybdate solution

Three aliquots of standard lead solution, containing approximately the same amount of lead as would be derived from samples of the ore to be analysed, were transferred to 400-ml beakers, 15 ml of 50% v/v sulphuric acid were added and the solutions evaporated to fumes of sulphur trioxide twice, the sides of the beaker being washed down with water each time, to remove nitric acid, and then to dryness to remove sulphuric acid. Ten ml of ammonium acetate–acetic acid solution were added, the beaker was covered, the solution diluted to ~ 150 ml with water, and boiled until all the lead sulphate had dissolved. The hot solution was titrated with ammonium molybdate solution, with freshly prepared 0·5% tannic acid solution as external indicator, until a drop of solution turned a drop of tannic acid solution yellow. The "true" lead equivalent of the ammonium molybdate solution was calculated from the mean.

The ammonium molybdate solution was also standardized with four aliquots (same as above) of standard lead solution which were evaporated to fumes of sulphur trioxide, as described under "standardization of thiosulphate", and carried through the procedure described below. The "apparent" lead equivalent of the solution was calculated from the mean.

Procedure

Following sample decomposition and dissolution of the salts as described for the chromate method, a small amount of filter pulp (~ 1/8 of a tablet) was added, the solution was cooled in an ice-bath for 45 min and the lead sulphate *etc.* was filtered off on Whatman No. 42 paper. The beaker was washed 3 times with cold 1% v/v sulphuric acid, the paper plus precipitate were washed once with the same solution, then the beaker and precipitate were each washed once with cold 1% v/v methanol.

The precipitate was transferred to the original beaker with a jet of water and the paper was shredded and added to the beaker. A small piece of moistened filter paper was used to clean the funnel and added to the beaker containing the lead sulphate. After addition of 10 ml of ammonium acetate–acetic acid solution and dilution to ~ 150 ml with water, the beaker was covered, the solution boiled for at least 20 min to ensure complete dissolution of the lead sulphate, then the solution was titrated as described above.

Recovery of lead from the filtrate. The combined filtrate and washings were evaporated to dryness to remove sulphuric acid, and lead was separated as the carbonate and determined by AAS as above.

ASTM (E-16) EDTA Method

Standardization of EDTA solution

Three aliquots of standard lead solution, containing approximately the same amount of lead as would be derived from samples of the ore to be analysed, were treated as described under "standardization of molybdate". Fifty ml of hydrochloric acid–sodium chloride solution were added, the solution was heated to boiling and boiled gently for 3–5 min to ensure complete dissolution of lead sulphate. After cooling to room temperature, 3 drops of concentrated fluoboric acid, 2 ml of freshly prepared 2·5% ascorbic acid solution and 6 drops of 0·2% Xylenol Orange solution were added, with stirring after each addition, then ~ 1-g portions of hexamine were added until the solution turned pale purple. The solution was titrated with EDTA solution, more hexamine being added as the colour began to fade. Near the end-point, 2 g of hexamine were added and the solution was titrated to a pure yellow. The "true" lead equivalent of the EDTA solution was calculated from the mean.

The EDTA solution was also standardized with four aliquots (same as above) of standard lead solution which were evaporated to fumes of sulphur trioxide, as described under "standardization of thiosulphate", and carried through the procedure described below. The "apparent" lead equivalent of the solution was calculated from the mean.

Procedure

Following sample decomposition as described above, 150 ml of water and 3 or 4 drops of 30% hydrogen peroxide solution were added and the solution was boiled vigorously for 10–15 min to destroy the excess of peroxide and dissolve the soluble salts. A small amount of filter paper pulp was added and the lead sulphate (and insoluble material) was filtered off as in the molybdate method. The beaker, and the paper plus precipitate, were each washed twice with 0·5% v/v sulphuric acid–1% sodium sulphate solution, then the beaker and precipitate were each washed once with cold water.

The precipitate and paper were transferred to the original beaker, as described above, 50 ml of hydrochloric acid–sodium chloride solution were added, the solution was boiled to dissolve the lead sulphate and subsequently titrated as described above.

The lead in the filtrate was recovered and determined as before.

NaDDTC–EDTA Method

Standardization of EDTA solution

Three 15-ml portions of standard lead solution were transferred to 250-ml beakers, 5 ml of concentrated perchloric acid were added to each and the solutions evaporated to dryness to remove the nitric and perchloric acids. Ten g of ammonium chloride and ~100 ml of water were added and the solution was heated to dissolve the lead salts. After addition of 30 ml of pH-6 acetate buffer solution, the solution was cooled to room temperature, then the pH was adjusted to 5·8–6·0 (pH-meter) with concentrated and 10% v/v ammonia solutions and 10% v/v hydrochloric acid, if necessary. Six drops of 0·2% Xylenol Orange solution were added and the solution was titrated with EDTA solution. Near the end-point the pH of the solution was re-adjusted, if necessary, to 5·0–5·5 with 10% ammonia solution and the titration was continued to a pure yellow end-point. The lead equivalent of the EDTA solution was calculated from the mean.

Procedure

Following sample decomposition as described above, 25 ml of water were added to the sample solution and it was heated to dissolve the soluble salts. After addition of 20 ml of 20% tartaric acid solution, the solution was cooled to room temperature, 30 ml of concentrated ammonia solution were added (carefully to avoid spattering) and the solution was allowed to stand for several hr to ensure the complete dissolution of lead sulphate. The pH was adjusted to 10·0 ± 0·1 (pH-meter) with concentrated ammonia solution, 10 ml were added in excess and the whole was transferred to a 250-ml separatory funnel. After addition of 30 ml of freshly prepared 20% potassium cyanide solution, the solution was allowed to stand for at least 5 min to ensure complete complexation of copper, zinc, iron and other interfering elements. Sufficient 5% NaDDTC solution was added, during three extraction stages, to ensure the complete precipitation of lead (4, 3 and 2 ml for KC-1, and 2, 1 and 0·5 ml for MP-1) and the lead complex was extracted by shaking for ~1 min each time, first with 15 ml, then with 10-ml portions of chloroform. The aqueous phase was washed by shaking for ~30 sec with 10 ml of chloroform, then the combined extracts were washed by shaking them in a 125-ml separatory funnel for ~30 sec with 10 ml of tartaric acid–potassium cyanide wash solution, containing 1 ml of 5% NaDDTC solution, to remove co-extracted interfering elements. The chloroform phase was drained into a 250-ml beaker and the aqueous layer washed 3 times by shaking for ~15 sec each time with 5-ml portions of chloroform. Ten ml each of water and concentrated nitric acid were added to the combined chloroform phases and the chloroform was removed by evaporation in a hot water-bath. After the addition of 10 ml of concentrated perchloric acid, the solution was covered and boiled to destroy organic material, then carefully evaporated to dryness to remove the nitric and perchloric acids. If organic material was still present, the residue was again treated with 10 ml each of concentrated nitric and perchloric acids and the solution boiled and evaporated to dryness. Following the addition of 10 g of ammonium chloride and 100 ml of water, the dissolution of the lead salts, and the addition of 30 ml of pH-6 acetate buffer solution, the solution was titrated as described above.

Modified NaDDTC–EDTA Method

Procedures for the separation of indium and bismuth

The following procedures were employed for the separation of indium and bismuth in MP-1 because it is known that they interfere in the determination of lead by the NaDDTC–EDTA method.

Separation of indium. After extraction of the lead diethyldithiocarbamate complex and evaporation of the final solution to dryness, 25 ml of 6*M* (~68%) hydrobromic acid were added to the residue and the solution was heated gently, if necessary, to dissolve the salts. The solution was transferred to a 125-ml separatory funnel and diluted to 50 ml with 6*M* hydrobromic acid. Fifty ml of pre-equilibrated di-isopropyl ether were added and the funnel was shaken for 2 min. The aqueous phase containing the lead was drained into a second 125-ml separatory funnel, the stem of the first funnel was washed with 6*M* hydrobromic acid (from a plastic wash-bottle), and the remaining indium was extracted as described above with a second 50-ml portion of the ether. The aqueous phase was drained into a 400-ml beaker and the stem of the funnel was washed with water. The ether in the first funnel was added to that in the second, and the first funnel was washed 3 times with 5-ml portions of 6*M* hydrobromic acid. The washings were drained into the second funnel, which was shaken for ~15 sec, and the aqueous phase was then added to the beaker. The ether phase was washed twice more with 5-ml portions of 6*M* hydrobromic acid, then the combined aqueous phases were heated gently to remove the residual ether. Five ml of concentrated perchloric acid were added and the solution was evaporated to dryness to remove the hydrobromic and perchloric acids.

Separation of bismuth. Ten g of ammonium chloride, 1 ml of 20% tartaric acid solution and ~100 ml of water were added to the residue obtained as just described and the solution was heated to dissolve the salts. After addition of 25 ml of concentrated hydrochloric acid, the solution was cooled to room temperature, transferred to a 250-ml separatory funnel, and diluted to ~150 ml with water. Fifteen ml of chloroform were added, followed by 3 ml of freshly prepared 5% potassium ethyl xanthate solution, and the yellow bismuth complex was extracted immediately (because of its instability) by shaking for ~1 min. The chloroform phase was discarded. The solution was

Table 4. Results obtained for KC-1 and MP-1 by the chromate method

	Pb found, %					
Sample	By standardization *vs.* potassium dichromate	In initial filtrate after lead sulphate separation	In paper and residue after lead sulphate separation	In filtrate after lead chromate separation	Total % Pb	By standardization *vs.* lead carried through procedure
KC-1 1	6·95$_2$	0·060	0·010	0·011	7·03$_3$	7·01$_4$
2	6·85$_4$	0·071	0·010	0·009	6·94$_4$	6·91$_6$
3	6·92$_7$	0·063	0·010	0·009	7·00$_9$	6·99$_0$
4	6·92$_0$	0·066	0·010	0·010	7·00$_6$	6·98$_3$
5	6·87$_2$	0·067	0·009	0·016	6·96$_4$	6·93$_4$
Mean					6·99$_1$	6·96$_7$
Standard deviation, %					0·036	0·041
Overall mean					6·97$_9$	
95% Confidence limits*					6·95$_2$–7·00$_7$	
MP-1 1	1·84$_0$	0·032	0·003	0·014	1·88$_9$	1·89$_4$
2	1·85$_0$	0·030	0·003	0·011	1·89$_4$	1·90$_5$
3	1·86$_1$	0·031	0·003	0·010	1·90$_5$	1·91$_5$
4	1·86$_1$	0·029	0·002	0·010	1·90$_2$	1·91$_5$
5	1·81$_4$	0·034	0·003	0·014	1·86$_5$	1·86$_7$
Mean					1·89$_1$	1·89$_9$
Standard deviation, %					0·016	0·020
Overall mean					1·89$_5$	
95% Confidence limits*					1·88$_3$–1·90$_8$	

* Calculated for all 10 results.

extracted three more times with 10 ml of chloroform and 0·5 ml of xanthate solution each time. The aqueous phase was drained into a 400-ml beaker, heated gently to remove the residual chloroform and evaporated to ~100 ml. Fifteen ml each of concentrated nitric and perchloric acids were added, the beaker was covered and the solution boiled to destroy the organic material and ammonium salts, then evaporated to ~75 ml. The solution was boiled with a further 15-ml portion of concentrated nitric acid, then carefully evaporated to dryness in an aluminium (beaker-style) evaporator to remove the nitric and perchloric acids. After addition of 10 g of ammonium chloride and 100 ml of water, dissolution of the lead salts, and addition of 30 ml of pH-6 acetate buffer solution, the solution was titrated as described above.

RESULTS AND DISCUSSION

The results obtained for lead in KC-1 and MP-1 by the four titrimetric methods are shown in Tables 4–7. No difficulties were encountered in applying the EDTA methods to the analysis of the certified ores. However, in initial tests with the chromate method,[6] in which filter paper (Whatman No. 42) was used for the filtration of the lead chromate precipitate, a considerable and variable amount of precipitate (equivalent to 0·3–1·1 mg of lead) was lost because of its tendency to creep up the sides of the funnel and then be washed down behind the paper during the washing stage. Further work showed that lead chromate was also lost during filtration, by suction, through a fine-porosity porcelain crucible. When a fine-porosity crucible containing a pad of filter paper pulp was used the loss of lead was 0·09–0·16 mg. In initial tests with the molybdate method[4,5] no end-point could be obtained with tannic acid as indicator when the recommended concentration of ammonium molyb-

Table 5. Results obtained for KC-1 and MP-1 by the molybdate method

	Pb found, %			
Sample	By standardization *vs.* pure lead	In initial filtrate after lead sulphate separation	Total % Pb	By standardization *vs.* lead carried through procedure
KC-1 1	6·97$_0$	0·058	7·02$_8$	7·04$_8$
2	6·90$_2$	0·060	6·96$_2$	6·97$_8$
3	6·93$_6$	0·063	6·99$_9$	7·01$_3$
4	6·87$_2$	0·060	6·93$_2$	6·94$_8$
5	6·83$_3$	0·061	6·89$_4$	6·90$_9$
Mean			6·96$_3$	6·97$_9$
Standard deviation, %			0·053	0·054
Overall mean			6·97$_1$	
95% Confidence limits*			6·93$_4$–7·00$_8$	
MP-1 1	1·85$_3$	0·037	1·89$_0$	1·88$_6$
2	1·91$_6$	0·036	1·95$_2$	1·94$_9$
3	1·90$_4$	0·037	1·94$_1$	1·93$_7$
4	1·88$_2$	0·035	1·91$_7$	1·91$_5$
5	1·92$_0$	0·036	1·95$_6$	1·95$_4$
Mean			1·93$_1$	1·92$_8$
Standard deviation, %			0·028	0·028
Overall mean			1·93$_0$	
95% Confidence limits*			1·91$_1$–1·94$_8$	

* Calculated for all 10 results.

Table 6. Results obtained for KC-1 and MP-1 by the ASTM (E-16) EDTA method

	Pb found, %			
Sample	By standardization *vs.* pure lead	In initial filtrate after lead sulphate separation	Total % Pb	By standardization *vs.* lead carried through procedure
KC-1 1	6·97$_9$	0·073	7·05$_2$	7·04$_3$
2	6·95$_8$	0·085	7·04$_3$	7·02$_2$
3	6·95$_6$	0·080	7·03$_6$	7·02$_0$
4	6·99$_9$	0·071	7·07$_0$	7·06$_4$
5	6·97$_4$	0·086	7·06$_0$	7·03$_9$
Mean			7·05$_2$	7·03$_8$
Standard deviation, %			0·013	0·018
Overall mean			7·04$_5$	
95% Confidence limits*			7·03$_3$–7·05$_7$	
MP-1 1	1·93$_0$	0·037	1·96$_7$	1·96$_0$
2	1·91$_1$	0·037	1·94$_8$	1·94$_1$
3	1·94$_2$	0·037	1·97$_9$	1·97$_3$
4	1·94$_2$	0·036	1·97$_8$	1·97$_3$
5	1·90$_0$	0·041	1·94$_1$	1·93$_1$
Mean			1·96$_3$	1·95$_6$
Standard deviation, %			0·017	0·019
Overall mean			1·96$_0$	
95% Confidence limits*			1·94$_7$–1·97$_2$	

* Calculated for all ten results.

Table 7. Results obtained for KC-1 and MP-1 by the NaDDTC–EDTA method

Sample	Pb found, %, by standardization *vs.* pure lead KC-1	MP-1
1	6·98$_4$	2·02$_9$
2	6·97$_0$	2·02$_7$
3	6·95$_8$	2·02$_2$
4	6·96$_6$	2·02$_7$
5	6·95$_2$	2·02$_7$
Mean	6·96$_6$	2·02$_6$
Standard deviation, %	0·012	0·003
95% Confidence limits	6·95$_1$–6·98$_1$	2·02$_3$–2·03$_0$

date was used (*i.e.*, 1 ml ≡ 5 mg of lead). Even with double the concentration the end-point was rather indistinct.

Table 8 shows that only the molybdate method gives really good agreement with the recommended values for both ores. Tables 4–6 show that the solubility losses inherent in the first three methods during the separations of lead are a significant source of negative error if the titrant is standardized directly against pure potassium dichromate in the chromate method and against pure lead in the other methods. The relative error is substantially greater for MP-1 than for KC-1 because of its lower lead content. In most cases, the precision is slightly poorer when the titrant is standardized against pure lead carried through the procedure in order to cancel out solubility losses, because the amount of lead remaining in the lead sulphate filtrate is not constant. This is why, in the evaluation tests, four aliquots of standard lead solution, containing approximately the same amount of lead as would be derived from the ore samples, were carried through the procedure and averaged for standardization purposes.

Theoretically, the molybdate and ASTM EDTA methods are prone to positive error because of the co-precipitation or retention of sulphates and hydrolysis products of interfering elements (calcium, strontium, bismuth, antimony, silver, copper, iron and zinc)[10–12] and the subsequent co-titration of these elements.[4,13,14] This readily explains the high results obtained for lead in both KC-1 and MP-1 by the ASTM EDTA method because large amounts of zinc and iron are present in both ores, and a relatively large amount of copper is present in MP-1 (Table 3). Similarly, the higher result obtained for MP-1 by the molybdate method than by the chromate method could be due to the high calcium content of this ore. Retention of calcium sulphate with lead sulphate would result in the formation of insoluble calcium molybdate during the titration with ammonium molybdate solution.[13] Positive error due to retention of interfering elements with lead sulphate would not occur readily in the chromate method because of the additional separation of lead from interfering elements by precipitation as the chromate.

Table 8. Correlation of overall mean lead results for KC-1 and MP-1 with the titrimetric method employed

Method	Overall mean lead results, % KC-1	MP-1
Chromate	6·97$_9$	1·89$_5$
Molybdate	6·97$_1$	1·93$_0$
ASTM (E–16) EDTA	7·04$_5$	1·96$_0$
NaDDTC–EDTA	6·96$_6$	2·02$_6$
CCRMP recommended value	6·98	1·93

The high result obtained for MP-1 by the NaDDTC–EDTA method (Table 7) is caused by the presence of bismuth and indium in this ore. These elements are completely co-extracted with the lead as diethyldithiocarbamate complexes from ammoniacal potassium cyanide media (pH 10) and, because of hydrolysis, are subsequently only partly co-titrated with EDTA.[8,9] When bismuth and indium are not present, this method is considered to be the best of the methods evaluated because it is based on complete separation and titration of lead. For this reason, an attempt was made to modify the method to obviate the interference of indium and bismuth. A search of the literature did not reveal any method for the simultaneous separation of indium and bismuth from lead, but it is known that indium can readily be separated from lead by ether extraction of its bromo-complex from 4–6*M* hydrobromic acid media.[15,16] Although bismuth and lead can be determined in the same solution by successive titration with EDTA at pH 2 and 5·5 with Xylenol Orange as indicator,[8] the author experienced difficulty in determining the end-point for the bismuth titration and did not pursue this approach. It is known that bismuth can be extracted as the xanthate complex from acidic media.[17,18] Tests (Table 9) showed that bismuth can be separated from lead by chloroform extraction of its xanthate from ~2*M* hydrochloric acid–tartaric acid media, and confirmed that indium can be separated from lead by di-isopropyl ether extraction of its bromo-complex from 6*M* hydrobromic acid media.[16]

Table 10 shows the results obtained for MP-1 by the NaDDTC–EDTA method modified for separation of indium and bismuth. The mean value is lower than the recommended value but in reasonably good agreement with that obtained by the chromate method and the mean value obtained by Laboratory

Table 9. Recovery of lead in synthetic solutions after the separation of indium and bismuth by extraction as the bromo- and xanthate-complexes, respectively

Pb taken, *mg*	In taken, *mg*	Bi taken, *mg*	Pb found, *mg*
10·58	4·97	—	10·68
21·15	4·97	—	21·12
42·30	4·97	—	42·36
84·60	4·97	—	84·62
10·58	—	4·62*	10·60
21·15	—	4·62*	21·34
42·30	—	4·62*	42·28
84·60	—	4·62*	84·57

* Bismuth extracted in five stages using 3, 3, 2, 0·5 and 0·5 ml of 5% potassium ethyl xanthate solution, respectively.

Table 10. Results obtained for MP-1 by the modified NaDDTC–EDTA method after the separation of indium and bismuth

Sample	Pb found, %, by standardization *vs.* pure lead
1	$1{\cdot}86_7$
2	$1{\cdot}89_6$
3	$1{\cdot}88_4$
4	$1{\cdot}88_6$
5	$1{\cdot}88_4$
Mean	$1{\cdot}88_3$
Standard deviation, %	0·010
95% Confidence limits	$1{\cdot}87_0$–$1{\cdot}89_6$

12 (Table 2). This laboratory also used a modification of the NaDDTC–EDTA method in which indium was separated from lead by butyl acetate extraction from 5*M* hydrobromic acid, followed by titration of bismuth at pH 2 and lead at pH 5·5.[19] Laboratory 12 also obtained a mean value of $1{\cdot}88_9\%$ for lead in MP-1 by atomic-absorption spectrophotometry (Table 2), and a mean value of $6{\cdot}96_7\%$ for lead in KC-1 (Table 1) by the NaDDTC–EDTA method. The latter value is in excellent agreement with the recommended value and the mean value obtained during the evaluation of this method (Table 7).

The foregoing results suggest that the recommended value for lead in MP-1 (1·93%) may be too high. This is also indicated by the results of a test in which a solution containing the same amounts of lead, bismuth and indium that are present in 2 g of MP-1 was titrated with standard EDTA solution to determine the approximate magnitude of the positive error due to bismuth and indium in the results shown in Table 7. Direct calculation of this error on the basis of the lead equivalents of the bismuth and indium present in the sample (Table 3) is not feasible because some hydrolysis of indium and particularly of bismuth occurs under the conditions employed for the titration of lead. The results of this test showed that the positive error due to bismuth and indium was equivalent to 0·140% lead. Consequently, on the basis of the mean value (2·026%) obtained for lead in MP-1 by the NaDDTC-EDTA method in the presence of bismuth and indium (Table 7), the value obtained after correcting for the positive error due to bismuth and indium ($1{\cdot}88_6\%$) is in good agreement with the mean value obtained (Table 10) after the separation of bismuth and indium.

CONCLUSIONS

This investigation has shown that the nature of the titrimetric method employed can cause a significant difference in the results obtained for lead. It is the author's opinion that the NaDDTC–EDTA method, modified, when necessary, to eliminate the interference of indium and/or bismuth, is the most satisfactory of the methods evaluated because it is based on complete separation of lead and direct standardization of the titrant against pure lead. Although this method is also subject to interference from thallium, which is co-extracted with lead as the diethyldithiocarbamate complex,[9] this element can be separated from lead in the same way as indium.[15] Moreover, the final titration procedure is superior to the ASTM procedure because sodium acetate has better buffering capacity than hexamine and because a sharper and more distinct end-point is obtained.

The molybdate and ASTM methods are not recommended for the exact, non-routine determination of lead in ores because these methods are prone to positive error resulting from the retention of interfering elements in the lead sulphate precipitate. Furthermore, the molybdate method is severely prone to "operator" error because of the difficult end-point. The high concentration of titrant required also causes error, when small or moderate amounts of lead are to be determined, because of the small volume needed.

Although the chromate method, as do the molybdate and ASTM methods, involves the incomplete separation of lead as the sulphate, further separation of lead from most of the interfering elements that are retained with the lead sulphate precipitate (with the exception of barium) is achieved during the subsequent precipitation of lead as the chromate. This method is recommended for the non-routine determination of lead in ores, if the titrant is standardized directly against pure potassium dichromate, and if the residual lead remaining in the filtrates and in the filter paper is determined by atomic-absorption spectrophotometry and appropriate corrections are made. The recovery and determination of the residual lead can be facilitated by combining all of the solutions obtained after the treatment of the filtrates and paper as described under "chromate method" and subsequently separating the lead as the carbonate.

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QUANTITATIVE SEPARATION OF GOLD FROM CADMIUM, INDIUM, ZINC AND OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN HYDROCHLORIC ACID–ACETONE MEDIUM

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Summary—Gold(III) can be separated from Cd, In, Zn, Ni, Cu(II), Mn(II), Co(II), Mg, Ca, Al, Fe(III), Ga and U(VI) by adsorbing these elements on a column of AG50W-X8 sulphonated polystyrene cation-exchange resin from 0·1*M* HCl containing 60% v/v acetone, while Au(III) passes through and can be eluted with the same reagent. Separations are sharp and quantitative. The amounts of gold retained by the resin are between 1 and 2 orders of magnitude lower than encountered during adsorption from aqueous 0·1*M* HCl. Recoveries for mg amounts of gold are 99·9% or better and for ng amounts are still better than 99%, as shown by radioactive tracer methods. Hg(II), Bi, Sn(IV), the platinum metals and some elements which tend to form oxy-anions in dilute acid accompany gold. All other elements, though not investigated in detail, should be retained, according to their known distribution coefficients. Relevant elution curves, results of quantitative separations of binary mixtures and of recovery tests are presented.

It has been shown that gold can be eluted from a column containing a sulphonated polystyrene cation-exchange resin by aqueous 0·2*M* hydrochloric acid and thus separated from cadmium which is retained under these conditions.[1] The separation is not quite quantitative, and μg amounts of gold are retained on a column of 30 ml of AG50W-X8 resin when 100 ml of gold(III) chloride solution in 0·1*M* hydrochloric acid containing 100 mg of gold are passed through it and the gold is eluted with another 300 ml of aqueous 0·1*M* hydrochloric acid.[2] When only μg amounts of gold are present a considerably larger fraction of the total gold can be retained. Pitts and Beamish[3] have investigated the separation of gold(III) from base metals in chloride solution and found that substantially low recoveries of gold occur when the base metal chloride concentration is above 0·05*M*. Losses are of the order of several per cent of the total gold present. Even at the lower base metal concentrations suggested by the authors, gold recoveries, according to their results, tend to be low by a few tenths of a per cent. Kutil and Čůta[4] also found that a small fraction of the gold(III) present is retained on a cation-exchange resin after elution with dilute hydrochloric acid. On the other hand, when gold is passed through a cation-exchange column in 0·2*M* hydrochloric acid containing 90% v/v acetone, the amount of gold retained becomes negligible (<0·5 μg out of 100 mg).[2] Apparently an association complex between $HAuCl_4$ and acetone is formed which tends to remain in the acetone-rich phase outside the resin particles, thus preventing interaction between gold(III) and the resin. Cadmium and indium are eluted together with gold(III) under these conditions. Toerien and Levin[5] have separated gold(III) and platinum metals from base metals by elution with 0·1*M* hydrobromic acid containing 60% v/v tetrahydrofuran from AG50W-X8 cation-exchange resin. Cadmium and indium were not included in their study. Cadmium will probably accompany gold(III). The distribution coefficient of cadmium in 0·1*M* hydrobromic acid containing 60% v/v acetone is 7·1,[6] and that in 0·1*M* hydrobromic acid containing 60% v/v tetrahydrofuran should not be greatly different, because the distribution coefficients of elements in mixtures of hydrobromic acid with these two solvents are very similar.[7] For retention of cadmium, hydrochloric acid would be preferable to hydrobromic acid as the medium because the chloride complexes of cadmium are less stable than the bromide complexes. In 0·1*M* hydrochloric acid containing 90% v/v acetone the distribution coefficient of cadmium is only 2·1,[2] but when the acetone concentration is decreased to 60% the coefficient increases to 93, while that for gold remains less than 1.[2] This seems to offer prospects for a good separation provided the amounts of gold retained by the column remain negligible at the lower acetone concentration. The quantitative aspects of this separation have not received attention and therefore were investigated in detail.

EXPERIMENTAL

Reagents and apparatus

Chemicals used were of analytical-grade purity. Water was distilled and then passed through an Elgastat deminer-

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alizer. The resin was the AG50W-X8 sulphonated polystyrene cation-exchanger of 200–400 mesh particle size (Bio-Rad Laboratories, Richmond, California). Resin used for column work was stirred in a beaker with 0·1*M* hydrochloric acid containing 60% v/v acetone and the slurry transferred to the column with the same reagent.

Borosilicate glass tubes of either 21 or 15 mm bore with fused-in glass sinters of No. 2 porosity and a burette tap at the bottom, and either a B19 or a B14 ground-glass joint at the top, were used for making the columns.

Atomic-absorption measurements were carried out either with a Perkin-Elmer 303 or with a Varian-Techtron AA-5 instrument, and for spectrophotometric determinations a Zeiss PMQ II spectrophotometer was used.

Elution curves

Fifty ml of a solution containing 0·25 mmole of gold(III) chloride and 1 mmole of cadmium chloride in 0·10*M* hydrochloric acid containing 60% v/v acetone were passed through a 30-ml column containing 10 g of AG50-X8 resin (200–400 mesh). The resin column was 15 cm long and 1·5 cm in diameter and had been equilibrated by passage of 50 ml of 0·1*M* hydrochloric acid containing 60% v/v acetone (*i.e.*, 0·25*M* aqueous hydrochloric acid mixed with acetone in a volume ratio of 2:3, disregarding volume changes during mixing). The elements were washed onto the column with 3 portions of about 10 ml of the same solution, the solution being drained to the top of the resin bed after each washing. Elution was then carried out with the same solution with a flow-rate of 2·0 ± 0·3 ml/min. Fractions of 25 ml were taken with an automatic fractionator from the beginning of the adsorption step and, after evaporation to remove acetone and suitable dilution with 0·1*M* hydrochloric acid, the amounts of the elements in the fractions were determined by atomic-absorption spectrometry using an air–acetylene flame and the 242·3 and 228·8 nm lines for gold and cadmium respectively. The experimental elution curve is shown in Fig. 1.

Figure 2 shows an elution curve for the Au(III)–In pair, obtained by using the same column and similar experimental conditions. Other elements such as Zn, Cu(II), Co(II), Ni, Mn(II), Mg, Ca, Al, Ga, U(VI) and Fe(III) are more strongly retained than indium and are not eluted in the first 1200 ml of eluate from a 30-ml resin column. When the column size was increased to 60 ml (20 g of resin) no cadmium or indium was found in the first 1000 ml of elutate when 1 mmole of either of these elements was present. Figure 3 shows an elution curve for the Au(III)–Cd pair with a column 20 cm in length and 2·0 cm in diameter, containing 20 g of resin. The flow-rate was 3·0 ± 0·3 ml/min in this case and elution with 0·1*M* hydrochloric acid containing 60% v/v acetone was interrupted after 400 ml had been passed. The cadmium was then eluted with 0·2*M* hydrobromic acid containing 50% v/v acetone.

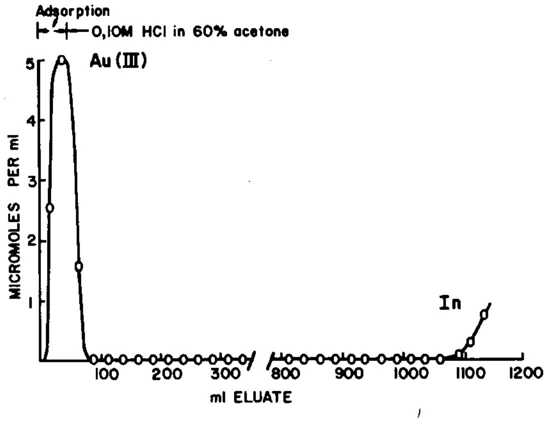

Fig. 2. Elution curve for Au(III)–In with 0·10*M* HCl in 60% v/v acetone. Column (15 × 1·5 cm), AG50W-X8 resin, 200–400 mesh. Flow-rate 2·0 ± 0·3 ml/min.

Retention of gold on the resin

About 50 mg of gold(III) as the chloride in 50 ml of 0·1*M* hydrochloric acid containing 60% v/v acetone were passed through a column containing 20 g of resin as described above. The gold was washed onto the resin and eluted with 300 ml of 0·1*M* hydrochloric acid containing 60% v/v acetone. The resin was then removed from the column and ashed in a new silica dish which had been cleaned by boiling in *aqua regia*. Ashing was carried out at low temperature (about 500°) initially, the temperature being finally increased to 650°. The ash was dissolved in *aqua regia* and the solution after evaporation to a small volume was transferred into a 50-ml beaker. It was evaporated almost to dryness, a few drops of nitric acid being added a few min before the evaporation was stopped, and made up to 5 ml with 1*M* hydrochloric acid in a volumetric flask. The amount of gold was then determined by atomic-absorption spectrometry using an air–acetylene flame, the 242·3 nm line and scale expansion. A similar experiment was carried out with a gold(III) solution in 0·1*M* aqueous hydrochloric acid and eluting with 300 ml of 0·1*M* aqueous hydrochloric acid. The results are shown in Table 1.

Quantitative separation of gold(III) from binary mixtures

Suitable aliquots of a standard solution of gold(III) chloride in dilute hydrochloric acid and of one other element were measured out and mixed. The mixtures were

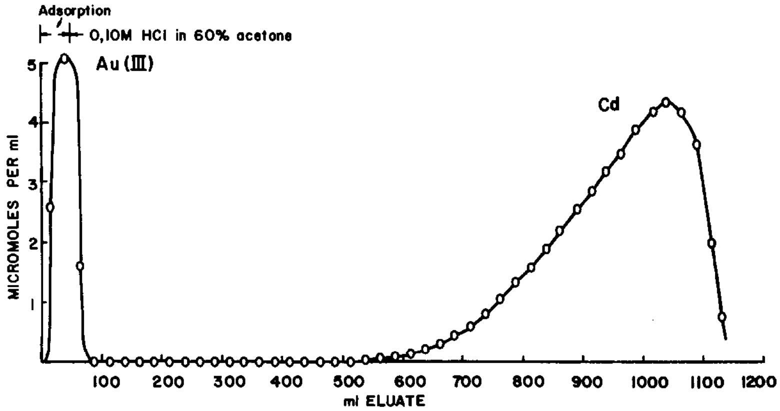

Fig. 1. Elution curve for Au(III)–Cd with 0·10*M* HCl in 60% v/v acetone. Column (15 × 1·5 cm), AG50W-X8 resin, 200–400 mesh. Flow-rate 2·0 ± 0·3 ml/min.

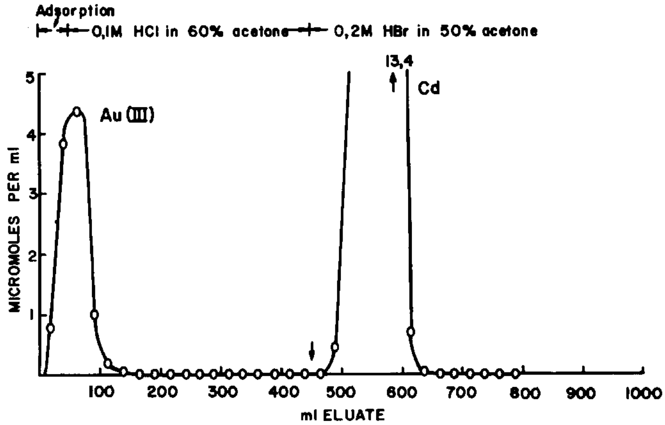

Fig. 3. Elution curve for Au(III)–Cd. Column (19 × 2·0 cm), AG50W-X8 resin, 200–400 mesh. Flow-rate 3·0 ± 0·3 ml/min.

Table 1. Amount of gold retained by resin

0·1*M* aqueous HCl Column no.	Au, μg	0·1*M* HCl in 60% acetone Column no.	Au, μg
1	13·3	4	$0{\cdot}4_0$
2	8·4	5	$0{\cdot}4_8$
3	17·1	6	$0{\cdot}2_8$

adjusted to contain 0·1*M* hydrochloric acid and 60% v/v acetone (volume of about 150 ml) and were passed through columns containing 20 g of AG50W-X8 resin (200–400 mesh). When 5 g of gold were present the solutions were adjusted to a volume of about 500 ml before being passed through the columns. The columns were 20 cm in length and 2·0 cm in diameter and had been equilibrated by passage of 50 ml of the eluting agent. Gold(III) was then eluted with 300 ml of 0·1*M* hydrochloric acid containing 60% v/v acetone, followed by the elution of the other element with 300 ml of 1·0*M* hydrochloric acid in the case of Cd and In and 300 ml of 3·0*M* hydrochloric acid in the case of Zn, Cu(II) and other elements. The flow-rate was 3·0 ± 0·5 ml/min. The gold(III) and "other element" fractions were collected separately, the effluent from the adsorption step being included in the gold(III) fraction, and after evaporation to dryness on the water-bath the amounts of the elements in the fractions were determined (Table 2). The results of the analyses are presented in Table 3.

Table 2. Analytical methods used

Element	Method
Au	Gravimetrically as the metal after precipitation with SO_2. Small amounts by atomic-absorption spectrometry.
Cd	Complexometrically with EDTA in slight excess of ammonia with Methylthymol Blue as indicator. Small amounts by atomic-absorption spectrometry.
In, Ga, Fe(III), Al	Complexometrically with DCTA; back-titration with $ZnSO_4$ at pH 5·5 with Xylenol Orange as indicator. Small amounts of indium by atomic-absorption spectrometry.
Zn	Complexometrically with EDTA at pH 5·5 with Xylenol Orange as indicator.
Co(II)	Complexometrically with EDTA, Naphthyl Azoxine S as indicator at pH 6 (pyridine buffer).
Ni	Complexometrically in slight excess of ammonia with EDTA; Murexide as indicator.
Cu(II)	Complexometrically with EDTA, Methylthymol Blue in presence of trace of 1,10-phenanthroline as indicator at pH 5.
Ca, Mn(II)	Complexometrically with EDTA in presence of excess of ammonia, Methylthymol Blue as indicator. Hydroxylamine hydrochloride present for Mn(II)
Mg	Complexometrically with EDTA at pH 10 with Eriochrome Blueblack B as indicator.
U(VI)	Gravimetrically as U_3O_8 after precipitation with CO_2-free ammonia.

Separation of nanogram amounts of gold(III)

Triplicate 1-g samples of the standard granite rock NIM-G were weighed out accurately and dissolved as described previously.[8] To the resulting solution were added 5 ml of a solution containing a mixture of radioactive gold isotopes, mainly gold-196 (6·2 d) and gold-194 (39·5 hr). These had been obtained by bombarding a target of pure platinum with 16-MeV deuterons in the cyclotron of the NPRL in Pretoria and separating gold from platinum by solvent extraction as chloride into ethyl acetate. The total amount of gold present was less than 500 ng originating from impurities in the platinum target (according to specifications) and 9 ng present in 1 g of granite as determined by neutron-activation analysis.[9] The solutions were adjusted to about 150 ml in volume, 0·1*M* in hydrochloric acid and 60% v/v in acetone concentration and gold was separated from the major rock-forming elements as described in the previous paragraph. The eluate was evaporated to dryness and the residue taken up in *aqua regia*. The resin was removed from the columns and ashed in silica dishes at low temperature after the rock-forming elements had been eluted, and the ash was dissolved in *aqua regia*. Undissolved material was fused with a small amount of potassium bisulphate before dissolution in dilute hydro-

Table 3. Results of analyses of synthetic mixtures

Taken			Found	
Au, *mg*	Other element (*mg*)		Au, *mg*	Other element *mg*
207·4	Cd	125·6	207·3 ± 0·2	125·6 ± 0·1
21·2	Cd	128·5	21·1 ± 0·1	128·5 ± 0·2
0·0488	Cd	254·6	0·0488 ± 0·0004	254·6 ± 0·1
200·4	Cd	12·90	200·3 ± 0·2	12·90 ± 0·01
411·5	Cd	0·114	411·3 ± 0·4	0·114 ± 0·001
5002	Cd	0·0238	5001 ± 1	0·0240 ± 0·0003
205·3	In	87·47	205·4 ± 0·1	87·53 ± 0·18
205·3	Zn	70·90	205·2 ± 0·2	70·93 ± 0·05
209·7	Ni	59·29	209·6 ± 0·1	59·29 ± 0·02
209·7	Cu(II)	64·12	209·6 ± 0·1	64·11 ± 0·02
0·0244	Cu(II)	1086	0·0242 ± 0·0004	1082 ± 2
208·5	Mn(II)	55·96	208·5 ± 0·1	55·97 ± 0·03
208·5	Co(II)	60·07	208·4 ± 0·2	60·06 ± 0·03
208·5	Mg	24·88	208·4 ± 0·1	24·88 ± 0·02
208·5	Ca	40·29	208·5 ± 0·2	40·30 ± 0·02
208·5	Al	28·12	208·6 ± 0·2	28·12 ± 0·02
208·5	Fe(III)	56·06	208·4 ± 0·1	56·07 ± 0·03
208·5	Ga	69·56	208·5 ± 0·1	69·55 ± 0·03
208·5	U(VI)	239·2	208·4 ± 0·2	239·1 ± 0·1

Table 4. Separation of nanogram amounts of gold

Taken (standard), *cps*	Eluting solution, *cps*	Resin ash, *cps*
513·9	508·1	1·6
518·6	508·2	1·4
505·4	507·7	1·0

chloric acid. The activity of the gold-containing fractions, the solutions of the ash and 3 solutions containing 5 ml of the radioactive gold standard, which had been measured out together with the solutions added to the dissolved rock samples, was then measured with a gamma-spectrometer under identical conditions (solution volume and counting position). Results are presented in Table 4.

RESULTS AND DISCUSSION

The method described provides a useful means for the separation of micro or macro amounts of gold from Cd, In, Zn, Ni, Cu(II), Mn(II), Co(II), Mg, Ca, Al, Fe(III), Ga, U(VI). Many other elements which have not been investigated in detail should also be separated according to their known distribution coefficients.[2] They include Be, Sr, Ba, Li, Na, K, Rb, Cs, Ti, Zr, Hf, Th, Sc, Y, lanthanides and Cr(III). The only species to accompany gold are the platinum metals, Hg(II), Bi(III), Sn(IV) and some of those elements which tend to form oxy-anions in dilute acids. The mixed-solvent eluting agent reduces the amount of gold retained by the resin by more than an order of magnitude (Table 1), while Cd and In are still retained. For large amounts of gold, recoveries are better than 99·9%, while even for ng amounts, 99% or more can be recovered (Table 4). In another experiment in which special precautions were taken to keep gold(III) in the oxidized state, only 0·1% of 500 ng of gold were found to be lost by adsorption on the resin and on the walls of beakers. When 5 g of gold were present (Table 3) 27·5 μg were found with the cadmium and 18·3 μg were found to be still on the column. Certain precautions always have to be taken to minimize losses of gold on the column. Evaporation in hydrochloric acid of high concentration reduces and precipitates gold. With small gold concentrations this is not visible. Solutions of gold in hydrochloric acid should therefore always be reoxidized after evaporation. The most convenient way is to add 5 or 6 drops of nitric acid to the last ml of hydrochloric acid which remains and heat the solution for several min before dilution and addition of acetone.

Separation of the other elements from gold is sharp and recoveries are quantitative. Cadmium is the most critical of the elements separated and shows fairly severe "heading" (Fig. 1), but the separation factor and distribution coefficient of cadmium are large enough to guarantee a quantitative recovery, provided a large enough column is used. No cadmium (<0·2 μg) was found in the gold-containing eluate after 48·8 μg of gold had been separated from 254·6 mg of cadmium on a 60-ml column. Smaller columns can be used when smaller amounts of cadmium are present. The separation of other elements is less critical and much smaller columns can be used for separating small amounts of Cu(II), Co(II), Mn(II), Ni, Zn, Fe(III) *etc.* from large amounts of gold.

The method is very well suited for the separation of small or trace amounts of many other elements from large amounts of gold. It is also quite useful for separating small amounts of gold from large amounts of other elements and in this respect compares quite well with a recently published method using DEAE-cellulose for the selective adsorption of gold.[10] The chloride concentration in the DEAE-cellulose method is limited to below 0·05*M*. This restricts the amounts of other elements from which the gold can be separated, because the distribution coefficient of gold is not very high (about 200 in 0·05*M* hydrochloric acid). Only a limited amount of solution therefore can be passed through a 1-g (about 15 ml) column before gold breaks through, and the 100-mg amounts of other elements separated from gold by Kuroda *et al.*[10] are near the maximum which a column of that size can handle. On a 60-ml column of AG50W-X8 resin, 1 g of Cu(II) (Table 3) and many other species can be retained, and a 90-ml column can quantitatively absorb more than 2 g of many ions. About 384 μg of Cu were found with the gold when about 1 g of Cu(II) was separated from 24·4 μg of Au(III), and no copper was found (<0·4 μg) when 1 mmole of copper was separated from 1 mmole of gold. The amount of Cu(II) passing through the column seemed to be much more dependent on the Cu(II) concentration during the adsorption step than on the total amount of Cu(II) present. Furthermore, in the cation-exchange separation the gold passes through the column directly, whereas it has to be eluted in the second step when DEAE-cellulose is used. In the cellulose method Se(IV) and, by a special extra step, also Pd(II), Pt(IV) and Hg(II), which accompany gold in the resin procedure, can be separated. The resin procedure, on the other hand, seems to be useful for the group separation of the precious metals Au, Pt, Pd, Ir and Rh from minerals and rocks, before their combined determination by sensitive methods such as spark-source mass-spectrometry or neutron-activation analysis.

An apparently very selective method for the separation of gold from other elements has been published by Fritz and Millen[11] who used an Amberlyst XAD-7 polyacrylic anion-exchanger. Indium has not been included in their investigation, but will probably also be separated. Unfortunately the quantitative investigations were carried out only on about 0·6-mg amounts of gold, and data on the quantitative analytical behaviour of large or very small amounts of gold were not included. However, in a patent it has been shown that about 100% recovery of gold can be obtained from $2{\cdot}79 \times 10^{-6}M$ solution, with the same resin.[12] The present method is more suitable for the separation of most elements in trace and ultratrace amounts from large amounts of gold. The method is also applicable to the separation of very small amounts of gold (< 1 μg), and is useful over a very wide concentration range of gold and other elements.

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TRACE METALS SPECIES IN SEA-WATER—I

REMOVAL OF TRACE METALS FROM SEA-WATER BY A CHELATING RESIN

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Summary—A significant fraction of the copper, lead, cadmium and zinc in sea-water exists in a form which is not retained by a chelating resin (Chelex-100) or extracted by ammonium pyrrolidinedithiocarbamate. Anodic stripping voltammetric results suggest that the major part of the unavailable trace metal is adsorbed on, or occluded in, organic or inorganic colloidal particles. An ionic equilibria computer program was used to predict the effect of various complexing agents on trace metal species in sea-water. Citric acid and amino-acids, with the exception of *l*-cysteine, were shown to be unimportant as complexing agents, and the ability of an EDTA-like ligand to complex Cu, Pb, Cd and Zn is controlled entirely by the concentrations of the ligand and of "labile" Fe(III) and Cr(III) in sea-water, since these two ions together will react quantitatively with EDTA. *l*-Cysteine, if present in sea-water, would also complex the trace metals.

Atomic-absorption spectrophotometry (AAS) is commonly used to determine many trace heavy metals in sea-water.[1] Because of interference by the sodium chloride matrix, and because their concentrations are too low for direct determination, the heavy metals must first be separated and concentrated from the sea-water sample.

Although liquid–liquid extraction of the trace metals by using a chelating agent such as ammonium pyrrolidinedithiocarbamate (APDC) often provides sufficient concentration for the non-flame AAS techniques, solvent extraction is inadequate for the less sensitive flame AAS methods. This is because the degree of extraction decreases as the aqueous-to-organic phase volume ratio is increased, effectively limiting the sample size which can be used, and the concentration factor which can be achieved.[1]

For this reason the application of chelating resins to sea-water analysis has become increasingly popular.[2–8] Chelating resins are simpler to use and less time-consuming than solvent extraction, and allow much higher concentration factors to be attained. In addition, the sample is not contaminated with heavy metal impurities from buffers and organic reagents. Most laboratories appear to use a chelating resin column in the manner originally described by Riley and Taylor,[2] *i.e.*, the sea-water at natural pH (pH 8·1) is passed through a 6 × 1·2 cm column of 50–100 mesh, hydrogen-form Chelex-100 resin. After passage of a sufficient volume of sea-water (1–10 litres), the adsorbed metals are eluted with a suitable solvent, usually 2*M* nitric acid. The nitric acid eluate is then analysed for trace metals directly, or after extraction.[6] Chelating resins have also been used by several workers for the preparation of "stripped" sea-water (*i.e.*, free from heavy metals) for productivity and other studies.[5,8]

Riley and Taylor[2] and later workers[5] checked the quantitative nature of adsorption of heavy metals from sea-water onto Chelex-100 resin, by spiking the sample with ionic radiotracers and measuring the activity of the effluent and eluent. Most metals were found to be quantitatively adsorbed at pH 8. This type of standard addition procedure using either active or inactive ionic tracers is commonly used for checking recoveries during the analysis of natural waters. The procedure, however, is prone to error because the heavy metal in the sample may not exist entirely in the free ionic form, but may be present partly as colloidal and/or complexed forms which will not equilibrate with the added ionic spike during the time of the separation experiment. In this case, measurement of the recovery of the spike will bear no relation to the recovery of the metal originally present in the water sample.

We have studied the retention of copper, lead, cadmium and zinc from sea-water on a column of Chelex-100 chelating resin by analysing the original sea-water and the column effluent for these metals, using direct anodic stripping voltammetry (ASV). Retention of the metals naturally present in sea-water was not quantitative.[9] We also did a few experiments to measure the efficiency of APDC extraction of these metals from sea-water. In addition, a computer study was made of the likely effect of several organic ligands on trace metal species in sea-water.

EXPERIMENTAL

Apparatus

The polarograph–voltammeter, used in conjunction with a Beckman electrode-rotator and a polished glassy-carbon electrode, has been described previously.[10] The hanging mercury-drop electrode assembly was used with a Princeton Applied Research Model 174 voltammeter.[11]

Table 1. Metal impurities in reagents used

Reagent	Impurity, μg/l.			
	Cu	Pb	Cd	Zn
Distilled, demineralized water*	0·18	0·14	0·05	0·36
2*M* Suprapur HNO$_3$	0·18	0·16	0·05	<1·0
2*M* Suprapur sodium acetate	—	—	—	<2·5
10^{-2}*M* G.R. mercuric nitrate	3·2	3·5	0·56	—

* Sample taken from polyethylene storage tank.

All separation experiments and voltammetric measurements were made at 25·0 ± 0·5°. Electrode potentials are referred to the SCE.

Reagents

The chelating resin used was Chelex-100 (Bio-Rad Laboratories), 50–100 mesh, supplied in the sodium form. To convert the resin into the H$^+$-form, a portion was suspended in 2*M* nitric acid, decanted several times to remove fines, then loaded into a 0·8-cm bore glass tube fitted with a Teflon stop-cock. After washing, the height of the column was 10 cm. The resin was washed with 30 ml of 2*M* nitric acid, then with water until the pH of the effluent was above 4·5.

Synthetic sea-water was prepared[12] from reagent-grade salts. The chlorides were first heated to 600° to remove any organic matter. The salts were then individually dissolved in water, mixed, and diluted to volume. The solution was filtered through an acid-washed 0·4-μm Nuclepore filter.

Water supplied from a commercial demineralizer plant was passed through a laboratory demineralizer, then distilled from permanganate and stored in a carefully-cleaned 25-l. polyethylene tank. Merck Suprapur nitric acid and sodium acetate, and general-reagent grade mercuric nitrate were used throughout. Table 1 shows the concentrations of trace metal impurities found in these reagents by direct ASV measurements.

Collection and treatment of sea-water samples

Pacific Ocean surface samples were collected near shore, off Wattamolla, a relatively unpolluted area in the Royal National Park, Sydney. The 15-l. high-density polyethylene sample bottles were initially cleaned by soaking in 2*M* hydrochloric acid for 2 weeks, then rinsed thoroughly with water. The same bottles were used for over 2 years for sea-water samples, and were rinsed with acid and water between samples. Surface sea-water samples were taken about 10 cm below the surface, the bottles being rinsed six times with sea-water before the sample was taken. The samples were filtered within 2 hr of collection, and were usually analysed the same day. The samples were filtered through an acid-washed 0·4-μm Nuclepore membrane filter, the first litre of filtrate being discarded. Filtrates were stored at the natural pH in clean polyethylene or Pyrex bottles which had been soaked overnight in 2*M* hydrochloric acid, then rinsed with water before use. No significant changes were observed in the concentrations of trace metals in samples stored for up to 2 weeks in either Pyrex or polyethylene.

Experimental procedure

Filtered sea-water was loaded into a 5-l. Pyrex reservoir above the chelating resin column. The column tap was adjusted to give a flow-rate of 1·5 ml/min, the first 25 ml of effluent being discarded. The flow-rate was varied between 0·5 and 3·0 ml/min, and in this range was found to have no effect on the retention of the trace metals. New resin was used for each experiment.

Labile* Cu, Pb and Cd were determined in the effluent by adding 0·1 ml of 2*M* nitric acid and 0·1 ml of 0·01*M* mercuric nitrate per 25 ml of sea-water (*i.e.*, bringing the pH to 2·2). Deposition at the glassy-carbon electrode, rotated at 2000 rpm, was carried out at −0·9 V, and the d.c. stripping ramp was applied at 5 V/min up to a potential of −0·15 V. A preliminary 5-min deposition was made, and after stripping, a 10-min deposition was used for quantitative measurements. The Cu, Pb and Cd peaks occurred at −0·31, −0·49 and −0·70 V, respectively. The peak heights were found to be unchanged if the acidified sea-water sample was allowed to stand at 25° for up to 3 hr before measurement.

Total Cu, Pb and Cd were measured after adding 2·00 ml of 2*M* nitric acid to 25 ml of effluent (pH 0·7) and boiling gently in a covered beaker for 10–15 min. We found, in agreement with other workers,[13] that this procedure liberated all the trace metals in a sea-water sample. No increase in trace metal content was found when 25 ml of sea-water were taken almost to dryness with 2 ml of 15*M* nitric acid, or with a mixture of nitric and perchloric acids.

Slightly different procedures were used for the determination of zinc at the hanging mercury-drop electrode. For labile zinc, 0·1 ml of 2*M* sodium acetate and 0·05 ml of 2*M* nitric acid were added per 25 ml of sea-water (*i.e.*, bringing the pH to 5). Deposition was carried out at −1·2 V for 5 min, and a differential pulse scan (10-mV pulse modulation) was made at 2 mV/sec. The zinc peak occurred at −1·0 V. Total zinc was measured after adding 2·00 ml of 2*M* nitric acid to 25 ml of sea-water, boiling for 10–15 min, cooling, then pipetting a 10-ml portion into a 25-ml flask, adding 1·0 ml of 2*M* sodium acetate, and diluting to volume. Corrections were made for the evaporation during boiling, measured by weighing the beaker and contents before and after the boiling.

RESULTS

Chelating resin and solvent extraction studies

The effect of pH on the determination of "free" Cu, Pb and Cd in sea-water is shown in Fig. 1. A similar study using synthetic sea-water yielded curves of almost identical shape. A pH of 2·2 was chosen

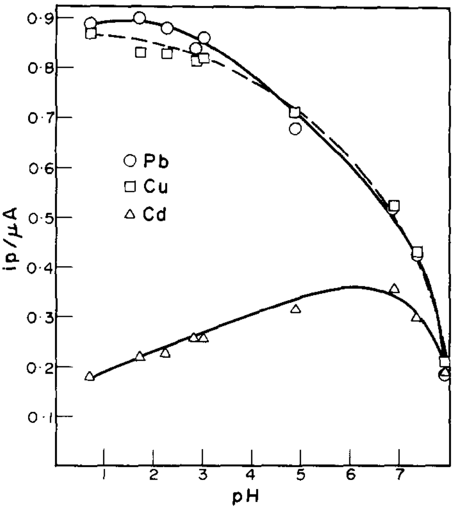

Fig. 1. Effect of pH on the sensitivity of the anodic stripping waves of Cd, Pb and Cu in sea-water. Sea-water contained (labile metal, μg/l.): Cd—0·15, Pb—0·45, Cu—0·46.

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* By "labile" we mean an easily dissociated complex species.

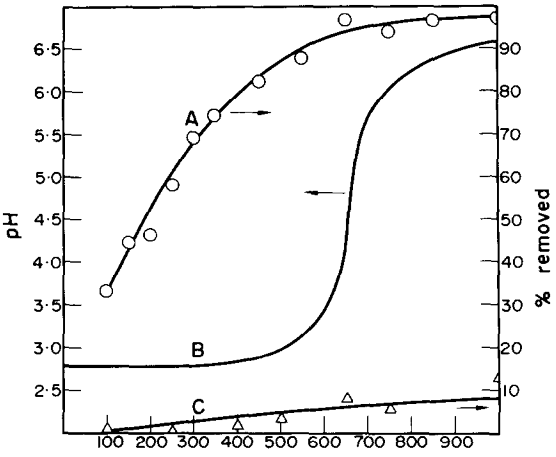

Fig. 2. Effect of volume of sea-water passed through column of Chelex-100 chelating resin (H^+-form) on pH of effluent and removal of zinc. *A*, removal of labile zinc; *B*, pH of effluent; *C*, removal of bound zinc.

for the determination of free metals, because at this pH all three metals give waves of reasonable sensitivity. Since the peak heights vary considerably with pH, both in natural and in organic-free synthetic sea-water, care should obviously be taken in ascribing such changes in sensitivity with pH to the presence of natural chelating agents in sea-water.

The pH of the effluent from a 10 × 0·8 cm column of Chelex-100 (H^+-form) was followed as a function of the volume of sea-water passed through the column. The results are shown in Fig. 2. The hydrogen form of Chelex-100 is gradually neutralized by the metals present in sea-water, and the plot of pH *vs.* volume of effluent had the shape of a typical acid–base titration curve, with the effluent pH finally rising to 7·4 after 4 litres of sea-water had been passed.

The effect of pH on the adsorption of trace metals by Chelex-100 has been studied by several workers.[7,14,15] To obtain greater than 98% retention of Cu, Pb, Cd and Zn, resin pH values higher than 1·7, 2·5, 2·9 and 2·5, respectively, are required. Retention of these metals increases with increasing pH until a constant distribution ratio is reached near pH 6.[7,14] We found that when a sample of sea-water was spiked with ionic Cu(II), Pb(II), Cd(II) and Zn(II), then passed through a column of Chelex-100 (H^+-form), the removal of the spikes from the first 100 ml of effluent (pH 2·8), was 99·7, 99·4, 80·0 and 97·3%, respectively. However, after passage of 1 litre of effluent, when the pH had risen to 6·6, the retention was greater than 99·5% for all four metals. If the Chelex-100 column was first buffered by treatment with 25 ml of 2*M* sodium acetate, then washed with water before passage of the sea-water sample, the initial effluent had a pH of 7·1. Under these conditions retention of Pb, Cd and Zn spikes in the first 100 ml of effluent increased to greater than 99·5%, but copper retention fell to 97·2%.

Figure 2 and Tables 2 and 3 show some of the results obtained for labile and bound (*i.e.*, total minus labile) metal in surface sea-water samples, and for the removal of these metals by Chelex-100. With the exception of copper, bound metals were very poorly extracted by the chelating resin, even at high pH. Labile zinc and copper were almost quantitatively retained after the passage of 1 litre of sample, but labile lead and cadmium were less efficiently removed. On the other hand, when synthetic sea-water was passed through a column of H^+-form Chelex-100, the metal impurities were removed to the same extent as ionic spikes. In the case of synthetic sea-water, values for labile and total metal are almost identical.

It was found possible to convert the trace metals in sea-water into a form which was retained on Chelex-100 by heating the sample after adjustment to pH 0·7, using the method described for determination of total metal. After cooling, the pH was adjusted to 8·1 with sodium hydroxide and the water passed through the column. However, the reagent-grade sodium hydroxide introduced such a high concentration of impurities that the blank value was higher than the natural heavy metal concentration.

The effect of irradiating a sample of sea-water with ultraviolet light before passing it through the resin column was also investigated. One litre of sea-water was treated with 1 ml of 30% hydrogen peroxide and irradiated in a narrow tube with a 35-W U-tube immersion ultraviolet lamp for 5 hr, with magnetic stirring. The temperature of the water rose to 60°, but the pH was found to be unchanged. Ultraviolet irradiation decreased the difference between the labile

Table 2. Removal of trace metals from sea-water by Chelex-100 chelating resin*

Volume of effluent,† *ml*	Total metal, *μg/l.*				Labile metal, *μg/l.*				Labile metal removed, %				Bound metal removed,‡ %			
	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cd
Initial	3·9	0·45	0·84	0·65	1·77	0·22	0·30	0·40	—	—	—	—	—	—	—	—
100	3·3	0·51	0·87	0·43	1·19	0·27	0·27	0·23	33	nil	10	43	0·9	nil	nil	20
250	2·9	0·40	0·80	0·30	0·75	0·15	0·25	0·13	58	32	17	68	nil	nil	nil	32
750	2·12	0·34	0·76	0·19	0·11	0·12	0·23	0·05	94	46	23	88	5·6	4·3	1·9	44
1000	1·94	0·33	0·71	0·20	0·05	0·09	0·18	0·06	97	59	40	85	13	nil	1·9	44
2000	—	0·25	0·69	0·17	—	0·05	0·18	0·03	—	77	40	93	—	13	5·6	44

* Sea-water at pH 8·1 passed through a 10 × 0·8 cm column of Chelex-100, H^+ form.

† Samples were collected from the column and analysed after passage of the stated volume of effluent.

‡ Bound metal = total metal − labile metal.

and total metal measurements, and improved the retention of cadmium and copper, but not of lead. Spectrophotometric examination of the irradiated water[16] could not detect any residual dissolved organic carbon compounds.

Some limited work was also carried out on the ability of a commonly-used solvent extraction technique[1] to measure Cu, Pb, Cd and Zn in sea-water. Portions of filtered sea-water (200 ml) were adjusted to pH 4·5 with hydrochloric acid after addition of 1·5 ml of 1% APDC (recrystallized) solution. The mixture was then shaken for 3 min with 10 ml of methyl isobutyl ketone (MIBK). After the phases had separated, 50 ml of the aqueous phase were treated with 5 ml of 2*M* nitric acid, and boiled to reduce the volume to 25 ml. After cooling, the solution was then analysed for Cu, Pb, Cd and Zn by ASV. At the thin-film electrode the cadmium wave suffered some interference from residual organic matter in these solutions.

Analysis of the aqueous phase by ASV showed that copper naturally present in sea-water was extracted completely by APDC at pH 4·5 from all sea-water samples studied. Extraction of lead varied between 35 and 65%, and was highest when the sea-water had a high labile:total lead ratio. Zinc extraction ranged from 23 to 59% of total zinc. If the sea-water was adjusted to pH 0·7, then heated, cooled, and sodium acetate added to adjust the pH to 4·5 before extraction, complete extraction of all three metals was achieved.

Suitable radioisotopes of Cu, Pb, Cd and Zn were used to spike sea-water samples and measure the degree of extraction of *ionic* metal by APDC in the pH range 3·5–8·1. Copper and lead gave 100% extraction in this range, zinc gave 98%, while cadmium showed 100% extraction between pH 8·1 and 4·5, but only 80% at pH 3·5.

Metal species studies

The use of individual metal-ion stability constants, or pairs of constants, to calculate the equilibrium concentration of a particular species is not valid in such a complex mixture as sea-water. The correct equilibrium concentration can be computed only by simultaneously taking into account all of the possible competing equilibria. This task is too laborious to be attempted by manual calculation. The ionic equilibria program COMICS[17] was corrected, modified, and improved by Sylva,[18] and used to calculate equilibrium concentrations of ions in a model sea-water. A further improvement of the program[19] enabled the data to be presented both as final equilibrium concentrations of each species, and the per cent distribution of a particular metal between various species.

For all calculations, the following total ligand and metal concentrations (*M*) were held constant: Cl^- 0·548; SO_4^{2-} $2{\cdot}82 \times 10^{-2}$; CO_3^{2-} $2{\cdot}40 \times 10^{-3}$; citrate $5{\cdot}00 \times 10^{-7}$; glycine $3{\cdot}00 \times 10^{-7}$; Cd^{2+} $1{\cdot}00 \times 10^{-9}$; Cu^{2+} $1{\cdot}50 \times 10^{-8}$; Pb^{2+} $1{\cdot}00 \times 10^{-9}$; Zn^{2+} $3{\cdot}00 \times 10^{-8}$; Ca^{2+} $1{\cdot}00 \times 10^{-2}$; Mg^{2+} $5{\cdot}40 \times 10^{-2}$. In addition, varying concentrations of *l*-cysteine, EDTA, iron and chromium were used in the calculations. The final pH was varied between 0·7 and 8·1. Glycine was used to represent (with the exception of *l*-cysteine) the free amino-acid group. This was considered valid because glycine is the predominant free dissolved amino-acid in sea-water,[20] and in any case, there is little variation in the stability of the complexes formed by most of the common amino-acids with a particular metal.[21,22] Other organic compounds identified in sea-water, such as fatty acids, sugars and phenols,[23] generally form weaker complexes with metals than do the amino-acids and citric acid, so they were not included in the model. EDTA was used to simulate a particularly powerful chelating agent (*e.g.*, humic acid). Stability constants were selected from Sillén's compilations,[21,22] and were corrected for ionic strength by using published activity coefficients.[24]

Some of the results obtained from these calculations are shown in Tables 4–7. In the absence of EDTA and *l*-cysteine (Table 4) the distribution of the Cu, Pb, Cd and Zn species is similar to that calculated by Zirino and Yamamoto.[24]

The effects of EDTA, NTA, and a synthetic organic mixture on the anodic stripping behavior of Cu, Pb, Cd and Zn in sea-water, and on the extraction of copper and zinc from sea-water by APDC, were investigated. A synthetic organic mixture was prepared, containing (in mg/l.); citric acid (250), malic acid (250), palmitic acid (250), *p*-hydroxybenzoic acid (2), glycine (150), humic acid (10), aspartic acid (50), leucine (50), and *l*-cysteine (10). Two ml of this mixture added to 200 ml of sea-water had no effect on the extraction of Cu and Zn spikes. Also, EDTA and NTA at the 125 μg/l. level did not decrease the extraction of Cu and Zn, but with EDTA at the 1·25 mg/l. level, only 35% of the zinc spike was extracted, although copper extraction was still unaffected. If distilled water was substituted for sea-water, similar results were obtained; the extraction of copper was not decreased, even by the higher concentration of EDTA, but only small amounts of zinc were extracted at the higher level of EDTA.

Addition of the organic mixture to both natural and synthetic sea-water (0·2 ml per 200 ml of water) had no effect on the Cu, Pb, Cd or Zn anodic stripping waves at either pH 6·0 or 4·6. At pH 4·6, aspartic acid at concentrations as high as $4 \times 10^{-6}M$ did not affect any of the metal waves. At pH 6·0, $2 \times 10^{-7}M$ EDTA did not diminish or shift the metal stripping waves, but at pH 4·6 the waves, particularly those of lead, were diminished by EDTA concentrations higher than $1 \times 10^{-8}M$.

DISCUSSION

It is apparent that Chelex-100 chelating resin cannot be used in the manner described by Riley and Taylor[2] for the quantitative concentration of Cu, Pb,

Table 3. Removal of trace metals from sea-water by Chelex-100 resin after passage of 1·0 litre of sea-water*

Sample No.	Resin form	pH of effluent	Total metal, µg/l. (original)				Labile metal, µg/l. (original)				Labile metal, removed, %				Bound metal removed,† %			
			Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
1	H^+	6·4	2·50	0·24	0·50	0·42	1·80	0·15	0·40	0·42	86	27	27	91	23	9	nil	—
2	H^+	6·5	6·2	0·58	0·87	0·69	1·55	0·12	0·36	0·33	—	29	34	69	—	nil	11	56
3‡§	H^+	6·4	4·8	0·23	0·96	0·45	2·40	0·13	0·80	0·35	85	67	69	96	12	5	5	27
4	H^+	6·5	—	0·23	0·74	0·65	—	0·08	0·30	0·40	—	50	25	97	—	18	19	55
4¶	H^+	2·0									—	9	22	40	—	nil	22	37
4	Na^+	7·7									—	100	87	91	—	23	12	44
4	NH_4^+	7·5									—	91	74	78	—	15	20	42

* Sea-water at pH 8·1 passed through a 10 × 0·8 cm column of Chelex-100. Effluent sampled after 1 litre had passed through column.

† Bound metal = total metal − labile metal.

‡ This sample collected 10 miles offshore.

§ Elution of the resin column with 2*M* HNO_3 after passage of 1 litre of sea-water gave the following apparent original metal contents (µg/l.): Cu—0·25, Pb—0·46, Cd—0·07.

¶ Sea-water adjusted to pH 1·8 (2 ml of 10*M* HC*l* per litre of sea-water) before passage through column.

Cd and Zn from sea-water. In a footnote to a later paper,[3] these authors mentioned that they had observed some initial leakage of zinc from a Chelex-100 column. They stated that the loss was equivalent to 3–4% of the zinc contained in the first litre of sea-water which passed through the column. We have found much greater losses, however. For example, from Fig. 2 it was calculated that the loss of labile zinc in the first litre was 25%, and the loss of bound zinc was 95%. This amounts to a 63% loss of total zinc in the first litre of sample. Conversion of the resin into the sodium or ammonium form improves the retention of labile metal, but has little effect on bound metal (Table 3). Because copper forms the strongest complex with Chelex-100,[15] it is removed from sea-water more efficiently than the other metals. However, at effluent pH values above 7, we found, in agreement with Holynska,[7] that the retention of copper decreases. Muzzarelli and Rocchetti[25] reported that Dowex A1 chelating resin removes only a small fraction of the total copper present in sea-water. Cadmium forms especially strong chloro-complexes,[21] and in saline waters its distribution ratio with Chelex-100 would be expected to be lower than in non-chloride media.[14]

Liquid–liquid extraction of sea-water with APDC–MIBK gave results similar to those obtained with the chelating resin, although removal of trace metals was generally more efficient by solvent extraction. Copper was extracted readily, but a preliminary acid treatment of the sample was necessary to attain complete extraction of lead and zinc with APDC.

Chelex-100 in the H^+-form removed trace metals from synthetic sea-water with an efficiency equal to the removal of ionic spikes, and there was very little difference between the ASV values for labile and total metal in synthetic sea-water. The entirely different behavior of natural sea-water shows that it contains a large fraction of the trace metals in a form which is not available to the resin. Even the "labile" metal in natural sea-water is not completely removed by the resin, indicating that the ASV method used to determine labile metal includes in the measurement some of the metal which will not react with the resin. Probably, at the low pH (pH 2·2) used for the determination of labile metal, some of the metal contained

Table 4. Calculated distribution of Cd, Cu, Pb and Zn species in sea-water in the absence of cysteine and EDTA*

Ligand	Fraction of total metal ion, %							
	Cd		Cu		Pb		Zn	
	pH 2·2	pH 8·1	pH 2·2	pH 8·1	pH 2·2	pH 8·1	pH 2·2	pH 8·1
Free ion	1·7	1·6	34·7	0·3	3·3	1·0	22·1	5·7
1-Cl	29·1	27·7	47·8	0·4	28·9	8·8	38·8	9·9
2-Cl	31·8	30·3	8·3	0·1	39·8	12·2	21·2	5·4
3-Cl	27·6	26·3	1·1	<0·1	17·3	5·3	5·8	1·5
4-Cl	9·6	9·1	0·2	<0·1	4·8	1·5	4·0	1·0
1-SO_4	0·3	0·3	7·6	0·1	5·8	1·9	7·8	2·2
1-CO_3	<0·1	0·7	<0·1	3·9	<0·1	67·8	<0·1	2·4
1-HCO_3	<0·1	0·1	<0·1	0·2	<0·1	0·2	<0·1	0·2
1-citrate	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1
1-glycinate	<0·1	<0·1	<0·1	0·3	<0·1	<0·1	<0·1	<0·1
1-OH	<0·1	4·0	<0·1	1·2	<0·1	1·3	<0·1	0·1
2-OH	<0·1	<0·1	<0·1	93·9	<0·1	<0·1	<0·1	71·7

* Fe(III) = $2 \times 10^{-9}M$, Cr(III) = $1 \times 10^{-9}M$.

Table 5. Calculated effect of EDTA on the distribution of Cd, Cu, Pb and Zn in sea-water*

pH	EDTA, M	Fraction of total metal as EDTA complex, % Cd	Cu	Pb	Zn
2·2	2×10^{-9}	<0·1	<0·1	<0·1	<0·1
	2×10^{-8}	<0·1	0·2	<0·1	<0·1
	2×10^{-7}	<0·1	2·6	0·1	0·1
4·5	2×10^{-9}	<0·1	<0·1	<0·1	<0·1
	2×10^{-8}	0·2	66·2	5·6	3·8
	2×10^{-7}	6·4	98·2	62·8	53·0
8·1	2×10^{-9}	<0·1	0·3	0·3	0·2
	2×10^{-8}	0·7	4·8	5·2	2·9
	2×10^{-7}	6·8	35·1	36·9	24·3

* Fe(III) = $2 \times 10^{-9}M$, Cr(III) = $1 \times 10^{-9}M$, *l*-cysteine = $5 \times 10^{-10}M$.

in colloidal particles which pass through the column will dissolve, and contribute to the value for labile metal (Table 3). Use of a Chelex-100 column in the Na^+-form appears to be a promising method for separating the ionic and colloidal forms of trace heavy metals in sea-water.

The exact nature of the form in which "soluble" trace metals exist in sea-water has been the subject of many studies and discussions.[26–33] It seems reasonable to assume that the soluble "bound" metal is present either as organic chelates or adsorbed on or occluded in organic or inorganic particles. Irradiation of a sea-water sample with ultraviolet light decreased, but did not eliminate, the difference between labile and total metal, which suggests that not all the bound metal is combined with a simple organic ligand.

If the bound metal were present as a simple metal chelate, the ligand would need to be very powerful to compete with the iminoacetate groups in Chelex-100, which form very strong complexes with heavy metal ions.[15] Alternatively, the complex could be inert, and not dissociate in the time of the separation experiment. Lowman and Ting[32] found that they could free the cobalt–vitamin B-12 complex (cobalamin) from Co^{2+} impurity by passing a solution of the mixture through a column of Chelex-100. The Co^{2+} was adsorbed, while the cobalamin passed into the effluent.

Colloidal particles are not retained by most ion-exchange resins because the resin pore size (about 30 Å) is too small to allow the colloids to enter the resin network.[34] Cation-exchange resins have been used in this manner to remove ionic impurities from colloidal zirconia and other sols.[34] Organic or inorganic colloidal particles in sea-water would therefore be expected to pass through a column of Chelex-100, carrying with them adsorbed trace metals. On heating in a strongly acid solution they would dissolve, or at least release the trace metal, and so give rise to the analytical figure for "bound" metal. Breger[35] has presented persuasive arguments that most of the "dissolved" organic matter in natural waters exists as colloidal particles. He believes that the study of the properties of high molecular weight compounds in natural waters has been neglected because these compounds are so difficult to characterize. Slowey and Hood[26] found that in the Gulf of Mexico an average of 43% of the zinc and 8% of the copper was in a non-dialysable form. Solubility of organic colloidal particles in MIBK could explain why we found that solvent extraction was more efficient than Chelex-100 in removing trace metals from sea-water.

Application of the computer program COMICS to predict the distribution of trace metals species in a

Table 6. Calculated distribution of Ca, Mg, Fe and Cr in sea-water*

	Per cent of total metal ion†							
	Ca		Mg		Fe		Cr	
Ligand	pH 2·2	pH 8·1	pH 2·2	pH 8·1	pH 2·2	pH 8·1	pH 2·2	pH 8·1
Free ion	93·5	92·2	93·5	89·4	0·7	<0·1	42·7	<0·1
	93·5	92·2	93·5	89·4	<0·1	<0·1	0·1	<0·1
1-Cl	<0·1	<0·1	<0·1	<0·1	1·6	<0·1	18·6	<0·1
	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1
1-SO_4	6·5	7·0	6·5	6·7	9·9	<0·1	37·2	<0·1
	6·5	7·0	6·5	6·7	<0·1	<0·1	0·1	<0·1
2-SO_4	<0·1	<0·1	<0·1	<0·1	86·3	<0·1	<0·1	<0·1
	<0·1	<0·1	<0·1	<0·1	0·1	<0·1	<0·1	<0·1
1-CO_3	<0·1	0·3	<0·1	0·1	<0·1	<0·1	<0·1	<0·1
	<0·1	0·3	<0·1	0·1	<0·1	<0·1	<0·1	<0·1
1-HCO_3	<0·1	0·5	<0·1	3·8	<0·1	<0·1	<0·1	<0·1
	<0·1	0·5	<0·1	3·8	<0·1	<0·1	<0·1	<0·1
1-OH	<0·1	<0·1	<0·1	<0·1	0·1	<0·1	0·4	99·9
	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	0·2
2-OH	<0·1	<0·1	<0·1	<0·1	<0·1	100·0	<0·1	<0·1
	<0·1	<0·1	<0·1	<0·1	<0·1	97·4	<0·1	<0·1
EDTA	—	—	—	—	—	—	—	—
	<0·1	<0·1	<0·1	<0·1	99·8	2·6	99·9	99·8

* Fe(III) = $2 \times 10^{-9}M$, Cr(III) = $1 \times 10^{-9}M$.

† First result shown for each ligand is in absence of EDTA and *l*-cysteine, the second result is in presence of $5 \times 10^{-10}M$ *l*-cysteine and $2 \times 10^{-8}M$ EDTA.

Table 7. Calculated effect of *l*-cysteine on the distribution of Cd, Cu, Pb and Zn in sea-water

	Fraction of total metal as cysteine complex,* %							
	Cd		Cu		Pb		Zn	
l-Cysteine, *M*	pH 4·5	pH 8·1	pH 4·5	pH 8·1	pH 4·5	pH 8·1	pH 4·5	pH 8·1
5×10^{-10}†	<0·1	<0·1	<0·1	<0·1	<0·1	0·3	<0·1	1·5
4×10^{-9}†	<0·1	<0·1	<0·1	<0·1	<0·1	2·3	0·2	11·5
4×10^{-8}†	<0·1	<0·1	<0·1	0·1	0·3	41·3	2·1	79·8
1×10^{-8}‡	<0·1	<0·1	<0·1	<0·1	0·1	6·3	0·5	27·9
4×10^{-8}‡	<0·1	<0·1	<0·1	<0·1	0·3	40·2	2·1	79·4

* Fe(III) = $2 \times 10^{-9}M$, Cr(III) = $1 \times 10^{-9}M$.
† No EDTA.
‡ Plus $2 \times 10^{-8}M$ EDTA.

model sea-water provided some interesting results (Tables 4–7), which should, however, be interpreted with some caution because of the limitations of this approach. Perhaps the most serious problem is the choice of the correct values for the relevant stability constants. Published values for any metal complex stability constant usually cover a wide range,[21,22] and this is particularly so in the case of the chloro-complexes. Because of the high concentration of chloride in sea-water, the chloride stability constants have a profound effect on the calculated distribution of species. Other problems are the lack of information on the existence or stability of polymerized species, on the lability of the complexes, and on the presence of unidentified chelating agents. With these reservations in mind, the following conclusions can be drawn from Tables 4–7. (*a*) At pH 2·2, the pH used for the determination of labile metal, Cu, Pb, Cd and Zn exist entirely as free metal ion, or as chloro- and sulphato-complexes, even in the presence of EDTA and *l*-cysteine. (*b*) At the natural pH of sea-water (pH 8·1), and in the absence of EDTA and *l*-cysteine, zinc and copper exist principally as the dihydroxy complexes, lead as the carbonato-complex, and cadmium as chloro-complexes. (*c*) Citrate and amino-acids (except *l*-cysteine) do not complex any significant amounts of metals over the range pH 0·7–8·1. Siegel[27] quoted ASV results which showed that aspartic acid added to sea-water diminished the stripping peak of copper. In agreement with Duursma[28] and with the results calculated from our computer model, we found that $4 \times 10^{-6}M$ aspartic acid had no effect on the stripping waves of Cu, Pb, Cd and Zn. (*d*) Even in the presence of a high concentration of EDTA ($2 \times 10^{-7}M$), no significant reaction occurs between EDTA and calcium and magnesium over the pH range studied. (*e*) EDTA has maximum complexing effect near pH 4·5.[36] (*f*) The concentrations of iron(III) and chromium(III) completely dictate the behaviour of EDTA in sea-water, since these two ions together react quantitatively with EDTA over the pH range 2·2–8·1, and the other heavy trace metals will form EDTA complexes only after ionic Fe and Cr have reacted completely.

The possibility that iron and chromium control the complexing behavior of powerful EDTA-like ligands in sea-water was originally proposed by Duursma.[28] Siegel[27] criticized the choice of EDTA to simulate a strong chelating agent, on the basis that EDTA shows an unusual preference for Fe(III). Although Siegel's arguments were not entirely convincing (he used an incorrect value for the Fe(III)–NTA stability constant[22]), it is true that certain ligands (*e.g.*, *l*-cysteine) can, at the natural pH of sea-water, react with other metals in the presence of an excess of Fe(III) (Table 7).

The difficulty in predicting the behavior of Fe(III) and Cr(III) in sea-water is that the "labile" concentrations of these ions are not known. The total concentration of soluble iron is about 5μg/l., and of chromium(III) is 0·5 μg/l.[37] However, much of this iron and chromium may exist as polymerized or other species which will not react with the added ligand. Florence[38] reported that only 10% of the total iron in tap-water would chemically exchange with the Bi–EDTA complex, while Benes and Steinnes[39] found that only 19% of the iron, and 49% of the chromium in river water was dialysable.

Fulvic and humic acids have often been suggested as the compounds in sea-water which react most powerfully with trace heavy metals.[31] However, the small amount of quantitative data so far published[31,40] suggests that fulvic acid forms weaker complexes with the transition metals than does EDTA.[36]

The stability constants of the *l*-cysteine complexes of Cu, Pb, Cd and Zn are particularly large,[22] and any significant concentration of this amino-acid in sea-water will have an important bearing on the complexing of zinc and other trace metals, since it will compete even with EDTA (Table 7). Siegel and Degens[20] and Degens *et al.*[23] could not detect any free *l*-cysteine in sea-water, and their results suggest that its concentration is less than 0·5 μg/l. ($4 \times 10^{-9}M$).

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APPLICATION OF A SIMPLE PHOTOIONIZATION DETECTOR FOR NON-DISPERSIVE ATOMIC SPECTROMETRY IN THE VACUUM ULTRAVIOLET REGION

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Summary—The construction and operation of a simple, solar-blind photoionization detector which responds to incident radiation between 125 and 140 nm is described. The detector, the response characteristics of which are controlled by the ionization potential of the ethylamine filler gas and the calcium fluoride window employed, is shown to provide for efficient detection of atomic line emission from carbon, oxygen and chlorine in this wavelength region. The spectral sources employed for non-dispersive work with this detector are a microwave-excited argon plasma and a demountable hollow-cathode lamp.

Because of the numerous problems associated with the production and detection of radiation at wavelengths shorter than 200 nm this region has been somewhat neglected for the purposes of routine analytical atomic spectrometry. The atoms of many elements, including the halogens, carbon, sulphur, oxygen, nitrogen, phosphorus and mercury, emit intense resonance-line radiation in this region. A simple, non-dispersive system for detecting the atomic-line emission of these elements would be attractive for their detection and determination by the techniques of atomic emission, absorption and fluorescence spectrometry. Conventional spectrometry in the "vacuum ultraviolet" region is usually undertaken with large vacuum spectrometers and photomultiplier detectors. By analogy with the advantages of non-dispersive detection systems rather than grating or prism/monochromator systems in analytical atomic spectroscopy in the near ultraviolet and visible regions of the spectrum, use of a non-dispersive detection system in the vacuum ultraviolet might be expected to yield advantages of simplicity, large aperture and suitability for operation in simultaneous multi-element analysis. The photoionization detector (PID) appears to offer such possibilities. A typical PID consists of a chamber containing a gas at low pressure and two electrodes across which a constant d.c. voltage is applied. When the chamber is irradiated by photons having sufficient energy to cause ionization of the gas, an ionization current is produced and may be registered in the external circuit. The magnitude of the current is proportional to the incident ionizing photon flux. The spectral response of a PID is controlled on the short wavelength (high energy) side by the transmission characteristics of the material from which the window is made and on the long wavelength side by the photoionization threshold of the filler gas. The construction and use of PID systems for physical research has been documented; detectors based on this principle have found application in the examination of the solar spectrum.[1,2] By careful selection of the window material and the filler gas, detectors with a spectral bandpass of only a few nm may be constructed, which will detect radiation in the range 105–200 nm. In addition to high spectral selectivity, detectors of this type have high quantum efficiencies, low noise levels and the capability of serving as gas-gain multipliers. They may also be made to have large optical aperture, are "solar-blind" and may be rugged and compact. This paper describes the construction and evaluation of a simple PID system designed for non-dispersive work in the spectral range 125–140 nm, and its use for the detection of such radiation from a microwave-excited argon plasma at atmospheric pressure or from a flow-through demountable hollow-cathode lamp source.

EXPERIMENTAL

Apparatus

Photoionization detector. The PID assembly used in this work is shown in Fig. 1. A Pyrex cylinder (90 mm in length, 29 mm diameter, 2 mm wall-thickness) fitted with a B14/23 ground-glass cone and socket at one end and a side-arm fitted with a three-way 2-mm bore tap was employed as the detector envelope. The electrode assembly, mounted onto glass-to-metal sealing rods through the ground-glass cone, consisted of a cylindrical sheet copper cathode (80 mm in length, 25 mm internal diameter, 0·19 mm thickness) along the central axis of which a 1-mm tungsten wire anode was located. The electrodes were insulated from each other by means of the glass and PTFE anode supports shown in Fig. 1. A polished calcium fluoride window (3 mm thickness, 25 mm diameter) was mounted in a cylindrical aluminium holder sealed with epoxy resin cement onto the end of the PID envelope. The aluminium window holder had an external annular depression in which an O-ring was positioned to permit vacuum sealing of the detector at the exit slit of the vacuum monochromator employed in some of the work. All components of the PID were carefully cleaned and degreased before assembly. The ground-glass joints were sealed with high-melting wax.

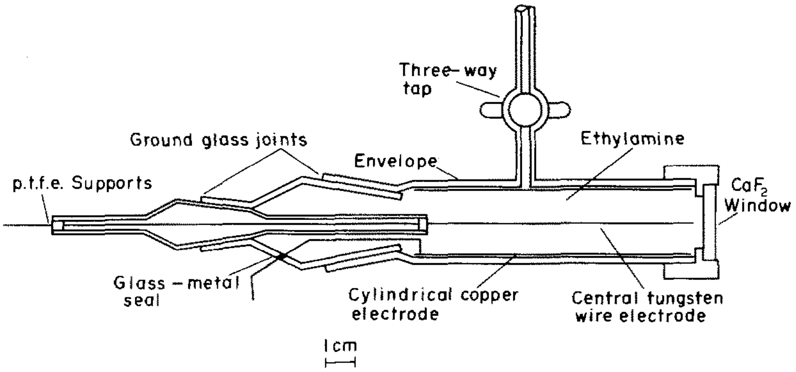

Fig. 1. Photoionization detector assembly.

A d.c. voltage (5–400 V) was provided across the detector from a dry battery supply. The photoionization current was registered on a picoammeter (P24, Knick, Berlin, Germany) and the voltage output from this device was displayed on a potentiometric chart recorder (Servoscribe Model RE 511).

Microwave plasma source. A microwave-excited argon plasma supported at atmospheric pressure in a fused silica tube (150 mm length, 2 mm i.d.) with a 1/4-wave resonant cavity, was employed. Power (*ca.* 50 W) was supplied at 2450 MHz from a 200-W microwave power supply (Microtron Mk III, EMS Ltd.). The argon flow-rate was variable between 0·5 and 1·0 l./min and the plasma discharge was viewed "end-on" along the central axis of the silica tube.

Demountable hollow-cathode lamp source. A commercial demountable hollow-cathode lamp source (Miniglow, Spectro Products Inc., North Haven, Conn., U.S.A.) was employed. The source was capable of operation at d.c. currents of between 5 and 50 mA and argon pressures between 2 and 10 mmHg. The lamp assembly was capable of accepting a variety of cathodes. The cathode shells used in this work were aluminium (22 mm length, 4 mm internal diameter, 1 mm wall thickness) into which the material to be examined was pressed. The cathode assembly was water-cooled. The silica window of the demountable hollow-cathode source was replaced by a calcium fluoride window (3 mm thickness) for the present studies.

Auxiliary equipment. The spectral emission characteristics of the source employed, and the spectral response characteristics of the PID, were established by using a 1-m normal-incidence vacuum grating monochromator (Model E760, Rank Hilger Ltd.). This was equipped with an end-window photomultiplier tube (EMI 625B) the silica window of which had been coated with sodium salicylate (1–1·5 mg/cm^2).

RESULTS AND DISCUSSION

For preliminary evaluation a PID was constructed to operate in the spectral range 120–140 nm, choice of this wavelength region being governed by the availability of suitable window materials and of filler materials having suitable ionization potential and vapour pressure to enable the PID to operate efficiently at room temperature. In addition, a number of useful atomic lines from carbon, oxygen, chlorine, bromine and sulphur lie in this wavelength range and were thus available for assessment of the response characteristics of the PID. The vapour of ethylamine, which has an ionization potential of 8·8 eV (141·0 nm) was employed as the filler material. The photoionization efficiency curve for ethylamine is shown in Fig. 2.[3] The short-wavelength response was controlled by the window material. In most of the work reported here a 3-mm calcium fluoride window was used. The transmission characteristics of this window are also shown in Fig. 2. The spectral response of the PID can be predicted to be between 120 and 140 nm.

A simple vacuum and purging system was constructed to permit the filling of the PID (Fig. 3.). Anhydrous ethylamine (10 ml), b.p. 16·6°, was placed in the pear-shaped flask and frozen by immersion of the flask in liquid nitrogen. The system was then evacuated with a two-stage rotary pump and flushed out several times with argon. After evacuation of the complete system tap A was closed to isolate the flask containing the ethylamine. The flask was then removed from the liquid nitrogen and allowed to warm to produce a steady increase in ethylamine vapour pressure. By first closing tap B and then opening tap A the system was flushed out several times with ethylamine vapour, followed each time by re-evacuation to a pressure of *ca.* 3 mmHg. Tap B was then finally closed and a preselected pressure of ethylamine vapour admitted to the system *via* tap A. With taps A and B both closed, the detector was sealed by closing tap C and removed from the system for use. Even with the simple PID system constructed for this study, the PID envelope would maintain a pressure as low as 1 mmHg for periods of over 8 hr and was simply and rapidly refilled when necessary.

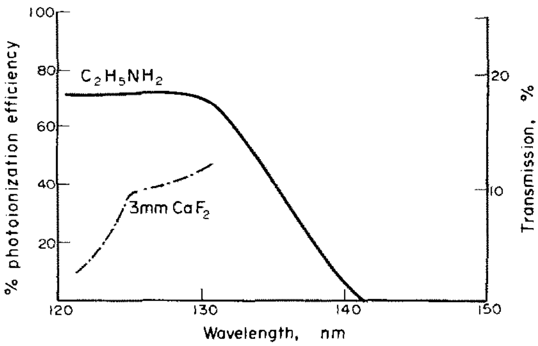

Fig. 2. Photoionization efficiency curve for ethylamine[3] and transmission characteristics of calcium fluoride window.

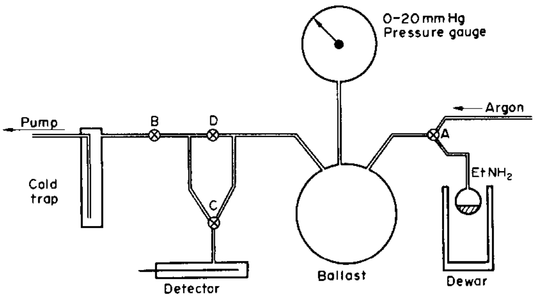

Fig. 3. Evacuation and purging system employed for filling PID detector.

Spectral response characteristics of the PID

The spectral response characteristics of the ethylamine PID were studied with both sources available, *i.e.*, a microwave-excited argon plasma and the demountable hollow-cathode lamp system. The background emission spectrum from the argon plasma in the wavelength range of interest was first examined with the vacuum monochromator and photomultiplier assembly. Figure 4 shows a typical spectrum obtained. The principal features of the emission spectrum may be identified as lines originating from impurities in the argon or from the walls of the silica plasma tubing, *i.e.*, lines of carbon and oxygen from carbon dioxide, hydrocarbons and water vapour. Emission spectra were then obtained from the plasma when small quantities of other vapours were introduced into the argon supply. Figure 5 shows the spectra obtained in the presence of carbon tetrachloride, sulphur dioxide and iodine. Though SO_2 and I_2 gave no emission in the wavelength range of interest, the emission spectra of the argon plasma alone or containing CCl_4 provided useful line emissions from carbon, oxygen and chlorine suitable for evaluation of the spectral response characteristics of the PID.

The PID was filled with ethylamine vapour at 2 mmHg and positioned at the exit slit of the vacuum monochromator; the window of the ionization chamber formed the vacuum seal with the monochromator. The argon plasma, operated at 65 W and an argon flow of 1 l./min, was viewed by the monochromator using a spectral half-band pass of 1·6 nm. The emission spectrum of the argon plasma was recorded with the PID operated at 85 V. The spectrum obtained is shown in Fig. 6, which also shows

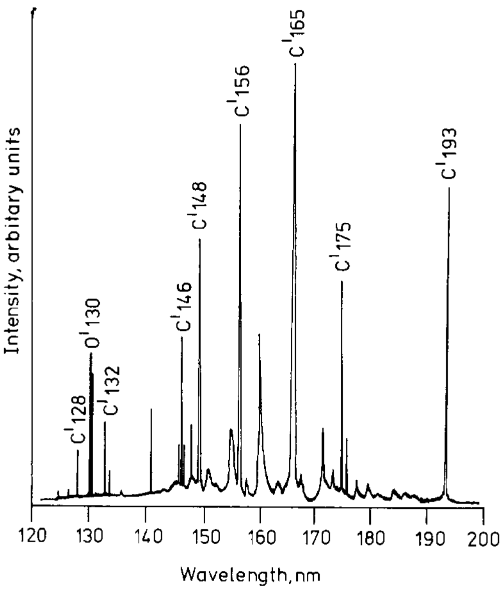

Fig. 4. Emission spectrum from microwave-excited atmospheric argon plasma between 120 and 200 nm. Microwave power, 65 W; E.M.I. 6256B photomultiplier at 1600 V, coated with sodium salicylate.

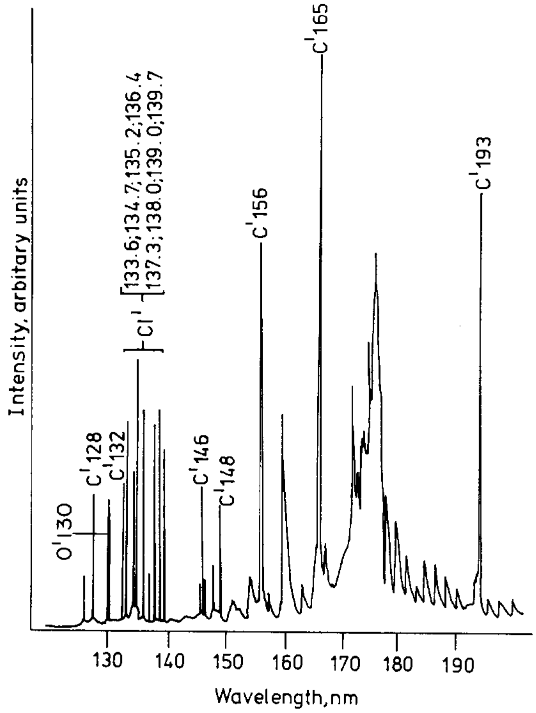

Fig. 5(*a*).

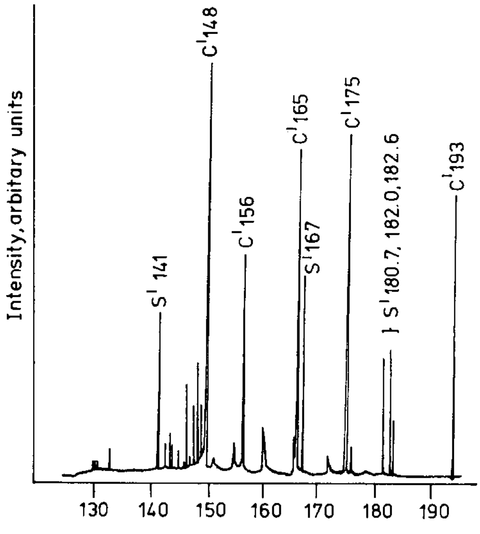

Fig. 5(*b*).

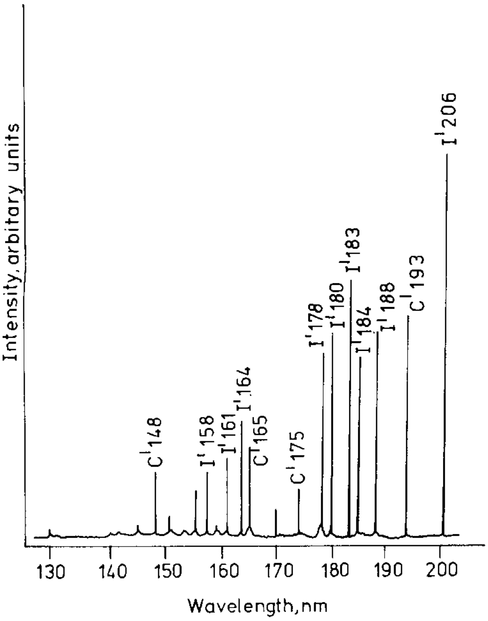

Fig. 5(*c*).

Fig. 5. Spectra from microwave-excited atmospheric argon plasma pressure of (*a*) CCl_4, (*b*) SO_2, (*c*) I_2, introduced into argon supply. Microwave power, 65 W, E.M.I. 6256B photomultiplier at 1600 V, coated with sodium salicylate.

the spectrum of the argon plasma obtained by using the vacuum monochromator at the same spectral band-pass (1·6 nm) but with the photomultiplier detector. It is clear that the PID responds only to radiation in the wavelength range predicted. Whereas the carbon and oxygen line emissions in the region 128–132 nm are observed, the more intense longer-wavelength carbon lines between 140 and 193 nm are not detected.

As a further test of the response characteristics of the ethylamine PID the demountable hollow-cathode lamp source with argon filler gas and an aluminium cathode containing a mixture of tungsten and mercuric chloride was employed. The spectrum from this source in the range 130–200 nm (obtained with the vacuum monochromator and photomultiplier detector) consists principally of atomic line emission from chlorine, oxygen, carbon and mercury, as shown in Fig. 7*a*. This spectrum was obtained with an argon-purged optical path (3 cm) between the source and the monochromator entrance slit. The experiment was then repeated with this 3-cm path-length purged with argon containing 1% methane. As methane absorbs strongly at wavelengths shorter than 140 nm the emission intensity from the source at short wavelengths is attenuated. The spectrum obtained under these conditions is shown in Fig. 7*b* and clearly demonstrates the absorption of the oxygen and chlorine atomic line emission between 130 and 140 nm and the unaffected intensities at longer wavelengths. These experiments were repeated with the PID in the non-dispersive mode, *i.e.*, with the radiation from the demountable hollow-cathode lamp source falling directly on to the detector *via* the 3-cm purged path without use of the vacuum monochromator. The re-

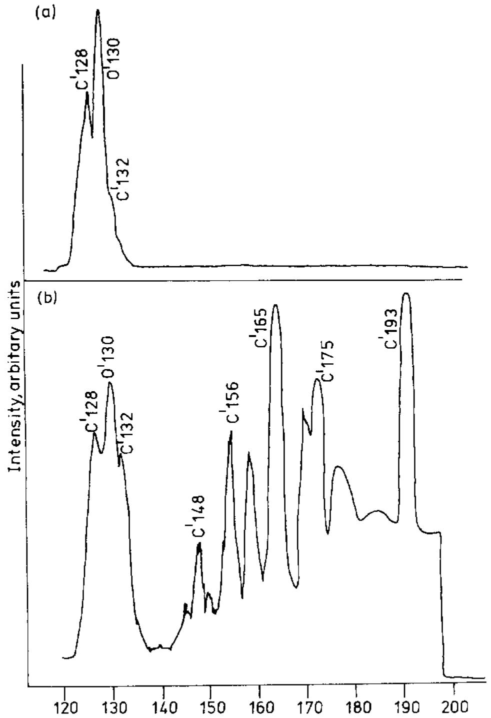

Fig. 6. Emission spectra from microwave-excited argon plasma, obtained by using vacuum monochromator (1·6 nm-bandpass) and (*a*) PID detector operated at 85 V, 2 mm Hg pressure of ethylamine. (*b*) E.M.I. 6256B photomultiplier at 700 V; coated with sodium salicylate.

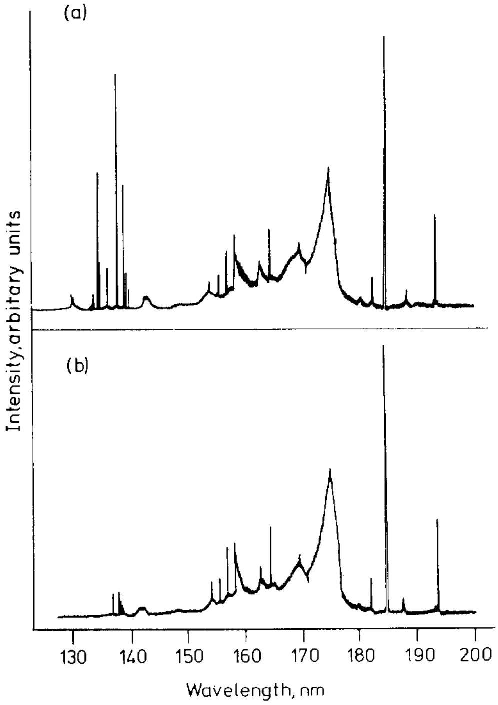

Fig. 7. Emission spectra from demountable hollow-cathode lamp source. Argon filler gas, $HgCl_2$/W cathode. (*a*) Optical path (3 cm) purged with argon. (*b*) Optical path (3 cm) purged with 1% CH_4 in argon.

sponse in the presence and absence of 1% methane in the argon purge-gas is shown in Fig. 8. The decrease in the presence of methane correlates well with that between 130 and 140 nm shown in Fig. 7. It is thus apparent that it is the incident radiation below 140 nm to which the PID responds.

Effect of ethylamine vapour pressure and applied voltage on response of PID

The radiation from the demountable hollow-cathode source with an aluminium cathode containing a mixture of tungsten powder and solid mercuric chloride was allowed to fall directly onto the PID in the non-dispersive mode. The effect of ethylamine pressure and the applied voltage on the response of the detector was examined. The current–voltage curves obtained are shown in Fig. 9.

For the detector geometry employed, in which a thin wire central electrode is located along the central axis of the large cylindrical electrode, the electric field E in the coaxial system at a distance r from the centre of the central wire electrode is given by

$$E = \frac{V}{r \ln [a/b]}$$

where V is the applied voltage and a and b are the radii of the cylindrical and central wire electrodes, respectively. In the applied voltage range between A and B (Fig. 9) for a given photon flux entering the detector the ions formed by the reaction.

$$C_2H_5NH_2 + h\nu \rightarrow C_2H_5NH_2^+ + e^-$$

are collected with increasing efficiency as the field strength in the chamber increases with increasing voltage. Further increase in applied voltage, in the range from B to C, can then not result in further collection efficiency for the given geometry and cell dimensions, and a "plateau region" of relatively constant output current is obtained. At higher applied voltages, as in the region of C and above in Fig. 9, the electrons produced by the initial photoionization of the ethylamine may achieve sufficient energy in the stronger field to cause secondary ionization on collision with ethylamine molecules, *i.e.*, the energy of a fraction of the photoelectrons becomes greater than the ionization potential of the filler material. As the applied voltage is increased the increasing field strength thus leads to increasing electron multiplication by secondary ionization and a consequent rapid increase in the current produced in the external circuit. This region is often referred to as the "gas-gain" region and can be employed to increase the sensitivity of the detector system. The effect shown in Fig. 9, where the PID current is inversely proportional to

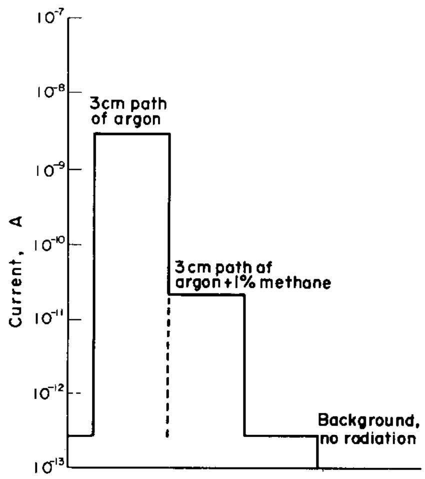

Fig. 8. PID currents observed in presence and absence of methane in optical path between hollow-cathode lamp ($HgCl_2$/W cathode) and detector.

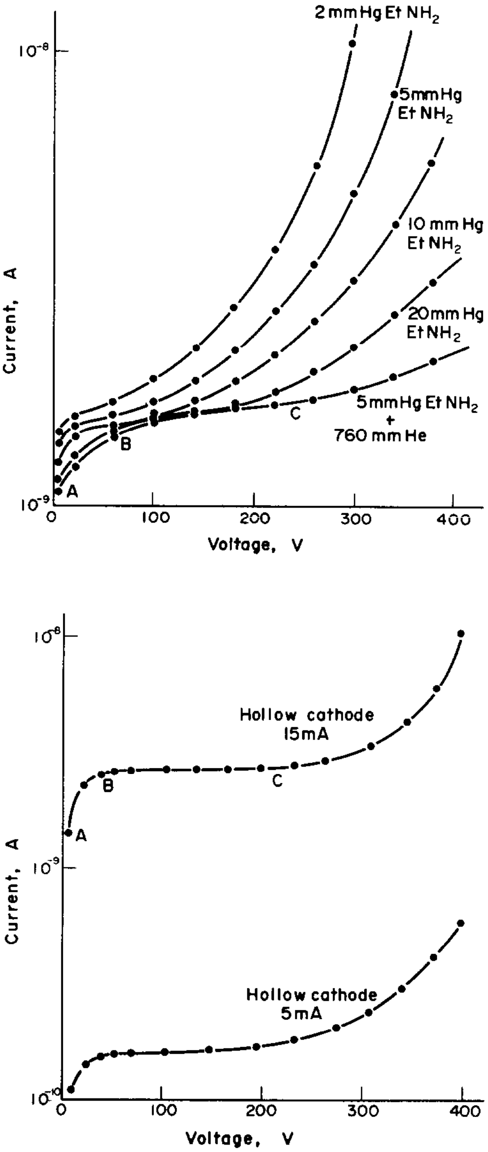

Fig. 9. (*a*) Effect of ethylamine vapour pressure and applied d.c. voltage on response of PID. (*b*) Dependence of PID response on applied d.c. voltage, with different operating currents for hollow-cathode lamp source.

Table 1. A selection of narrow bandpass PID systems in the wavelength range 105–184 nm

Window material	Approx. thickness, *mm*	Filler gas	I.P., *eV*	(Ref.)	Spectral range of PID, *nm*
Lithium fluoride	1	ethyl bromide	10·29	(2)	105–129
		nitric oxide	9·25	(2)	105–134
Calcium fluoride	3	benzene	9·25	(2,4)	122–134
		toluene	8·82	(2,4)	122–141
Sapphire	0·5	*p*-xylene	8·44	(2)	142–147
		trimethylamine	7·82	(5)	142–156
Fused quartz	1	dimethylaniline	7·14	(5)	160–172
		triphenylamine	6·89	(5)	160–180
		ferrocene	6·74	(5)	160–184

the pressure of ethylamine present over the range studied, can be explained on the basis of the mean free path of the photoelectrons. Thus, as the ethylamine pressure is increased, the mean free path of the electrons decreases so that there is insufficient time to permit their acceleration to energies sufficient to cause secondary ionization on collision with ethylamine molecules. This effectively delays the onset of the "gas-gain" region to higher applied voltages. The limiting case shown in Fig. 9 corresponds to the addition of helium as an inert filler gas at atmospheric pressure in the presence of 5 mmHg of ethylamine. Under these conditions the plateau region extends to above 300 V without significant secondary ionization.

Figure 9*b* demonstrates the dependence of the PID response on the incident radiation intensity from the source employed. An increase in operating current from 5 to 15 mA d.c. resulted in an increase in current of *ca.* one order of magnitude owing to the equivalent increase in observed intensity of the oxygen and chlorine atomic line emission between 125 and 140 nm. The proportionality between incident intensity and PID response is observed in both the plateau and gas-gain regions.

CONCLUSIONS

Our preliminary work reported here indicates that simple, high-efficiency, narrow spectral band-pass, solar-blind photoionization detectors may offer advantages for detection of radiation at short wavelengths in analytical atomic emission spectrometry. They should prove most valuable when used for non-dispersive, on-line detection systems. The most useful wavelength range for such detectors lies between 120 and 200 nm; Table 1 shows a selection of narrow spectral band-pass detectors which may be constructed with different window and filler materials. Detectors of this type may prove useful in continuous gas-analysis monitoring systems using plasma or glow-discharge sources, particularly for detection of oxygen, oxides of nitrogen and sulphur dioxide.

The detection and determination of low concentrations of organic compounds in the vapour phase, particularly those containing halogen, sulphur or phosphorus atoms, may also be facilitated by use of this type of detection system. Work is at present in progress on the development of such systems and the application of PID detectors in atomic-absorption and fluorescence spectrometry; this will be reported in a later communication.

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STUDIES ON EXTRACTION OF THORIUM BY THE *N*-OXIDES OF 5-(4-PYRIDYL)NONANE AND TRIOCTYLAMINE FROM DIFFERENT MINERAL ACID SOLUTIONS AND ITS SEPARATION FROM RARE EARTH ELEMENTS AND YTTRIUM

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Summary—The *N*-oxides of 5-(4-pyridyl)nonane and trioctylamine have been evaluated for use in the extraction of thorium from different mineral acid solutions. The influence of the concentration of the solvents and salting-out agents has been investigated. The possible mechanism of extraction is discussed in the light of the results of extraction isotherms, loading-ratio data and log–log plots of reagent concentration *vs.* distribution ratio. Separation factors for a number of metal ions are reported and a method for the separation of thorium from rare earth elements and yttrium is also suggested.

In the search for new solvent extraction systems, the variable that can be most profitably exploited is the molecular configuration of the solvent extraction reagents: through the variation of molecular parameters such as the type of functional group and the molecular geometry, new and useful properties can be created. A class of extractants that has received much attention in the last twenty years is that of neutral organophosphorus compounds, especially tri-n-butyl phosphate (TBP).[1] TBP and other phosphorus derivatives such as trioctylphosphine oxide are similar in their extraction behaviour and the type of complex they form.

Other oxide-type compounds formed from the elements in the vicinity of phosphorus in the Periodic Table might also be expected to act as solvent extraction reagents, *e.g.*, ketones, silicon oxides, amine oxides, sulphoxides and arsine oxides. The alkyl silicon oxides readily hydrolyse, however, and are obviously unsuitable. The arsine oxides are useful extraction reagents,[2–4] but their synthesis is rather difficult.[5] Ethers, ketones and alcohols have been extensively investigated and surveyed.[6] Although the sulphoxides have been investigated and used for some years[7–17] only a few investigators[18–25] have examined *N*-oxides as extractants. This communication is a part of a programme of systematic studies of *N*-oxides as solvents, and reports recent fundamental data on the extraction of thorium by the *N*-oxides of 5-(4-pyridyl)nonane and trioctylamine and the separation of the metal from rare earth elements.

EXPERIMENTAL

Reagents

5-(4-Pyridyl)nonane *N*-oxide (PyNOx) and trioctylamine oxide (TOAO) were prepared and authenticated as reported elsewhere.[24]

Mineral acid solutions were generally prepared from standard volumetric solution ampoules and all other chemicals used were of analytical-reagent grade.

Nuclides

The ^{230}Th tracer had a ^{230}Th:^{232}Th ratio of approximately 0·085 and was isolated[26] from Australian South Alligator River pitchblende, and the ^{234}Th was milked from uranium.[27] The other tracers were obtained either from Radiochemical Centre, Amersham or through (n, γ) reactions or by separation of the daughter product from the initial nuclide without a carrier (^{140}La, ^{90}Y).[28]

Measurement of distribution coefficients

Equal volumes (2 ml) of the aqueous and organic phases were shaken mechanically for 3 min in test-tubes with ground-glass stoppers at 22 ± 2°. Preliminary experiments showed that 3 min are sufficient for attainment of equilibrium. Portions of the extracts and aqueous phases were placed on stainless-steel or glass planchettes in the case of α- and β-emitters and counted by proportional and end-window Geiger counters respectively. The γ-activities were measured with a scintillation counter and NaI(Tl) crystal.

RESULTS AND DISCUSSION

The extraction of thorium as a function of nitric, hydrochloric and sulphuric acid concentration in the aqueous phase was studied. The results are presented in Fig. 1. Thorium is quantitatively extracted only from nitric acid, with maximum extraction from 0·1–0·5*M* concentration. The decrease in extraction at higher acid concentrations is apparently due to a

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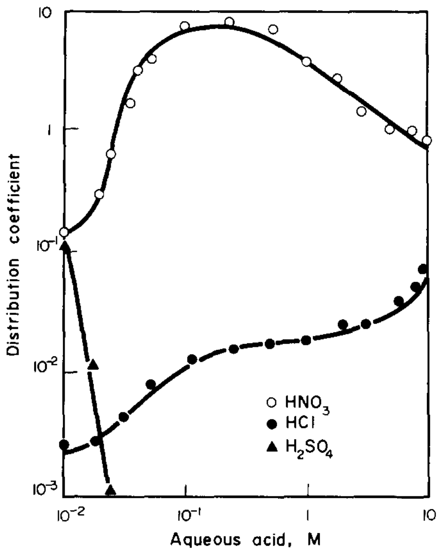

Fig. 1. Dependence of D_{Th} on the concentration of aqueous acids for extraction by 0·1*M* PyNOx in xylene.

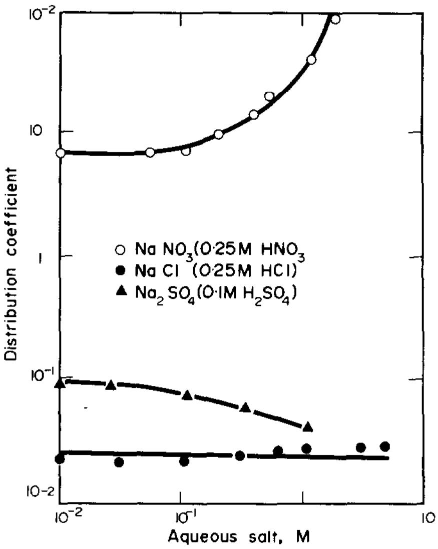

Fig. 2. Effect of salting-out agents on the extraction of thorium by 0·1*M* PyNOx in xylene.

decrease in the concentration of the free solvent through its combination with nitric acid and also to formation of inextractable anionic nitrate-complexes of thorium. Like sulphoxides,[29] PyNOx extracts thorium from very dilute nitric acid solutions much more efficiently than does TBP. In hydrochloric acid media extraction increases with concentration of the acid, possibly because neutral thorium chloride complexes are formed at high hydrochloric acid concentrations.[30] The poor extraction from sulphuric acid may be due to the formation of anionic sulphate complexes.

The effect of nitrate, chloride and sulphate ions on the extraction at constant acidity is shown in Fig. 2. The addition of nitrate ions to 0·25*M* nitric acid gives rise to high distribution coefficients similar to those with TBP,[31,32] probably because of salting-out action. In the hydrochloric acid system, chloride ions have little effect on extraction. This is in accordance with the fact that the thorium species present in up to 5*M* chloride solutions are reported to be the same irrespective of whether hydrogen ions or sodium ions are present.[33] Addition of sulphate ions to a dilute sulphuric acid solution gives rise to a steady decrease in the distribution coefficient of thorium, evidently because of the formation of anionic species which exist under these conditions.[34]

Extraction of thorium with PyNOx from nitric acid solutions can be represented as follows:

$$Th^{4+}_{aq} + 4NO^-_{3_{aq}} + n\text{PyNOx}_0 \rightleftharpoons Th(NO_3)_4.n\text{PyNOx}_0 \quad (1)$$

with equilibrium constant

$$K_1 = \frac{[Th(NO_3)_4.n\text{PyNOx}]_0}{[Th^{4+}]_{aq}\,[NO_3^-]^4_{aq}\,[\text{PyNOx}]^n_0} \quad (2)$$

The terms in brackets should be the activities, but concentrations may be used instead if they are low enough. Thus the metal distribution ratio is

$$D_{Th} = [(Th(NO_3)_4.n\text{PyNOx}]_0/[Th^{4+}]_{aq}$$
$$= K_1[\text{PyNOx}]^n_0 \quad (3)$$

Plots of log D_{Th} *vs.* log [PyNOx] are linear for 0·25*M* nitric acid medium, with a slope of about 2, indicating that a disolvate is formed, as with sulphoxides[29] and TBP.[31] Similar results were also obtained from the loading-ratio data.

Extraction of thorium by 0·1*M* TOAO in xylene from aqueous mineral acid solutions is shown in Fig. 3. In the nitric acid system, at low acidities thorium

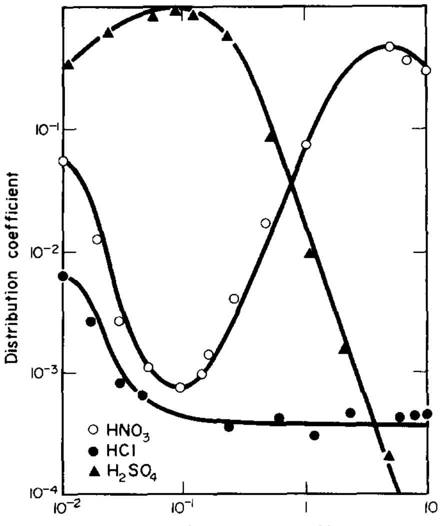

Fig. 3. Dependence of D_{Th} on the concentration of aqueous acids for extraction by 0·1*M* TOAO in xylene.

is highly hydrolysed and is probably extracted in the form of hydrolysed species. The extraction at high acidities of nitric acid resembles closely that with the unoxidized amine,[35] indicating that the extraction of hexanitrate complexes of thorium, which are present in this range of acidity,[35–38] is occurring by ion-pair formation. In the case of PyNOx, however, the extraction is considered to be of neutral complexes since the basicity of heterocyclic amine oxides is much lower than that of aliphatic amine oxides and the formation of the ion-pair structure may not be favoured in the case of PyNOx.

In hydrochloric acid media thorium extraction from low acid concentrations resembles the nitric acid system and can, therefore, be explained accordingly. The poor extraction from dilute and concentrated solutions is evidently due to absence of neutral or anionic chloro-complexes of thorium. Extraction from sulphuric acid solutions increases with increase in the acid concentration and reaches a maximum at about 0·1M hydrogen ion concentration before decreasing at higher acidities. Sulphate complexes of thorium are possibly extracted from dilute sulphuric acid solutions and the decrease in extraction may be considered as due to an increase in the bisulphate concentration in the aqueous phase.

Extraction of thorium by 0·1M TOAO/xylene from varying nitrate, chloride and sulphate concentrations at constant acidity is shown in Fig. 4. Chloride ions, added to 1M hydrochloric acid, have little effect on the extraction, as in the PyNOx system. The addition of nitrate ions to the nitric acid system increases the extraction. This may be explained as due to salting-out action and/or the increased formation of extractable complexes. The addition of sulphate ions to 0·1M sulphuric acid decreases the extraction, as in the PyNOx system.

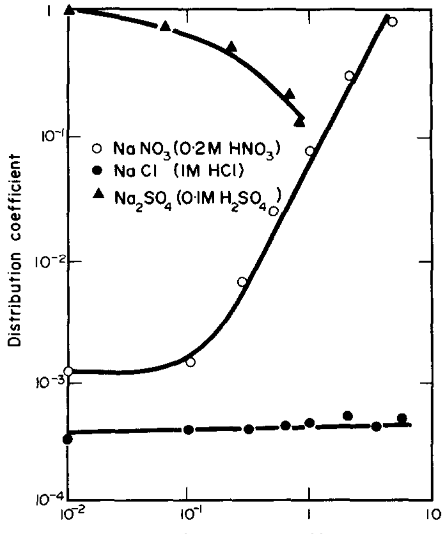

Fig. 4. Effect of salting-out agents on the extraction of thorium by 0·1M TOAO in xylene.

Table 1. Separation factors for various metal ions with respect to thorium(IV) extracted into 0·1M PyNOx in xylene from 0·25M nitric acid

Ion	Concentration, M	Separation factor
Te(VII)	C.F.	0·76
U(VI)	10^{-3}	0·78
Cr(VI)	5×10^{-2}	0·80
Mo(VI)	10^{-5}	0·816
W(VI)	10^{-7}	0·8
Nb(V)	C.F.	2×10^{2}
Ta(V)	10^{-9}	5·3
Hf(IV)	10^{-9}	5·28
Zr(IV)	10^{-9}	4
Ce(IV)	10^{-8}	8·8
Fe(III)	10^{-5}	40
Au(III)	10^{-8}	0·02
Y(III)	C.F.	$1·2 \times 10^{4}$
Ce(III)	10^{-8}	$1·26 \times 10^{4}$
La(III)	C.F.	$\sim 5 \times 10^{4}$
Eu(III)	10^{-8}	$\sim 5 \times 10^{4}$
Pr(III)	10^{-8}	$\sim 5 \times 10^{4}$
In(III)	10^{-9}	$1·6 \times 10^{3}$
Sr(II)	10^{-9}	$1·04 \times 10^{3}$
Ba(II)	10^{-9}	$0·96 \times 10^{3}$
Zn(II)	10^{-8}	4×10^{4}
Co(II)	10^{-9}	$3·6 \times 10^{4}$
Mn(II)	10^{-4}	$1·6 \times 10^{5}$
Cs(I)	10^{-8}	$1·36 \times 10^{5}$
Ag(I)	10^{-7}	$1·6 \times 10^{3}$

C.F. Carrier-free.

In the nitric and sulphuric acid systems plots of log D_{Th} *vs.* log [PyNOx] are linear for 6M nitric and 0·2M sulphuric acid, with a slope of about 2, suggesting that thorium is extracted as a disolvate in both cases.

Back-extraction of thorium

Thorium extracted into the organic phase from nitric acid solutions by PyNOx may be readily stripped with dilute sulphuric or hydrochloric acid. Quantitative stripping of thorium is achieved in 2 min with 0·5–1M sulphuric acid.

Extraction behaviour of other metal ions

The extraction behaviour of other heavy metal ions and fission products from 0·25M nitric acid by 0·1M PyNOx in xylene was investigated and the results are shown in Table 1. It is evident that thorium can be separated from the rare earth elements and yttrium. The data were tested by extracting thorium from a 0·05M thorium test solution containing not more than 0·5 mg/ml of Ce, La, Eu and Y in 0·25M nitric acid with an equal volume of a 0·1M solution of PyNOx in xylene. The equilibration time was 3 min. After centrifugation the organic phase was removed and thorium was stripped with an equal volume of 0·5–1M sulphuric acid. The γ-spectrum showed the absence of Ce, La, Eu and Y in the back-extract.

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ANREICHERUNG VON SPUREN Au UND Pd AUS REINSTMETALLEN Cd, In, Ni, Pb UND Zn MIT NACHFOLGENDER BESTIMMUNG IN DER GRAPHITROHR-KÜVETTE

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Zusammenfassung—Es wurde ein Verfahren zur Bestimmung von Spuren Au und Pd in Reinstmetallen Zn, Cd, In, Ni und Pb entwickelt. Nach Lösen des Probenmaterials werden die Spuren aus etwa 2*M* salzsaurer Lösung als Dithizon-Chelate ausgefällt, wobei überschüssiges Dithizon als Spurenfänger dient. Niederschlag und Cellulosenitrat-Membranfilter werden gemeinsam zu 1,0 ml in Dimethylsulfoxid gelöst. Anteile dieser Lösung (50 μl) werden durch flammenlose AAS in der Graphitrohr-Küvette analysiert. Für die relative Standardabweichung der Anreicherung und Bestimmung von etwa $5 \cdot 10^{-7}\%$ Au bzw. Pd wurden, je nach Probenmaterial, Werte zwischen 4% und 12% ermittelt; für Einwaagen von 10 g Metall wurden Nachweisgrenzen im Bereich $2–5 \cdot 10^{-8}\%$ Au bzw. $0,6–1 \cdot 10^{-7}\%$ Pd berechnet. Dabei wurde vereinfachend angenommen, daß vor allem der Störpegel der Bestimmungsmethode die Nachweisgrenze des gesamten Analysenverfahrens bestimmt.

Die "flammenlosen" Verfahren der Atomabsorptions-Spektrometrie (AAS) gehören heute zu den nachweisstärksten Bestimmungsmethoden für Elementspuren. Ihre Anwendbarkeit und Leistungsfähigkeit bei der Spurenanalyse von Reinststoffen ist jedoch durch eine Reihe von Merkmalen gekennzeichnet, die wesentlich durch Art und Menge des zu untersuchenden Materials in der Probenlösung mitbestimmt werden. Zum Beispiel gilt das hohe Nachweisvermögen des Verfahrens vor allem für Spuren*mengen*; wegen der nur im unteren Mikroliter-Bereich liegenden Volumina an eingesetzter Probenlösung ist das Nachweisvermögen für Spuren*konzentrationen* weniger ausgeprägt. Die Mehrzahl der flammenlosen AAS-Verfahren ist ihrer Natur nach deshalb eher zur Mikro- als zur Spurenanalyse geeignet.

Um Spurenverunreinigungen um $10^{-7}\%$—etwa in Reinstmetallen und Metallsalzen—bestimmen zu können, ist, von Ausnahmen abgesehen, die Abtrennung der Matrix sowie die Anreicherung der Spuren aus einer größeren Probeneinwaage unumgänglich. Die oft beträchtliche Störung der Spurenbestimmung durch Fremdsalze in der Probenlösung verlangt möglichst matrixfreie Spurenkonzentrate. Dabei sind Verbundverfahren aus chemischer Anreicherung und flammenloser AAS vor allem dann von Interesse, wenn nur einzelne Elemente im Probenmaterial zu bestimmen sind. Für Multi-Element-Analysen ist dieses Verfahren schon wegen der relativ langen Analysenzeiten und der für jedes Element notwendigen Umrüstung des AAS-Geräts (Wechsel der Hohlkathoden-Lampen sowie Änderung der Einstellungen an Monochromator, Meßelektronik und Heizautomatik für die Ofen-Anordnung) nur wenig geeignet.

Ziel der im folgenden beschriebenen Arbeit war, ein Verbundverfahren für Spuren Gold und Palladium in Reinstmetallen zu entwickeln, bei dem durch flammenlose AAS mit der Graphitrohr-Küvette Au bzw. Pd in Gehalten von $10^{-7}\%$ und darunter erfaßt werden können. Höchstens in so niedriger Konzentration werden diese Elemente—wenn überhaupt—in vielen im Handel befindlichen Materialien gefunden. Entsprechend dieser Analysenaufgabe und entsprechend der Leistungsfähigkeit des Bestimmungsverfahrens mußte ein Anreicherungsprozeß unter folgenden allgemeinen Gesichtspunkten entwickelt werden:

1. Trennung von Spuren und Matrix aus Einwaagen bis zu 10 g Probenmaterial;
2. Anreicherung der Spuren in ein weitgehend matrixfreies Spurenkonzentrat mit definiertem kleinen Probenvolumen (1 ml);
3. Vermeiden von Stoffen, die eine Störung der Spurenbestimmung verursachen.

Zur selektiven Abtrennung kleiner Mengen Gold und Palladium ist als chelatbildendes Reagenz das seit langem in der Spurenanalyse verwendete Dithizon geeignet.[1] Zwar reagiert Dithizon mit mehr als 30 Kationen zu stabilen Chelaten, Bildung und Stabilität hängen aber u.a. stark vom pH-Wert der Lösung ab. Dies wird in einer Vielzahl von Varianten vor allem zur extraktiven Trennung der Metalldithizonate ausgenutzt. In Lösungen mit pH-Werten <1 werden vor allem die Chelate der Metallkationen Hg^{2+}, Ag^{+}, Pd^{2+} und Au^{3+} gebildet; durch Einstellen einer hohen Acidität kann man erreichen, daß andere Metalle an der Reaktion mit dem Chelatbildner gehindert werden, auch wenn sie in wesentlich höherer Konzentration als die Edelmetall-Spuren in der Probenlösung enthalten sind.

Die Dithizon-Komplexe von Pd^{2+} und Au^{3+} sind sehr stabil: $PdDz_2$ (Dz = Dithizon), einmal gebildet, wird auch durch 12*N* Schwefelsäure nicht mehr zerlegt.[1] Auch das Gold-Dithizonat ist gegenüber Säuren sehr beständig, wobei, je nach Art der Arbeitsbedingungen, Verbindungen unterschiedlicher Ligandenzahl entstehen sollen.[2] In einer Arbeit von Cox und Servant[3] wird die Bildung definierter Gold-Dithizonate überhaupt infrage gestellt und die als solche beschriebenen Farbkomplexe eher als Oxidationsprodukte des Dithizons bedeutet. Au^{3+}- oder Au^{+}-Ionen werden von den Autoren lediglich als Oxidationsmittel in dieser Reaktion angesehen. Die Ergebnisse der folgenden Arbeit zeigen, daß Spuren Gold nach Reaktion mit Dithizon zumindest in einer in organischen Lösungsmitteln löslichen Form enthalten sind. Nähere Untersuchungen dazu haben wir nicht durchgeführt.

EXPERIMENTELLER TEIL

Beim augenblicklichen Entwicklungsstand der flammenlosen AAS-Verfahren sind Arbeitsvorschriften nur selten mit gleichbleibenden Ergebnissen auf Geräte anderer Laboratorien übertragbar. Wegen der komplizierten Vorgänge und Abhängigkeiten im Absorptionsvolumen des Graphitrohres[4] gilt dies auch für Geräte desselben Herstellers, oft sogar für zeitlich auseinanderliegende Wiederholungmessungen an demselben Gerät. Bei einer Übernahme von Arbeitsvorschriften aus der Literatur müssen in der Regel vor allem die Betriebsdaten für den Graphitrohr-Ofen (Temperatur–Zeit-Ablauf der Heizautomatik) überprüft und gegebenenfalls der eigenen Meßapparatur angepaßt werden. In diesem Sinne sind auch die hier mitgeteilten Apparate-Parameter unserer Untersuchungen zu verstehen.

Geräte

Perkin-Elmer Atomabsorptions-Spektrometer Modell 300 mit Untergrund-Kompensator und Hohlkathoden-Lampen für Gold und Palladium. Graphitrohr-Küvette mit Heizautomatik HGA 72.[5] Für vergleichende Untersuchungen wurde in Einzelfällen das neuere Modell HGA 74 verwendet. Die Meßsignale wurden mit einem Kompensations-Schreiber (Eingang 5 mV, Vorschub 3 cm/min) registriert.

Heizprogramm für den Graphitrohr-Ofen HGA 72

a	Verdampfen des Lösungsmittels:	60 sec bei 200°
b	Zersetzen organischer Rückstände:	in *ca.* 45 sec weiterer linearer Temperaturanstieg (Temperatur-Gleitprogramm) auf 750° (Au) bzw. 700° (Pd) danach jeweils 60 sec Verweilzeit bei der Endtemperatur
c	Atomisieren:	15 sec bei etwa 2600° (höchste am Meßgerät angezeigte Temperatur)

Alle Temperaturangaben sind Werte des Meßgeräts der Heizautomatik. Die Messungen wurden in N_2-Schutzgas-Atmosphäre (1,7 l./min) durchgeführt.

Untersuchungen zur selektiven Anreicherung von Spuren Au und Pd

Bei unserem Verfahren werden zur Anreicherung von Gold und Palladium die Dithizonchelate der Spuren aus saurer Lösung ausgefällt. Das Fällungsreagenz Dithizon wird zu wenigen Milligramm als Acetonlösung zugesetzt. Da es in nicht zu starken Säuren ebenfalls schwerlöslich ist, dient der Reagenzüberschuß zugleich als "Spurenfänger". Spuren und Matrix werden durch Filtrieren der Suspension über ein Membranfilter voneinander getrennt. Filter und Niederschlag werden in einem definierten Volumen eines geeigneten Lösungsmittels klar gelöst; in aliquoten Teilen der Lösung werden Gold und Palladium bestimmt.

Bei Auswahl der Arbeitsbedingungen wurden vor allem die Einflüsse der Acidität sowie die von Filtermaterial und Dithizonmenge auf den Anreicherungs- und Bestimmungsprozess untersucht. Dabei zeigte es sich, daß die Acidität der Probenlösung in weiten Grenzen variieren kann, ohne daß die Vollständigkeit der Spurenanreicherung beeinträchtigt wird. Der Säurezusatz muß lediglich so hoch gewählt werden, daß Matrixbestandteile nicht mehr mit Dithizon reagieren; andererseits muß der Spurenfänger zur Sorption der Edelmetall-Chelate in filtrierbarer Menge ausfallen. Beide Voraussetzungen sind im Bereich von etwa 1,5 bis 4*N* Säure erfüllt. Schwierigkeiten ergeben sich lediglich durch mitgerissenes Kupfer, das schon in Mikrogramm-Mengen bei der AAS-Bestimmung der Spuren stört. Da die Sorption so geringer Mengen Kupfer auch in stark saurer lösung nicht verhindert werden kann, muß die Störung durch ein besonderes Eichverfahren eliminiert werden. Spuren und Spurenfänger werden, für alle untersuchten Probenmaterialien einheitlich, in etwa 2*N* Säure ausgefällt. Wichtig ist, daß nitrose Gase aus dem Löseprozeß der Metallproben vollständig entfernt sind; andernfalls wird ein Teil des Dithizons oxidiert, und man erhält —vor allem beim Palladium—zu kleine Analysenwerte. Aus diesem Grunde wird die Salpetersäure nach Lösen der Metalle unter Zusatz konzentrierter Salzsäure jeweils sorgfältig abgeraucht. Die Spurenfällung wird deshalb auch in *salzsaurer* Lösung durchgeführt. Als Spurenfänger wird eine nur geringe Dithizonmenge verwendet, um den bei der nachfolgenden Spurenbestimmung durch "Rauchpeaks" verursachten Untergrund an unspezifischer Absorption möglichst niedrig zu halten. Abbildung 1 zeigt die Abhängigkeit der Anreicherungs-Ausbeuten (100 ng Au bzw. Pd) vom Reagenzzusatz. Zwei mg Dithizon reichen danach voll aus, um maximale Ausbeuten zu erzielen. Dies gilt auch dann, wenn Kupfer in Mengen bis zu 10 mg im eingewogenen Probenmaterial enthalten ist.

Menge und Beschaffenheit von Niederschlag und Filter

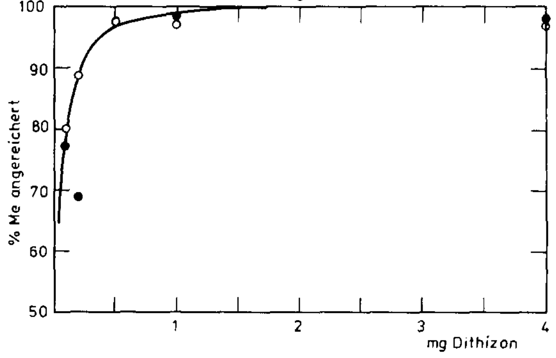

Abb. 1. Abhängigkeit der Anreicherung von 100 ng Au (○) bzw. Pd (●) von der als Spurenfänger eingesetzten Dithizonmenge.

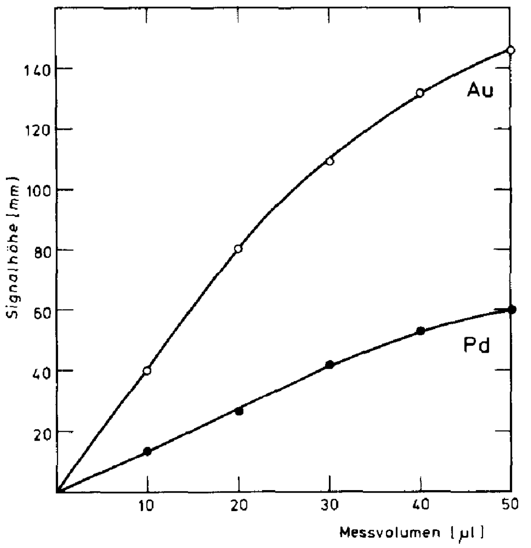

Abb. 2. Abhängigkeit der Signalhöhe (registrierte Peakhöhen) vom injizierten Probenvolumen bei der Bestimmung von Au und Pd in der Graphitrohr-Küvette HGA 72 (DMSO-Lösung mit 0,1 μg/ml Au bzw. Pd).

sind von besonderer Bedeutung, um klare homogene Spurenkonzentrat-Lösungen geringer Viskosität zu erhalten, aus denen ohne merklichen Verlust die zur Bestimmung notwendigen μl-Volumina dosiert werden können. Nach zahlreichen Voruntersuchungen mit unterschiedlichen Filtermaterialien sowie den zum Lösen von Filter und Niederschlag geeigneten Lösungsmitteln wurden Cellulosenitrat-Membranfilter sowie Dimethylsulfoxid (DMSO) gewählt. Durch Erwärmen im Wasserbad lösen sich Filter und Niederschlag in 1 ml DMSO zu einer für die Spurenbestimmung geeigneten Lösung, die, im Meßkolben verschlossen und unter Lichtausschluß aufbewahrt, auch bei nur wenigen Nanogramm angereicherter Edelmetalle über mehrere Wochen titerstabil bleibt.

Untersuchungen zur Dosierung der Meßlösungen

Zur Dosierung der Meßlösungen wurden Mikroliter-Pipetten (Eppendorf, Hamburg) verwendet. Abbildung 2 zeigt, daß die Signalhöhen bei ansteigend injizierten Probenvolumina (Lösung mit 0,1 μg/ml Au) nichtlinear größer werden. Oberhalb von etwa 50 μl wird die Reproduzierbarkeit der Meßwerte zunehmend schlechter. Ursache hierfür ist die unvollständige Verdampfung von DMSO im Graphitrohr: bei größeren DMSO-Volumina schlagen sich Teile des Dampfes bzw. höhersiedender Zersetzungsprodukte an kälteren Stellen des Rohres nieder und verursachen in der Atomisierungsstufe des Heizprogramms einen mehr oder weniger starken "Rauchpeak", dessen unspezifische Lichtabsorption durch den Untergrund-Kompensator nicht immer voll eliminiert wird. Auch mit den von der Gerätefirma angebotenen "Spezial-Graphitrohren" (Art.-Nr. 062628) mit innen ausgefrästem Ring zur Aufnahme größerer Probenvolumina wurden mit über 50 μl hinausgehenden Probenvolumina keine brauchbaren Ergebnisse erzielt. Sowohl für die Bestimmung von Gold als auch für die von Palladium wurde das Meßvolumen deshalb nach oben hin auf 50 μl begrenzt.

Zur Störung der Spurenbestimmung durch Kupfer

Es wurde bereits darauf hingewiesen, daß die Analyse von Spuren Gold und Palladium unter den Bedingungen unserer Arbeitsvorschrift durch Kupfer gestört wird: in Gegenwart von Kupfer erhält man deutlich verminderte Analysensignale (Abb. 3). Die erste Vermutung, daß Kupfer bereits die quantitative Anreicherung der Edelmetallspuren behindere, erwies sich als falsch; gestört wird vielmehr die eigentliche Bestimmung der Spuren und zwar durch dasjenige Kupfer, das im Anreicherungsprozeß als Dithizon-Chelat mit erfaßt wird und in die DMSO-Lösung der Spuren gelangt. Um das Ausmaß der Störung zu ermitteln, wurden zu einer Serie 2*N* salzsaurer Lösungen mit je 0,1 μg Au^{3+} und Pd^{2+} in 150 ml ansteigende Mengen Cu^{2+} (als $CuCl_2$-Lösung) gegeben. Die Edelmetallspuren wurden entsprechend der Arbeitsvorschrift angereichert und in der Graphitrohr-Küvette bestimmt. Die Höhe der Signale wurde gegen den Kupferzusatz aufgetragen. Nach Aussage der Diagramme (Abb. 3) sinken die Meßsignale sowohl für Gold als auch für Palladium zunächst rasch auf einen Wert, der nur etwa die Hälfte des Wertes für kupferfreie Probenlösungen erreicht, bleibt dann aber über einen Bereich mehrerer Milligramm Kupfer praktisch unverändert. Der Kurvenverlauf hängt jedoch von den Anreicherungsbedingungen, insbesondere von Acidität und Chelatbildner-Menge ab, so daß jede Veränderung der Parameter auch auf das Ausmaß der Kupferstörung einwirkt. Zahlreiche Versuche, die eigentliche Ursache für diese Störung zu finden bzw. sie zu beseitigen, brachten keinen Erfolg.

Um den Einfluß wechselnder Kupfermengen bei der Analyse unterschiedlich reiner Metalle zu stabilisieren, haben wir im folgenden jedem Probenmaterial mit Eigenverunreinigungen von mehr als 10 μg Kupfer pro Einwaage einheitlich 2 mg Cu^{2+} zugesetzt und den dadurch bedingten Verlust an Empfindlichkeit bei der Spurenbestimmung in Kauf genommen. Der Störeinnfluß des Kupfers wurde in diesem Fall als systematischer Fehler des Bestimmungsverfahrens bei der Eichung berücksichtigt.

Eichung des Analysenverfahrens

In der Graphitrohr-Küvette können Spuren nur anhand jeweils mitgeführter Leitproben sicher bestimmt werden. Bewährt haben sich das Eichzusatz-Verfahren sowie die sich der Analyse unmittelbar anschließende Eichung durch Standardlösungen mit abgestuften Spurengehalten. Wegen der Störungen durch viele Arten von Fremdstoffen muß besonders bei den flammenlosen AAS-Verfahren sorgfältig darauf geachtet werden, daß Proben- und Standardlösungen möglichst identisch zusammengesetzt sind. Für unser Verfahren bedeutet das, daß zur Eichung DMSO-Lösungen verwendet werden müssen, die neben den Spuren den Chelatbildner Dithizon sowie das Filtermaterial gelöst enthalten. Zu ihrer Herstellung haben wir entsprechend der

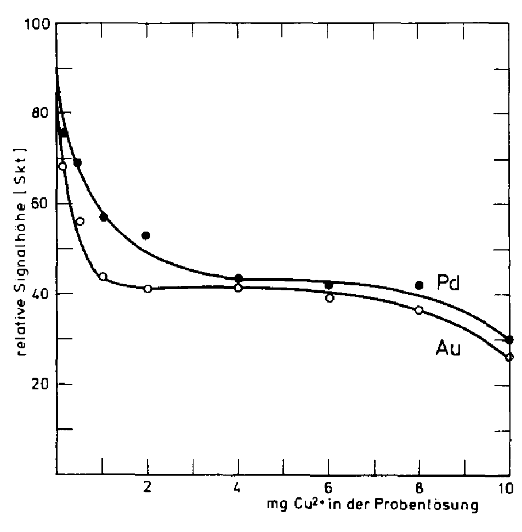

Abb. 3. Änderung der relativen Signalhöhen durch den Kupfergehalt des Probenmaterials (kupferfreie Lösungen zu 100 Skt angenommen).

Arbeitsvorschrift abgestufte Mengen Gold und Palladium aus etwa 2*N* salzsaurer Lösung (eventuell nach Zusatz von je 2 mg Cu^{2+} als $CuCl_2$) mit Dithizon ausgefällt und den Niederschlag einschließlich Filter in DMSO gelöst. Da solche Lösungen über mehrere Wochen titerstabil sind, können die Standardlösungen als Vorrat auch in größeren Volumina als 1 ml angesetzt werden. Sie müssen allerdings das Filtermaterial und Dithizon in der entsprechend erhöhten Menge enthalten.

Arbeitsvorschriften zum Lösen der Probenmaterialien

In den im folgenden beschriebenen Löseprozessen für die Reinstmetalle Zn, Cd, In, Ni und Pb sind vor allem zwei Gesichtspunkte bestimmend. 1. Die Edelmetallspuren müssen neben der unedleren Matrix quantitativ in Lösung gebracht werden. Obwohl sich die Probenmaterialien bereits in Salzsäure bzw. in Salpetersäure allein lösen, ist besonders für Gold eine Mischung aus beiden Säuren erforderlich. Im Verlaufe des Lösevorgangs muß deshalb "Königswasser" entstehen, damit sonst ungelöst bleibende Goldspuren sicher erfaßt werden. 2. Wegen der hohen Oxidationsempfindlichkeit des als Spurenfänger verwendeten Dithizons müssen nitrose Gase und andere oxidierende Stoffe vollständig aus der Probenlösung entfernt werden. Aus diesem Grund werden die Metallsalze nach Lösen der Proben mehrfach mit konzentrierter Salzsäure abgeraucht. Die Wirksamkeit der Salzsäure ist bei den verschiedenen Metallen sehr unterschiedlich; sie ist besonders groß, wenn das Nitrat bereits durch Bildung wenig dissoziierter Chloride oder Chlorokomplexe aus den Metallsalzen verdrängt wird. Aus diesem Grund ist die Behandlung des Nickels hier am langwierigsten. Die Umsetzung mit Salzsäure kann bei allen Salzen wesentlich beschleunigt werden, wenn man die Lösungen während des Einengens, etwa mit einem heizbaren Magnetrührer, intensiv durchmischt. Die beim Lösen des Bleis unvermeidbare $PbCl_2$-Suspension wird jedoch am besten mit Hilfe von Oberflächenstrahlern eingeengt. Sofern das Probenmaterial mehr als etwa 10 μg Cu pro Einwaage enthält, setzt man, um Störungen durch Kupfer bei der Eichung eliminieren zu können, zu Beginn des Löseprozesses 2 mg Cu in Form von $CuCl_2$-Lösung zu. Ein Kupferzusatz in gleicher Höhe muß anschließend auch bei der Herstellung der Eichlösungen verwendet werden (siehe auch dort).

Zink, Cadmium, Indium

10 g zerspantes Metall werden in einem 250-ml Becherglas (hohe Form) mit 5–10 ml Wasser sowie 30 ml 37%iger Salzsäure versetzt. Portionsweise werden nun insgesamt 5 ml 65%iger Salpetersäure zugesetzt (bei Zink sind 3 ml ausreichend), wobei die Größe der Portionen sowie die Temperatur dem Ablauf der Lösereaktion angepaßt werden. Wenn das Probenmaterial gelöst ist, werden weitere 2 ml 65%iger Salpetersäure zugegeben. Die Lösung wird weitgehend eingeengt. Nach Zusatz von 5 ml 37%iger Salzsäure (bei Cadmium sind 10 ml erforderlich) wird erneut eingeengt. Der Vorgang wird noch zweimal wiederholt. Der Kristallbrei wird anschließend mit 20 ml 37%iger Salzsäure sowie 50 ml Wasser gelöst und etwa 1 min zum Sieden erhitzt. Nach Abkühlen auf Raumtemperatur wird die Lösung mit Wasser auf 150 ml verdünnt. Aus dieser etwa 2*N* salzsauren Probenlösung werden Gold und Palladium entsprechend der Anreicherungsvorschrift abgetrennt.

Nickel

10 g Nickel werden in einem 250-ml Becherglas (hohe Form) mit 5 ml Wasser versetzt; portionsweise wird 65% ige Salpetersäure zugegeben, bis das Probenmaterial gelöst ist. Je nach Beschaffenheit des Materials (Pulver, Späne, Kugeln) benötigt man dazu 40–80 ml. Die Lösetemperatur wird dem Ablauf der Reaktion angepaßt. Die Lösung wird eingeengt, mit 30 ml 37%iger Salzsäure versetzt und unter Rühren (heizbarer Magnetrührer) erneut bis zur beginnenden Salzausscheidung eingeengt. Dieser Vorgang wird mit 10-ml Portionen wiederholt, bis auf Zusatz einiger Tropfen 48%iger Bromwasserstoffsäure kein Brom mehr freigesetzt wird (Gesamtverbrauch etwa 150 ml Salzsäure). Die Lösung wird nun bis fast zur Trockne gebracht. Der Kristallbrei wird in 20 ml 37%iger Salzsäure sowie 50 ml Wasser gelöst und etwa 1 min zum Sieden erhitzt. Nach Abkühlen auf Raumtemperatur wird die Lösung auf 150 ml mit Wasser verdünnt. Aus dieser etwa 2*N* salzsauren Probenlösung werden Gold und Palladium entsprechend der Anreicherungsvorschrift abgetrennt.

Blei

10 g zerspantes Blei werden in einem 250-ml Becherglas (hohe Form) mit etwa 20 ml Wasser erhitzt. Durch Zusatz von insgesamt 12 ml 65%iger Salpetersäure in mehreren Portionen wird das Probenmaterial vollständig gelöst. Dann werden 30 ml 37%iger Salzsäure zugesetzt. Mit Hilfe von Oberflächenstrahlern wird die $PbCl_2$-Suspension bis zur Trockne eingedampft; der Vorgang wird die Lösung auf 150 ml mit Wasser verdünnt. Aus Rückstand wird in 20 ml 37% iger Salzsäure sowie 50 ml Wasser suspendiert, die Suspension wird unter fließendem Wasser abgekühlt. Anschließend wird das Bleichlorid über ein weiches Filter abfiltriert. Das Filtrat wird etwa 1 min zum Sieden erhitzt. Nach Abkühlen auf Raumtemperatur wird die Lösung auf 150 ml mit Wasser verdünnt. Aus dieser etwa 2*N* salzsauren Probenlösung werden Gold und Palladium entsprechend der Anreicherungsvorschrift abgetrennt.

Arbeitsvorschrift zur Anreicherung von Spuren Au und Pd

Die etwa 2*N* salzsaure Lösung der zur Analyse eingesetzten Metalle wird unter intensivem Rühren mit 2,0 ml einer 0,1% igen Lösung von Dithizon in Aceton versetzt. Noch vorhandene Reste oxidierender Stoffe werden durch Zugeben von 1 ml 10%iger Ascorbinsäure-Lösung sofort nach Zusatz des Dithizons zerstört. Dithizon- wie Ascorbinsäure-Lösung müssen täglich frisch angesetzt werden. Unmittelbar nach der Fällung wird der Niederschlag mit Hilfe einer zerlegbaren Hahn'schen Nutsche[6] über ein Cellulosenitrat-Membranfilter (Schleicher & Schüll, Selectron AE 99; Porengröße 8 μm, Filterdicke 180 μm, Durchmesser 25 mm) abgesaugt. Probengefäß und Nutsche werden mit wenigen ml Wasser, dem etwas Netzmittel (z.B. "Zephirol") zugesetzt wurde, gespült. Durch das Netzmittel wird verhindert, daß fein verteilte Partikel des Niederschlags an den Gefäßwandungen hochkriechen.

Der Dithizon-Niederschlag wird zusammen mit dem Filter in ein 1 ml-Meßkölbchen gebracht, mit etwa 0,8 ml Dimethylsulfoxid (Merck, zur Analyse) versetzt und 5 min im Wasserbad bei etwa 80° erhitzt. Nach dem Abkühlen wird mit DMSO zur Marke aufgefüllt und die Lösung gut durchmischt. Nach einer Standzeit von etwa 1 Std. werden Gold und Palladium in Teilen von je 50 μl dieser Lösung bestimmt. Zur Analyse wurden aus jeder Lösung drei aufeinanderfolgende Parallelbestimmungen durchgeführt, deren Signale gemittelt wurden.

ERGEBNISSE DER UNTERSUCHUNGEN

Zur Entwicklung und Bewertung des Analysenverfahrens wurden handelsübliche Reinstmetalle eingesetzt. Analysenwerte der Hersteller über die Gehalte an Gold und Palladium standen nicht zur Verfügung. In Tabelle 1 sind Angaben über die Herkunft einiger Metalle mit den von uns ermittelten Daten zusammengestellt. Die Mehrzahl der Zahlenwerte gibt die aus den Untergrundstreuungen errechnete "Garantiegrenze für Reinheit" wieder.[7] Zur

Tabelle 1. Reinstmetallproben, deren Herkunft und Analysenwerte

Probenmaterial		Analysendaten Au, %	 Pd, %
Zink	Merck, Darmstadt, gekörnt, z.A. mind. 99,9% Zn Art.-Nr. 8780	$<6\cdot10^{-8}$*	$<2\cdot10^{-7}$*
Cadmium	Riedel-de Haën, Seelze-Hannover, Stangen, Art.-Nr. 11704	$<1\cdot10^{-7}$*	$<2\cdot10^{-7}$*
	Preussag AG, Metall, Goslar, Stangen, mind. 99,9998% Cd	$<1\cdot10^{-7}$*	$<2\cdot10^{-7}$*
Indium	Preussag AG, Metall, Goslar, Barren, 99,9995% In	$2\cdot10^{-7}$	$<1\cdot10^{-7}$*
Nickel	Merck, Darmstadt, Kugeln, mind. 99,7% Ni Art.-Nr. 6701	$2\cdot10^{-7}$	$2\cdot10^{-7}$
Blei	Merck, Darmstadt, fein gekörnt, Art.-Nr. 7363	$3\cdot10^{-8}$	$<1\cdot10^{-7}$*
	Nordd. Affinerie, Hamburg, Feinblei-Muster 5A/72 fein gekörnt	$6\cdot10^{-8}$	$<1\cdot10^{-7}$*

* “Garantiegrenze für Reinheit”[7]

Ermittlung der relativen Standardabweichung $s/\bar{x}$ des Analysenverfahrens haben wir den Metalleinwaagen Spuren Gold und Palladium als Lösungen zugesetzt, so daß einheitlich für sämtliche Probenmaterialien Gehalte von $5\cdot10^{-7}$% Gold bzw. Palladium eingestellt wurden. Der Berechnung lagen 10 vollständige Analysen zugrunde (Tabelle 2). Ein Vergleich mit matrixfreien Probenlösungen zeigte, daß bei der Anreicherung der Spuren Gold und Palladium jeweils um 90% der zugesetzten Elementspurenmenge wiedergefunden werden. Der Wert für die Anreicherungsausbeute wurde bei der Verfahrenseichung berücksichtigt.

Die tabellierten Daten für die Nachweisgrenze (3σ-Grenze) wurden aus den Untergrundstreuungen allein des Bestimmungsverfahrens errechnet; sie stellen also nur Schätzwerte für die Nachweisgrenze des Gesamtverfahrens dar, die unter günstigen Umständen erreicht werden könnten. Dieses Vorgehen schien uns wegen der Kostbarkeit eines Teils der Probenmaterialien sowie wegen des Fehlens meßbarer Reagenzienblindwerte für Gold und Palladium in den benutzten “analysenreinen” Chemikalien vertretbar.

Tabelle 2. Analysenergebnisse

Probenmaterial (Au- bzw. Pd-gehalt: $5\cdot10^{-7}$%) (siehe Text)	rel. Standardabweichung $100\,s/\bar{x}$ %, ($N = 10$) Au	 Pd	Nachweisgrenze (3σ-Grenze) (siehe Text) Au, %	 Pd, %
10 g Zn	7,6	4,6	$3\cdot10^{-8}$	$1\cdot10^{-7}$
10 g Cd	5,4	5,2	$5\cdot10^{-8}$	$8\cdot10^{-8}$
10 g In	3,9	4,5	$3\cdot10^{-8}$	$7\cdot10^{-8}$
10 g Ni	12	12	$3\cdot10^{-8}$	$7\cdot10^{-8}$
10 g Pb	6,7	11	$2\cdot10^{-8}$	$6\cdot10^{-8}$
1 g Pb*	4,3	7,0	$6\cdot10^{-7}$	$1\cdot10^{-6}$

* mit $5\cdot10^{-6}$% Au bzw. Pd.

In einer Serie von Messungen wurde versucht, die mit der Graphitrohr-Küvette HGA 72 erhaltenen Ergebnisse auf das neuere Modell HGA 74 zu übertragen. Beide Geräte unterscheiden sich sowohl in der eigentlichen Küvette als auch in der Auslegung der Heizautomatik. Einflüsse auf Empfindlichkeit und Nachweisvermögen des Bestimmungsverfahrens waren vor allem durch die bei der HGA 74 abgeänderte interne Schutzgasführung, die veränderte Anstiegsrate im Temperatursprung der Atomisierungsstufe sowie durch die kleinere Dimensionierung des Graphitrohres zu erwarten. Ein unmittelbarer Vergleich beider Modelle sowie eine zu verallgemeinernde Aussage über die Leistungsfähigkeit sind mit wenigen Meßreihen kaum möglich.

Die Übertragung der unveränderten Arbeitsvorschrift unseres Bestimmungsverfahrens für Gold und Palladium erwies sich erwartungsgemäß als nicht möglich: 50 µl der an Dithizon und Cellulosenitrat relativ konzentrierten DMSO-Lösung des Spurenkonzentrats verursachten bei Verwenden der HGA 74 Rauchpeaks, die nur in Ausnahmefällen durch den Untergrundkompensator eliminiert werden konnten; stark streuende Signale waren die Folge. Gleichzeitig wurde die Lebensdauer der Graphitrohre durch die großen Stoffmengen merklich verringert. Erst bei Vermindern des eingegebenen Probenvolumens auf 20 µl konnten die angereicherten Elemente Au und Pd ohne Schwierigkeit bestimmt werden. Die Ergebnisse der mit beiden HGA-Systemen an 20 µl-Anteilen der Spurenkonzentrate durchgeführten Parallelmessungen können folgendermaßen zusammengefaßt werden.

Empfindlichkeit und Genauigkeit der Bestimmung beider Elemente ändern sich beim Wechsel der Graphitrohr-Küvette nur unwesentlich, sofern die durchfließende Inertgas-Menge (N_2) im Augenblick der Bestimmung etwa die gleiche ist. Die Gasströmung bestimmt die Verweilzeit der Atome in der Küvette und damit Empfindlichkeit und Nachweisvermögen der Messung. Bei der HGA 74 kann der Gasstrom in der Atomisierungsstufe der Heizautomatik wahlweise reduziert oder ganz abgestellt werden; die HGA 72 erlaubt die Messung nur bei vollem oder bei ganz abgestelltem Gasfluß. Das Erste ist u.U. günstig, um Reste organischer Stoffe noch im Temperaturanstieg der Atomisierungsstufe aus dem Meßraum zu entfernen. Sind Störungen durch Rauchpeaks nicht zu erwarten, so wird die Empfindlichkeit der Bestimmung des Goldes um mehr als das Doppelte verbessert, wenn bei abgeschaltetem Schutzgasfluß gemessen wird; die Signale des Palladiums verändern sich dagegen nur unwesentlich. Dies gilt für beide Systeme. Wegen der Möglichkeit, größere Probenvolumina mit entsprechend größeren absoluten Proben- und Spurenmengen störungsfrei bei der Bestimmung einsetzen zu können, haben wir die Küvette HGA 72 in den Untersuchungen dieser Arbeit dem neueren Modell vorgezogen: die höhere Probeneingabe erbrachte einen Gewinn an Empfindlichkeit und Nachweisvermögen um etwa den Faktor 2.

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DEVELOPMENT AND PUBLICATION OF SOLVENT EXTRACTION METHODS

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Summary—Guidelines are set for the development of solvent extraction separation methods and for their preparation for publication. The necessity of establishing the novelty of and need for the new method is emphasized. The various items that require specification are discussed, and the criteria for successful application of the method, *viz.* completeness of extraction, selectivity and freedom from interference, are laid down.

Solvent extraction is a separation method, and as such has been used for centuries in such enterprises as the perfume industry. Applications in analytical chemistry may quite arbitrarily be said to start with the observation by Peligot, of the extractability of uranyl nitrate by ether, in 1842.[1] An established item in the classical scheme of qualitative analysis of the metal cations is the extraction of cobalt thiocyanate into amyl alcohol to form a deep blue layer.[2,3] The separation of iron(III) chloride from hydrochloric acid media by extraction with ether[4] is another early instance of the application of solvent extraction in analytical chemistry. Recent interest is evidenced by the five hundred papers in the field published annually and their biennial review by Freiser in *Analytical Chemistry*,[5] (lamentably not since 1968). In this proliferation of papers many worthwhile new methods are published, but trivial work is not excluded, nor is faulty reporting of otherwise good work. It is the purpose of this paper to point out those features of the solvent extraction methods that must be considered in any investigation, and to set guidelines for proper reporting of the results, when indeed a significant piece of work in the field of analytical chemical solvent extraction has been accomplished.

Solvent extraction has basically two functions in analytical chemistry. One is as a selective separation method, capable of handling both macro and trace quantities of the substances to be determined. It is thus a step in the isolation, concentration and purification of the substance to be determined, and is followed by several other steps leading to the final determination. The other is as a penultimate step, serving to bring the substance to be determined into a particularly favorable environment, as for some spectrophotometric determinations or radioactive counting procedures with liquid scintillators. The requirements for both modes of application are essentially the same, and prospective authors should pay attention to the following points, so that their efforts can be appreciated and evaluated on a sound basis.

ESTABLISHMENT OF THE NOVELTY OF A METHOD

As has been mentioned above, solvent extraction had an early start. It has come of age in the forties and early fifties, when many chelating agents have been established as useful extractants,[6] following the pioneering work of Fischer on dithizone[7] and of Kolthoff and Sandell on the quantitative aspects of chelate extraction.[8] Since then, highly selective chelating extractants have been found for most of the elements, capable of separating them from almost all others. It is true that this statement should be limited to metallic elements, and among these are several which are selectively extractable only as a group, not individually, *e.g.*, the alkali metals or the rare-earth metals, and that there is certainly further scope for development. When a new method involving chelating extractants for metals is offered, the following questions must be answered satisfactorily, in order to establish the novelty of the method.

1. Do satisfactory separation methods already exist to deal with the problem at hand? If the answer is *no*, the researcher and author must satisfy himself that he has interpreted the word *satisfactory* properly. Thus, an existing method need not use solvent extraction to be satisfactory; it may use *e.g.* ion-exchange or precipitation. If the answer is *yes*, the next question must be conscientiously answered.

2. Is the proposed method indeed superior to the existing methods? If the answer is *yes*, this must be demonstrated clearly, in quantitative terms. *Superior* may apply within the existing limits of applicability of the methods, or it may mean a *significant* broadening of these to cover new ground. If the answer is *no*, it is very difficult to justify the development and publication of just another method, which does no better than established methods.

A solvent extraction method consists of a combination of an extractant, a diluent (if necessary), a modifying reagent (if necessary) and certain conditions in the aqueous solution, *e.g.* controlled pH, presence of a ligand, presence of a salting-out agent, and external conditions such as temperature, time of contact, intensity of agitation. The novelty of a method rests usually in the choice of the extractant, less often in the choice of the diluent or other constituents of the organic solvent phase, or the other conditions.

If, indeed, a new extractant is proposed, it should be demonstrated that it is superior for effecting the separations to which existing extractants are applied, under the optimal conditions for applying them. That is, the comparison should be fair, and a new extractant should not be deemed superior if it outperforms existing extractants only under conditions suitable for its own application.

REQUIRED SPECIFICATIONS

Having satisfied himself, in a manner that can withstand eventual critical examination by the scientific community, that a new solvent extraction method ought to be developed, the analytical researcher must obtain the information required to specify the following data for the method that he proposes.

The solvent

The solvent is usually a composite organic phase, which may consist of the extractant(s), and/or diluent(s), and/or modifier(s). Sometimes the solvent is a single substance, which may be the extractant, or a more or less inert solvent in which a complex (chelate) formed in the aqueous phase preferentially dissolves.

The *extractant*, or extracting agent, which is the active substance in the organic phase primarily responsible for the transfer of the solute from the aqueous phase, through chelation, solvation, ion-association or some other adduct formation, must be completely specified. The specification includes the chemical composition, the structure, and if necessary, the particular isomer or conformation intended, and not merely a trivial or a trade name. It is realized that sometimes this information is not available, that a natural substance or an undisclosed commercial substance may be used to good advantage, but these must be instances explicitly justified by the circumstances. If impure materials or mixtures of materials are used, this must be clearly specified. In fact, mixtures may be superior to pure substances as extractants, with respect to cost or to performance, The cost aspect is illustrated by the use of "amyl alcohol" in preference to n-pentanol; improved performance may be due to synergistic properties of the mixture. Thus, "oppa," octylpyrophosphoric acid prepared by reacting n-octanol with phosphorus pentoxide at a proper stoichiometry, is far superior to pure *P,P'*-dioctylpyrophosphate for the extraction of uranium (IV) from phosphoric acid solutions.[9]

The *extractant concentration* range must be specified. In many cases it must stand in some stoichiometric ratio to the solute to be extracted, and a certain excess must be established. On the other hand, a large excess should sometimes be avoided, in order to repress side-reactions with this solute (formation of non-extractable higher complexes), or to repress extraction of impurities, or simply to avoid waste. The minimal and maximal concentrations at which the extractant is to be usefully applied should be established and specified. This specification should preferably be expressed in a manner readily understood, *e.g.*, the weight or volume (at a specified temperature) of the extractant taken and the final volume it was diluted to. These manipulations are ordinarily carried out in the analytical laboratory by means of pipettes and volumetric flasks, and therefore specifications such a $1 + 4$ or $1:4$, when a volume x is diluted in a volumetric flask of capacity $5x$, are to be avoided. It should be noted that this specification does *not* yield the *equilibrium* concentration of the extractant in the liquid–liquid distribution equilibrium. This is an additional item of information which is useful to specify, and authors are urged to do so, but not instead of the initial composition of the solvent to be used.

The *nature of the diluent* employed must be specified. Sometimes it is immaterial which of a large class of diluents, *e.g.*, hydrocarbons, is utilized. This must be clearly indicated, together with the name of the diluent actually used. Care must be taken in this, since seemingly inert diluents often play an important role in the extraction. If no diluent is used, *i.e.*, the neat extractant is employed, this must also be specified.

The *nature and concentration range of modifiers*, when employed, must be specified. A modifier is a substance dissolved in the organic phase to improve its properties, *e.g.*, the solubility of the extractant, or the interfacial properties. It may also exert a synergistic effect. Again, if any one from a class of substances, *e.g.*, surface-active agents, may serve, this should be established, and the particular members of this class tested should be specified. It is useful, if possible, to find out the mode of action of the modifier and disclose it. Its concentration range, however, *must* be specified, since an excess may have a deleterious effect.

The aqueous phase

Ordinarily, the aqueous solution from which a solute is to be extracted contains besides this solute some acids and salts, more rarely some organic substances. These may arise from treatment of the matrix from which the solute is to be separated, or they may be added for a purpose. The purpose may be the enhancement of the extractability of the desired solute, and/or the masking or holding back of impurities or interferences.

The *matrix* present in the aqueous phase, and which must be tolerated in the extraction method, must be specified. It is useless for analytical purposes (though not for preparative ones) if the sample must be present in the form of an essentially pure substance. The samples to be analysed provide this matrix, and the kind of matrices for which the extraction method is intended, and which will contribute constituents to the aqueous phase (*e.g.*, sea-water, silicate rocks, ferrous alloys, environmental samples) must be specified. Furthermore, certain reagents are added in the initial treatment of the sample (dissolution, prior separations) and they ordinarily remain in the aqueous phase. These should also be specified; or certain combinations of them ruled out if incompatible with the extraction method.

The *acidity* or the *pH* of the aqueous phase is usually of cardinal importance and must be specified. Chelating extractants of metals, being as a rule weak acids, have limited ranges of pH where they may be applied. The pH control employed, the buffer used, the tolerance to presence of strong acids or bases must be established and specified. Other extraction systems, on the other hand, may require a high acidity, above some threshold value, to be operative. This must then be established. Specification of the acidity is facilitated by the concept of pH_{50}, *i.e.*, the pH at which the distribution coefficient is unity, and 50% of the solute is extracted if the phase (volume) ratio is unity.

The *ligands, complexing agents* or *masking agents* added to the aqueous phase and their required or permitted concentration ranges must be specified. Sometimes, ligands are a part of the matrix, or have been added in the course of sample preparation or previous separation steps. It may be obvious to the researcher and author that a particular ligand for the metal ion is present, say chloride if the sample is customarily dissolved in hydrochloric acid. However, if the presence of chloride in the extraction step is not specified, nor its role explained, an unwary reader may for his own reasons substitute another acid in the sample dissolution step, and find to his dismay that the extraction does not proceed as expected. Similarly, most ion-pair extraction methods require a large counter-ion, say perchlorate in a particular instance. The perchlorate would have been added "naturally" if the sample had been decomposed with perchloric acid, and though nitric acid could be substituted for the decomposition, its anion might not be adequate for the extraction.

The concentration range of the ligand, complexing or masking agents is of importance, since too little may not be adequate, and too much may lead to side-reactions leading to non-extractable species. The wider the tolerance of the method, the better it is in this respect.

Salting-out agents may be required, in order to "push" the extractable solute into the organic phase. Often the ligand provided also performs this role, but sometimes reagents with highly hydrated ions or functional groups have to be added, to lower effectively the water activity in the aqueous phase. The necessity to do this should be discerned by the researcher, but obviously it would be advantageous if the procedure can dispense with this reagent. However, some highly selective extractants are too water-soluble if a salting-out agent is not employed, and its nature and minimal concentration should be specified. The researcher, however, must clarify its role, since if its only function is as a salting-out agent, often any of a large group of reagents may be adequate, and the less restrictive the procedure, the more it can be adapted for wide use.

The extraction conditions

A range of conditions can be used for the extraction of the desired solute, but it is important to find those where the separation is best, *i.e.*, as much as possible of the desired solute and as little as possible of the impurities are transferred, while reagent consumption is tolerable. Attention must be paid to the achievement of a *clean* separation, so that neither of the liquid phases is contaminated by the other.

The *phase ratio, i.e.*, the ratio of the quantity (usually volume) of the organic phase to that of the aqueous phase, is often implicitly unity, and if the distribution coefficient (or distribution ratio D) is reported, this is of minor importance. However, if the recovery factor R, the fraction of the total quantity of solute which is extracted, or the extraction factor, the ratio of its quantity in the two phases, is reported, it is essential to report also the phase ratio. It is usually difficult under analytical conditions to work outside the range of phase ratios from 0·2 to 5·0, and a procedure that requires exceptionally small or large phase ratios is to be questioned.

The *duration* and *intensity of agitation* of the two liquid phases with each other are, again, of minor importance in the usual cases. Most liquid–liquid distribution equilibria are established within 30 sec with manual shaking. On the other hand, there are chelating agents where slow kinetics of isomerization or some other step, and metal ions where slow kinetics of loss of water from the hydration sphere, lead to an overall slow extraction. Examples are the rate-controlling enolization of thenoyltrifluoroacetate,[10] and the reluctant extraction of chromium(III), unless refluxed with an extractant such as acetylacetone.[11] Researchers must, therefore, ensure that prolonged mutual contact is unnecessary, or else specify its necessity. In the latter case, account must be taken of the possibility of extractant decomposition on prolonged agitation with the aqueous phase (and air) since some extractants, notably dithizone,[12] are unstable in solution. Furthermore, use may be made of differences in the rate of extraction of two solutes in order to effect a separation between them which could not be achieved under equilibrium conditions. It is useful if this possibility is pointed out, even if not utilized for a given problem, in cases where slow extraction steps can be identified.

It is difficult to specify the intensity of the agitation, and usually it is immaterial. Occasionally, however, problems may be encountered in this respect, in particular in the presence of surface-active agents. A cautionary remark in such cases should be included, in view of the following.

A *clean phase-separation* is an essential part of an extractive separation procedure. It is extremely difficult to prevent entrainment of less than 0·1% of the wrong liquid phase, as little droplets dispersed in the bulk, or as a film or discrete drops at the surface, which will contaminate a sampling device such as a pipette. On the other hand, this limit should be approached as best as one can, and therefore conditions which favour emulsification, such as violent agitation of the phases, or the presence of surface-active agents, should be avoided as far as possible. The means employed to effect a clean separation should be mentioned in the procedure. Since one advantage of solvent extraction methods is their rapidity, a procedure which produces clean phases after 30 sec of standing is to be preferred to one that requires considerably longer standing or centrifugation. Proper choice of diluent and/or modifier and/or salting-out agents can be of great help in this respect.

The *temperature* at which the solvent extraction is carried out is usually of little consequence provided it is near room temperature, understood in this context as anywhere between 15° and 35°, dictated by climate. It is urged, however, that the temperature limits at which the results were obtained are specified, so that other workers can utilize the data for other studies. It cannot be expected that extractions for analytical purposes should be carried out in a thermostat, but there is no rule against its employment during the development of the method. If the optimal temperature for a given extractive separation is not the ambient temperature, it should of course be specified, together with the tolerance, i.e., permissible deviation.

APPLICATION OF SOLVENT EXTRACTION

In order for a solvent extraction separation method to be useful, the following have to be established: completeness of the extraction, the required selectivity, and freedom from interferences. The method must be tested with respect to all three criteria, and the results must be reported, with a valid statistical evaluation of the numerical data.

Completeness of extraction

Few, if any, analytical determinations aim at an error of less than 0·1%, hence extraction should be 99·9% complete to satisfy ordinary requirements. With a phase ratio of unity, this means a distribution coefficient of $\geq 10^3$. Higher distribution coefficients, though occurring in systems with appropriate extraction equilibrium constants and concentration ranges of the reagents, can only rarely be measured, because of the entrainment problems discussed above. Lower distribution coefficients can be tolerated, if one of the following steps is taken: the phase ratio is varied in favour of the organic phase (within the limits delineated above); a numerical correction is applied for the fraction which was not extracted (the standard procedure of correcting for *chemical yield* in radiochemical methods); best of all, extraction is repeated with fresh portions of organic solvent. The lowest practical distribution coefficient for analytical solvent extraction is about 10.

If the method is to be applied within a wide range of *extrahend* (solute to be extracted) concentrations, it is necessary to establish that either the distribution coefficients are independent of the extrahend concentration within that range, or are sufficiently large anyway. It is one of the advantages of solvent extraction methods that they can handle trace concentrations of the extrahend, since only homogeneous solutions of it in liquid phases are involved. Solvent extraction methods, therefore, seldom have inherent lower limits, practical lower limits being dictated by the effects of impurities. The upper limit of applicability is usually given by the consumption of a stoichiometric quantity of the extractant, and the necessity of some excess of the latter, which may be limited by its solubility, and the procedure must be cognizant of this.

Selectivity

As a separation method, solvent extraction presupposes high selectivity for the solute of interest. Applications where this is unnecessary are known—extraction as a concentration procedure, which is limited by phase-ratio considerations, or the transfer of the solutes into an organic environment for spectrophotometric or radiometric (liquid scintillation counting) determinations which can take care of the selectivity requirements and do not require selectivity in the extraction step. Ordinarily, however, selectivity is an essential requirement, and its achievement must be demonstrated quantitatively. It is expressed by means of separation factors, which are the ratios of the distribution coefficients of the solute of interest and of the impurities, measured under the same conditions, or by means of the *enrichment factors*, *S*, which are the factors by which the original ratios of quantities of the solute of interest and the impurities must be multiplied to give the ratios after extraction. The selectivity desired depends on the ultimate determination methods to be used after the solvent extraction separation step. Usually, procedures in which the impurities have distribution coefficients $D > 0{\cdot}1$ should be avoided, and in cases where $0{\cdot}001 < D < 0{\cdot}1$ one or more *scrubbing* steps should be employed. In these, the loaded solvent is contacted with a suitable aqueous phase, which selectively removes the contaminants from it. This may entail a slight loss of the extrahend; likewise, a slight loss of extrahend may be brought about by choosing conditions (*e.g.*, pH or extractant concentration) which depress the D values of the impurities to below 0·001, without lowering that of the extrahend much below 10^3.

The actual selectivity attained by the method *under working conditions* must be reported, not that calculated from the equilibrium constants and the reagent concentrations. Although this calculation can provide a rough guide to the attainable selectivities, major deviations may be caused by the multicomponent nature of analytical samples, and the particular contributions to the extraction system from the sample matrix, which may not have been considered in the work that led to the equilibrium constants.

Since, however, it is impractical to test the selectivity under all possible conditions, and undesirable to limit unduly the applicability of the method, it is useful to provide not only the actually determined selectivities but also the equilibrium constants involved (see below), so that the application can be extended where appropriate.

Interferences

Extraction systems are seldom specific for a given solute, but those impurities which are co-extracted with the extrahend of interest because of insufficient selectivity cannot properly be called interferences as far as the solvent extraction separation itself is concerned. They may interfere, of course, in subsequent determination steps. Interferences are those solutes which make the extraction of the extrahend less complete. This can occur mainly through two processes: binding of the extrahend in the aqueous phase, or binding of the extractant in the organic phase. If the extrahend is a metal cation, then other ligands are interferents of the first kind, if they form competitive and non-extractable complexes. Other metal cations (or hydrogen ions) are then interferents of the second kind, if they form competitive extractable complexes with the extractant. Other cations may also interfere by removing the extractant from the organic phase into the aqueous phase, if they form strong, competitive non-extractable complexes with the extractant, binding it in the aqueous phase.

It is impractical to test for all possible interferences, and therefore, again, it is useful to know the extraction equilibrium constant and any other association constants which are relevant. With this knowledge it is possible to predict whether a given solute would constitute under given conditions a serious interference or not. A serious interference, in this context, is a reduction of the distribution coefficient D of the extrahend from above 10^3 to, say $< 10^2$. A predicted interference, or non-interference, should in any case be verified by a concrete experimental example.

ADDITIONAL CONSIDERATIONS

There are several additional points which it is worthwhile to consider when developing a solvent extraction separation method. Although not as essential to the proper operation of a separation procedure as those discussed above, they permit eventual future improvements, and a widening of the applicability of the method. These are on the one hand physico-chemical details of the liquid–liquid distribution equilibrium, and on the other hand considerations relating to multi-sample, on-line, or automatic analysis.

Physical-chemical details

It is recommended that the extraction equilibrium reaction be identified, with respect to the stoichiometries involved, and the species which the extrahend forms with the extractant in the organic phase. Any side-reactions occurring in the system, such as acid dissociation of the extractant or dimerization of the extracted species, should preferably also be identified. The extraction equilibrium constant[13] K_{ex} of the distribution reaction should be determined, either as a conditional equilibrium quotient or as the thermodynamic equilibrium constant. The value of the former is dependent on the conditions, such as the concentrations of reactants and the acidity, while the latter takes into account the relevant activity coefficients. Values of the equilibrium constants of the side-reactions mentioned above should also be known.

It should be understood that the determination of these constants is optional, and its lack does not necessarily detract from the usefulness of a solvent extraction method for the particular problem for which it has been developed. However, in view of the proliferation of existing solvent extraction methods, commented on at the beginning of this article, the justification of the development of an additional method rests mainly on the wider scope it may offer. For its realization the information discussed above is indispensable, whereas the elucidation of the actual mechanism of the extraction reaction, in terms of the sequence of steps that lead to the equilibrium distribution, usually is not. The mechanism of solvent extraction reactions is rarely known and more rarely required, except in those cases where differences in the rate of extraction are utilized. In this particular application, a detailed knowledge of the mechanism is of great help.

Practical details

Thought should be given to the implication of extending the solvent extraction separation to large series of samples. For the ultimate exploitation of a method, situations such as large numbers of samples from environmental studies, or from industrial quality-control stations, or the need for continuous on-line monitoring of a system, should be considered. The rapidity of the usual solvent extraction separations (*e.g.*, 30 sec phase mixing, 30 sec phase separation) recommends them for such applications. The on-line approach is now realized with devices such as the AK-UFVE.[14] For such multi-sample applications, considerations such as the cost and availability of the extractant and other reagents at the required purity become important. Also, the chemical stability of solvent phases (avoidance of the necessity to prepare daily fresh extractant solutions, as is the case with dithizone[12]), the flammability and toxicity of diluents (even simple diluents such as toluene become a problem in this respect if handled in large quantities over a prolonged period), *etc.*, must be considered. Often it is possible to choose reagents that are least problematic in this respect, even though they may not produce optimal results if only a single separation is to be performed.

It is urged that consideration be given to these points in any case when a solvent extraction method is developed, even if they are not directly relevant to the particular application envisaged for it. The superiority of a new method over existing ones is certainly measurable by practical criteria as discussed here.

PUBLICATION

When a new solvent extraction separation method is being made ready for publication, all the points above must have been taken care of. First the necessity for the new method must have been established. Then all the relevant items must have been specified, *i.e.*, the composition of the solvent, the composition of the aqueous phase, and the extraction conditions. A definite procedure for the separation must be worked out. The function of each item in this procedure, and the range within which quantities may be varied must also be specified. It must then be shown that the desired extraction has been achieved, and with it the desired separation from the other solutes, and that the method works with respect to completeness of extraction, its selectivity, and its freedom from interferences, when the reagents and conditions are within the specification. The optional information, such as equilibrium constants, if determined, must also be ready.

In order to convince readers of the merits of the new solvent extraction method, it must now be compared in a fair way with existing solutions to the separation problem at hand. A statistical analysis of the results must be included, to show the significance of a claimed quantitative superiority.

It is desirable that internationally agreed-on nomenclature, symbols, and units be used. As regards the names of reagents, common abbreviations (see, *e.g.*, ref. 15) may be used, but they must be defined where first used in the text. Trade names and trivial names should also be accompanied by chemical names. The sources of uncommon reagents should be given.

Some of the terms relating to solvent extraction have been used rather loosely in the past. This paper contains definitions of some of the important terms, following the recommendations of international bodies.[16,17] A clear distinction must be made, *e.g.*, between the extraction (equilibrium) constant, K_{ex} pertaining to the distribution reaction, the distribution or partition constant, K_D, which is the ratio of the activities of a definite chemical species in the two phases, and the distribution coefficient or ratio, D, which is the ratio of the total analytical concentrations of a solute in the two phases. Similarly, a clear distinction must be made between the separation factor, which is the ratio of the respective distribution coefficients of two solutes measured under the same conditions, and the decontamination or enrichment factor, S, which is the ratio of the proportions of contaminant to desired product before and after treatment.

Results from a comparative study of several extractants, or several sets of extraction conditions, applied to a series of extrahends (say metal cations) are profitably displayed in distribution charts.[18] These consist of a series of "distribution strips," one for each extractant or set of extraction conditions, each strip being a one-dimensional plot of the logarithms of the distribution ratios of the extrahends. From such charts distribution ratios D and separation factors between any two extrahends may be readily read, and extraction processes can be readily compared.

CONCLUSIONS

Solvent extraction is a very powerful analytical separation method, and many applications have been and are being published. Therefore, those intending to add yet another publication in this field will do well to follow this guide, so that their contribution is significant, and of real help to others, *i.e.*, the scientific community for which the intended publication is prepared.

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X-RAY FLUORESCENCE SPECTROMETRY OF COPPER INTERMEDIATES

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Summary—Iron, magnetite, copper, copper(II) oxide, calcium carbonate, sulphur, silicon dioxide and aluminium oxide as components of copper intermediates (concentrates, slags, mattes, calcines and fluxes) in powdered (300–400 mesh) binary mixtures obey the Lachance–Traill equation, so the coefficients α_{AX} of interelement effects can easily be determined experimentally. They show a reasonable agreement with the theoretical values calculated from mass absorption coefficients. This fact can be the basis of a convenient routine method for the determination of intermediates. Since the intermediates exhibit differences in the distribution of their atoms (microcosmic inhomogeneity) a correction factor k_{dist} has to be used. Its value for the main components (concentrations $>5\%$) is in the range 0·92–1·24 The highest relative average deviation of the results from those of the classical "wet" methods is 2·7% for the major and 30% for the minor components.

X-Ray spectrometry is a most convenient routine method for the analysis of copper intermediates (concentrates, slags, mattes, calcines, and fluxes) because of its speed. Fusion of samples with sodium and lithium tetraborate is a favourite technique used in X-ray analysis, giving accurate results. The weighings and fusions are, however, tedious operations that become very inconvenient if a hundred or more specimens are to be assayed daily. Then the powder-specimen technique, in spite of its lower precision and accuracy, is the only convenient approach.[1]

Variations in particle size, density and adhesivity (due to electrostatic, magnetic and other factors) are the main sources of error in the powder technique. The problem of particle size can be settled by use of an efficient grinder. The other sources of error are largely eliminated by the constant properties of individual intermediates. Powder specimens exhibit strong interelement effects, however, so a proper mathematical correction of those effects is necessary.

EXPERIMENTAL

Apparatus

The instrument used was a Norelco Corporation (Mount Vernon, New York), X-ray vacuum spectrometer, with a chromium target tube.

The specimens were ground and mixed by means of a "Wigl Bug" (Crescent Dental Co., Inc., Chicago, Illinois) with a tungsten carbide capsule of 6 ml effective volume.

Materials

Iron, magnetite, copper, copper(II) oxide, calcium carbonate, sulphur, silicon dioxide and aluminium oxide powders were used as standards and for the preparation of binary mixtures. The mixtures were prepared in the "Wigl Bug" by 2 min grinding and mixing. The copper-intermediate specimens were the usual daily samples. To assay the individual elements the following "wet" methods were used: cerimetric potentiometric titration of iron, electrolytic gravimetry for copper, permanganate titration for calcium, barium sulphate gravimetry for sulphur, silicon dioxide gravimetry for silicon and aluminium phosphate gravimetry for aluminium.[2] All chemicals used were Baker analysed reagents.

Measurement

Plastic cups of 7 ml effective volume with a 1-mm hole in the bottom (for measurements in vacuum) were used. About 2 g of specimen were placed in each cup, covered with Spex-Film (Spex Industries, Inc., Metuchen, New Jersey), inserted into the metallic holder, tapped gently on a bakelite plate and inserted into the spectrometer. The parameters of measurement for individual elements are listed in Table 1.

THEORETICAL

Lachance–Traill equation

If R_A is the relative X-ray fluorescence intensity of an element A such that

$$R_A = (I_A - I_{Ab})/(I_{A1} - I_{A1b}) \qquad (1)$$

where I_A and I_{A1} are the intensities for A in the sample and a pure specimen respectively and I_{Ab} and I_{A1b} are the corresponding background intensities, the Lachance–Traill equation[3,4] has the form

$$c_A/R_A = 1 + \sum_{B}^{Z} \alpha_{AX} c_X \qquad (2)$$

where c_A and c_X are the concentrations of elements A and X, respectively (as weight fractions of the total specimen amount), and α_{AX} is the coefficient for the influence of element X on the intensity for element A. It is assumed that the specimen consists of elements A, B,...Z.

Equation (2) is a simplified Gillam–Heal[5] and Shiraiwa–Fujino[6] equation describing the general relationship between the relative fluorescent intensity of

Table 1. Instrument settings for individual elements

Parameter	Element*					
	Fe	Cu	Ca	S	Si	Al
Pulse-height analyser base-line, *V*	8·0	9·0	6·0	12·0	11·0	9·0
Pulse-height analyser window, *V*	25·0	46·0	21·0	16·0	13·0	12·0
Measurement time, *sec*	20	10	10	20	50	50
Spectrometer angle, 2θ	57·55°	45·05°	14·95°	45·87°	79·21°	115·09°
Crystal	LiF	LiF	PET†	PET	PET	PET
Path medium	air	air	vac‡	vac	vac	vac
Detector§	S	S	P	P	P	P
Detector voltage, *kV*	0·8	0·8	1·5	1·5	1·5	1·5

* X-Ray tube voltage 46 kV, current 18 mA, linear amplifier attenuation 5, and coarse collimation used throughout.

† Pentaerythritol.

‡ Pressure 0·2 mmHg (10% methane and 90% argon).

§ S is scintillation and P proportional detector. All the measured intensities were corrected for the counting dead-time.

an element and the concentrations of all elements present in the specimen. The application of that relationship to quantitative analysis is inconvenient, especially for multielement systems, because the mathematics is too complicated. There are many modifications of equation (2)[7] but the Lachance–Traill version is the most convenient for calculation.

The value of α_{AX} can either be determined experimentally from binary mixtures or calculated theoretically by means of the equation[3,4]

$$\alpha_{AX} = \frac{\mu_{X1}/\sin\theta_1 + \mu_{X2}/\sin\theta_2}{\mu_{A1}/\sin\theta_1 + \mu_{A2}/\sin\theta_2} - 1 \qquad (3)$$

where θ_1 is the angle at which radiation strikes the specimen and θ_2 is the angle of emergence of radiation. The mass-absorption coefficients μ_{A1}, μ_{X1} and μ_{A2}, μ_{X2} (for elements A and X) are measured at wavelengths of the absorption edge (subscripts 1) and characteristic line (subscripts 2) of element A. For the absorption edge an effective wavelength should be used:

$$\lambda_{E(\text{eff})} = \lambda_E - 0{\cdot}01 \qquad (4)$$

where λ_E is the value from tables. The correction is empirical and is connected with some losses of energy by scattering.[8]

Equation (3) is valid only for mixtures of pure elements since the values of the mass absorption coefficients were determined for those conditions. In practice, we often have mixtures of the oxides and carbonates. If the "dilution" by oxygen and carbon is the only effect we take into account, and the new mixture contains the elements A and X in the *same ratio* as the original mixture, then

$$R_A = R'_A \qquad (5)$$

where R'_A is the ratio of the net intensities of the new mixture and the new reference standard (*i.e.*, the corresponding oxide or carbonate).

For binary mixtures we obviously have

$$c_A = 1 - c_X \quad \text{and} \quad c'_A = 1 - c'_X \qquad (6)$$

and from equation (2)

$$(1 - c_X)/R_A = 1 + \alpha_{AX}c_X \qquad (7)$$

$$(1 - c'_X)/R'_A = 1 + \alpha'_{AX}c'_X. \qquad (8)$$

The combination of equations (5), (7) and (8) results in

$$(1 - c_X)/(1 + \alpha_{AX}c_X) = (1 - c'_X)/(1 + \alpha'_{AX}c'_X). \qquad (9)$$

If r_A represents the conversion factor from element A to its oxide (or carbonate), and r_X the corresponding factor for element X, we have

$$c'_X = c_Xr_X/[(1 - c_X)r_A + c_Xr_X]. \qquad (10)$$

Combining equations (9) and (10) we get

$$\alpha'_{AX} = r_A(1 + \alpha_{AX})/r_X - 1. \qquad (11)$$

Employing this equation we can calculate the influence-coefficient α'_{AX} of an oxide (or carbonate) mixture from the original coefficient α_{AX} calculated by means of equation (3), although this calculation is only approximate because of the simplifications made.

Structural and trace element effects

It is well known[9] that certain deviations sometimes occur if equation (2) is applied to multielement mixtures. Those deviations are explained by enhancement and polychromaticity effects and there have been attempts to correct them by expansion of the right-hand side of equation (2) to include terms with higher powers of the concentration.[7,10] In our opinion, this is completely justified only if the binary mixtures and sample specimens exhibit exactly the same distribution of atoms of the elements to be determined (microcosmic homogeneity). Unfortunately, the copper intermediates do not meet that condition. Both copper and iron are able to form with sulphur a great variety of compounds, the distribution of which in the test specimens is virtually unknown.[11] Since most of the bonds are covalent in character it is uncertain, even for pellets prepared by fusion, whether the condition of microcosmic homogeneity is met.

The uncertainty in the composition of the specimens (it also affects the system of iron and oxygen) leads to the fact that the equation

$$\sum_{A}^{Z} c_X = 1 \tag{12}$$

the validity of which is the necessary condition of equation (2), may not hold exactly, the sum coming to 0·90–0·95 instead of 1·00. Fortunately, the effect of those factors [microcosmic inhomogeneity plus failure of equation (12)] is relatively small and sometimes negligible; nevertheless, it requires the introduction of an additional distribution correction constant k_{dist} such that the final concentration of an element A is given by the equation

$$c_A^{\text{corr}} = k_{\text{dist}} c_A. \tag{13}$$

The values of k_{dist} can be calculated by measurement of a set of standards (concentrations c_A^{std}) and use of the equation

$$\sum c_A^{\text{std}} = k_{\text{dist}} \sum c_A. \tag{14}$$

The determination of c_A^{std} by "wet methods" must be performed with the greatest care and accuracy. Equation (14) is another approximation justified by the relatively constant composition of test specimens. A high value of k_{dist} can be due to incorrect values of α_{AX} and of the background.

RESULTS AND DISCUSSION

A typical dependence between the particle size and the fluorescence intensity is presented in Fig. 1. It shows that for particles finer than about 300 mesh the fluorescence intensity becomes independent of the particle size.

The behaviour of binary mixtures of the eight most common components of copper intermediates is illustrated in Fig. 2. The function of $c_A/R_A = f(c_A)$ shows very good agreement with the equation (2) so that no special treatment of the polychromaticity and enhancement effects is necessary. The values obtained for the influence coefficients α_{AX}, together with the theoretical values calculated by means of equations (3) and (11), are presented in Table 2. Taking into account the approximations in the theoretical calculation, there is reasonable agreement between the experimental and theoretical values. It should be kept in mind that the values can vary according to the geometry of the spectrometer.

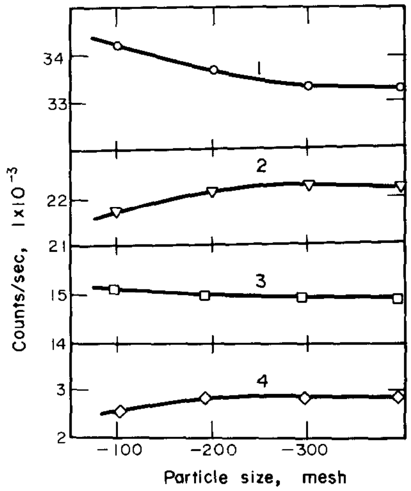

Fig. 1. Dependence of the fluorescence intensity on the particle size: 1—Cu, 2—Fe, 3—S, 4—Ca (Specimen: copper concentrate).

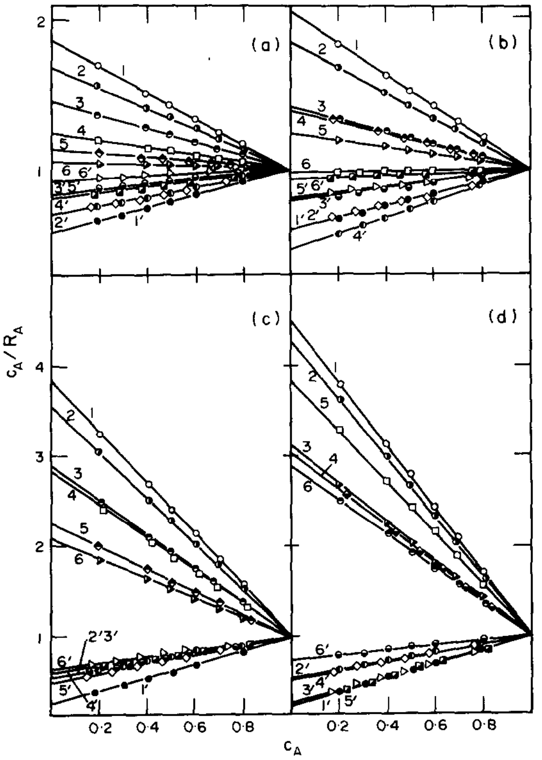

Fig. 2. Dependence $c_A/R_A = f(c_A)$ of binary mixtures. *a*: 1, $CaCO_3$–Fe; 1', Fe–$CaCO_3$; 2, $CaCO_3$–SiO_2; 2', SiO_2–$CaCO_3$; 3, $CaCO_3$–Fe_3O_4; 3', Fe_3O_4–$CaCO_3$; 4, S–CuO; 4', CuO–S; 5, S–Fe; 5', Fe–S; 6, Fe_3O_4–S; 6', S–Fe_3O_4. *b*: 1, Cu–Fe; 1', Fe–Cu; 2, $CaCO_3$–CuO; 2', CuO–$CaCO_3$; 3, $CaCO_3$–Al_2O_3; 3', Al_2O_3–$CaCO_3$; 4, S–Cu; 4', Cu–S; 5, S–SiO_2; 5', SiO_2–S; 6, S–Al_2O_3; 6', Al_2O_3–S. *c*: 1, SiO_2–Cu; 1', Cu–SiO_2; 2, Al_2O_3–Fe; 2', Fe–Al_2O_3; 3, SiO_2–Fe; 3'; Fe–SiO_2; 4, SiO_2–Fe_3O_4; 4', Fe_3O_4–SiO_2; 5, $CaCO_3$–Cu; 5', Cu–$CaCO_3$; 6, CuO–Fe_3O_4; 6', Fe_3O_4–CuO. *d*: 1, Al_2O_3–Cu; 1', Cu–Al_2O_3; 2, $CaCO_3$–S; 2', S–$CaCO_3$; 3, SiO_2–CuO; 3', CuO–SiO_2; 4, Al_2O_3–Fe_3O_4; 4', Fe_3O_4–Al_2O_3; 5, Al_2O_3–CuO; 5', CuO–Al_2O_3; 6, SiO_2–Al_2O_3; 6', Al_2O_3–SiO_2. The first component is A.

The estimated experimental values of α_{AX} were used in equation (2) for the assay of copper intermediates. The calculation was done by means of a general program for 3–6 components (machine model 1860, Monroe Co., Orange, New Jersey), which can be easily extended to any higher number of components. The results together with the results of "wet methods" are presented in Table 3. A relatively good agreement of both methods can be seen. Some higher deviations can be explained in terms of errors in both methods. The higher deviations of converter flux specimens are due to the low density. The instrumental drift was corrected by measurement of one standard. It is useful

Table 2. Influence-coefficients α_{AX}*

	X							
A	Fe	Fe_3O_4	Cu	CuO	$CaCO_3$	S	SiO_2	Al_2O_3
Fe	—	—	−0·40	—	−0·42	−0·15	−0·45	−0·47
			(−0·53)		(−0·44)	(−0·22)	(−0·74)	(−0·76)
Fe_3O_4	—	—	—	−0·37	−0·15	0·07	−0·42	−0·48
				(0·48)	(−0·22)	(0·08)	(−0·77)	(−0·67)
Cu	1·05	—	—	—	−0·52	−0·52	−0·75	−0·76
	(1·35)				(−0·56)	(−0·39)	(−0·80)	(−0·81)
CuO	—	1·09	—	—	−0·40	−0·19	−0·73	−0·75
		(1·12)			(−0·44)	(−0·24)	(−0·75)	(−0·77)
$CaCO_3$	0·87	0·45	1·28	0·85	—	3·31	0·67	0·43
	(0·77)	(0·28)	(1·22)	(0·78)		(3·22)	(0·44)	(0·30)
S	0·14	−0·08	0·40	0·25	−0·48	—	0·25	−0·01
	(0·17)	(−0·15)	(0·48)	(0·18)	(−0·76)		(0·10)	(−0·02)
SiO_2	1·91	1·85	2·85	2·12	−0·27	−0·18	—	1·94
	(2·36)	(1·43)	(3·26)	(2·40)	(−0·29)	(−0·19)		2·07
Al_2O_3	2·53	2·05	3·55	2·86	−0·20	−0·06	−0·25	—
	(2·67)	(1·65)	(3·71)	(2·76)	(−0·21)	(−0·06)	(−0·76)	

* Theoretical values are in parentheses; the values of characteristic line and absorption-edge wavelengths and the corresponding mass absorption coefficients were taken from ref. 1. $\theta_1 = 67°$ and $\theta_2 = 23°$.

Table 3. Analysis of copper intermediates*

Type	Fe, %	Cu, %	CaO, %	S, %	SiO_2, %	Al_2O_3, %
Calcine	31·3	26·5	1·1	25·3	4·8	1·7
	(33·6)	(26·80)	(1·32)	(25·40)	(4·4)	(1·8)
	31·7	26·5	1·1	24·9	4·7	1·7
	(32·0)	(26·65)	(0·92)	(25·26)	(4·6)	(1·6)
AD	0·9	0·3	0·1	0·6	0·2	0·1
k_{dist}	0·934	0·923	2·053	1·223	0·526	0·420
Converter flux	3†	2‡	0·4	1	73·7	10·0
	(4·4)	(2·23)	(0·36)	(1·96)	(74·19)	(10·52)
	2·2†	0·5‡	0·4	0·8	81·1	7·0
	(2·0)	(0·58)	(0·36)	(0·76)	(83·00)	(7·31)
AD	0·3	0·4	0·04	0·1	1·2	0·3
k_{dist}	1·226	1·560	7·869	1·437	1·034	0·862
Converter slag	48·0†	1·2‡	0·5	—	30·4	2·5
	(46·4)	(1·04)	(0·47)	—	(31·8)	(2·83)
	50·3†	2·6‡	0·6	—	24·1	2·3
	(50·4)	(2·60)	(0·71)	—	(23·7)	(2·19)
AD	1·0	0·3	0·1	—	0·6	0·2
k_{dist}	1·020	1·001	4·551	—	1·023	1·161
Reverberatory matte	30·5	37·6	—	26·5	—	—
	(30·6)	(38·62)	—	(27·02)	—	—
	28·7	41·7	—	26·7	—	—
	(28·8)	(41·68)	—	(26·60)	—	—
AD	0·2	0·3	—	0·2	—	—
k_{dist}	1·001	0·992	—	0·997	—	—
Reverberatory slag	33·1†	0·5‡	5·8	—	36·6	6·3
	(33·0)	(0·51)	(5·57)	—	(38·2)	(6·5)
	41·4†	0·6	2·1	—	34·1	5·4
	(41·5)	(0·56)	(2·07)	—	(34·3)	(5·1)
AD	0·2	0·04	0·1	—	0·7	0·3
k_{dist}	1·008	1·119	1·064	—	1·010	1·157
Copper concentrate	28·6	23·9	0·1	38·5	4·8	2·1
	(28·2)	(23·03)	(0·16)	(38·62)	(4·3)	(1·8)
	32·1	14·9	0·1	41·2	6·1	2·2
	(31·7)	(14·81)	(0·06)	(40·92)	(6·4)	(2·2)
AD	0·4	0·4	0·04	0·3	0·2	0·2
k_{dist}	1·240	0·956	2·333	1·055	0·545	0·445

* The result of the corresponding "wet" analysis is in parentheses: CaO was calculated from $CaCO_3$. Each value of k_{dist} (dimensionless) was calculated from the results for 16 standards, see equation (14). One "good" and one "bad" result is shown. AD is the average deviation for eight samples.

† Calculated from Fe_3O_4.

‡ Calculated from CuO.

Table 4. Some empirical methods investigated*

Reference	Equation	Comment
13	$c_A = k_A + I_A(k_{AA} + \sum_{B}^{Z} k_{AX} I_X)$	Poor results
12	$I_A = k_A + c_A(k_{AA} + \sum_{B}^{Z} k_{AX} I_X)$	Good for SiO_2 in converter flux
14	$c_A = k_A + \sum_{A}^{Z} k_{AX} I_X$	Good for narrow range of concentrations
12	$I_A = k_A + \sum_{A}^{Z} k_{AX} c_X$	Poor results

* For the meaning of individual symbols see the text; k_A, k_{AA}, k_{AX} are the empirical interdependent constants determined by least-squares method.

to repeat the standard measurement for each set of samples in the spectrometer.

The Rasberry–Heinrich[7] and Claisse–Quintin[10] methods give better results for copper intermediates than the Lachance–Traill method. However, even with those methods an additional correction for structural and trace-element effects is necessary. The iteration technique is the only mathematical approach by which those methods can be applied to multielement systems, which, together with the considerably higher number of correction constants, represents a drawback of those methods which is not always compensated by a better accuracy and precision.[12]

From the practical viewpoint of routine analysis, the present method and all methods employing true influence constants have one drawback. They require the intensity measurement of all components of a specimen to satisfy equation (12). That could sometimes be inconvenient, if the concentration of only one or two elements is of interest. In those cases, some workers prefer a solely empirical relationship between the concentrations of the given elements and their intensities (usually on the basis of a regression formula). That relationship is able to produce quite good results if the concentrations of all elements present are in a certain relatively narrow range. However, the trouble is that there is not sufficient evidence that that condition is obeyed. We have investigated several empirical regression methods. Their brief description and evaluation is given in Table 4.

The practical importance of the Lachance-Traill method was stressed recently by the fact that Norelco Corporation (Mount Vernon, New York) introduced it as a built-in method for their machines.

The computer program can be obtained upon request. It includes the counter dead-time, background, and instrumental-drift corrections.

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TRACE ANALYSIS FOR CHLORINATED HYDROCARBONS IN AIR BY QUANTITATIVE COMBUSTION AND COULOMETRIC CHLORIDE DETERMINATION

APPLICATION TO STANDARDIZATION OF VINYL CHLORIDE PERMEATION TUBES

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Summary—Methods for high-temperature combustion of vinyl chloride in air were studied theoretically and two types of gas mixtures were found to give 100% conversion into HCl. The chloride was determined by coulometric titration with silver, in 70% acetic acid. Good agreement between theoretical and experimental results was obtained. Permeation rates of vinyl chloride from fluorinated ethylene propylene permeation tubes were determined gravimetrically and with the coulometric method developed. The standard deviations of the methods were 0·002 and 0·001 μg/min respectively for permeation rates of 0·5 μg/min when the temperature was controlled to ± 0·02°. The coulometric mean value was 99·9% of the gravimetric mean; 1 ppm of vinyl chloride in air could be determined coulometrically with a standard deviation of about 0·002 ppm.

Vinyl chloride has been linked to several liver cancer deaths among production workers and the maximum concentration allowable in factories has consequently been decreased. Taking the U.S. as an example, from 1 January 1975, vinyl chloride in workplace air has to be reduced to 1 ppm (v/v), averaged over an 8-hr period.

Very few methods for the trace determination of vinyl chloride in air have been described in the literature. Vinyl chloride can be absorbed[1] on activated carbon and then converted into formaldehyde, which is measured spectrophotometrically at 594 nm. This method must be calibrated with a standard of vinyl chloride in air. However, no primary standard for vinyl chloride has yet been described in the literature as far as we know. A gas-chromatographic method[2] using the flame-ionization detector has recently been described. The detection limit is reported to be 0·05 ppm and the method is simple and rapid. However, the apparatus must be calibrated with standard samples of vinyl chloride in air. The standards used[2] were obtained by a dilution procedure which resulted in a precision of about 10% at the 1-ppm level. In a recent paper[3] the use of a vinyl chloride permeation tube for calibration of a gas-sampling valve for gas chromatography was described. However, no determinations of permeation rate were reported.

This paper reports the investigation of a permeation-tube gas standard for vinyl chloride in air. The permeation rate was determined by two independent methods; a gravimetric and a coulometric. The latter method required a high-temperature conversion step to convert the chlorine in vinyl chloride into hydrogen chloride. The chloride can be determined very accurately in the nanomole range with a coulometric procedure. The development of the coulometric method involved a theoretical study of the combustion conditions for quantitative conversion into hydrogen chloride. Of special interest with regard to the coulometric titration was the determination of combustion conditions for 100% recovery of hydrogen chloride with formation of a minimum amount of water.

Several coulometric methods for the determination of chlorinated hydrocarbons[4–6] have been described. The sample is combusted in oxygen and the HCl formed is titrated with silver ions. The most commonly used titration medium is a mixture of acetic acid and water. The main drawback of these coulometric methods is that the recovery of HCl is strongly dependent on the matrix. For a hydrocarbon sample containing traces of chlorine the recovery[6] is 100%, but for traces of chlorinated hydrocarbons in air the recovery is very dependent on the combustion conditions.[7] It has been observed that addition of water, *e.g.*, humidification of the combustion gases, increases the recovery.[7] The theoretical reasons for these variations are given below in this paper.

Permeation tube

From its boiling point and its vapour pressure at room temperature, vinyl chloride seems to have the fundamental physical properties required for the permeation-tube technique. The permeation rate F is affected by the temperature, T, according to

$$F = F_0 \exp(-E/RT) \qquad (1)$$

where E is the activation energy. The value of E is rather high (about 10 kcal/mole) for fluorinated ethylene propylene co-polymer (FEP), which means that the permeation rate is very temperature-sensitive.

High-temperature equilibria

The system investigated is given by reaction (2) which corresponds approximately to the combustion of 150 ml of air containing 1 ppm (v/v) of vinyl chloride. The primary aim was to determine the conditions for obtaining a 100% recovery of HCl; x and y represent varying additions of hydrogen and carbon monoxide respectively to the mixture.

$$120N_2 + 30O_2 + 1{\cdot}5 \times 10^{-4}CH_2{=}CHCl + xH_2 + yCO \rightarrow \text{Products} \quad (2)$$

Because of the great complexity of this system we chose to use the computer program SOLGAS[8] which is a general program for the determination of high-temperature equilibria in systems containing an ideal gas phase and condensed phases of invariant composition. This program uses the free-energy minimization principle which was introduced by White *et al.*[9] An introductory book on equilibrium calculations has been written by van Zeggeren and Storey.[10] Recently, a thorough discussion of the SOLGAS[8] computer program was given by Eriksson.[11]

In order to perform chemical equilibrium calculations it is necessary to ascertain that equilibrium in the system has been attained. Generally, the probability of reaching equilibrium increases with increasing temperature.

The system dealt with in this paper contains five elements: C, H, O, Cl and N. In our system [see equation (2)] the following gaseous products were considered at equilibrium and at a total pressure of 1 atm: CO, CO_2, H_2, O_2, H_2O, N_2, HCl, HClO, ClO, Cl, Cl_2, $COCl_2$, CCl_4, CH_2Cl_2 and $CHCl_3$. Substances like CH_4, NO and NO_2 which also are thought to be possible reaction products were cancelled because they were not present in such concentrations that they were able to affect the mass balances. The values of the Gibbs free energy of formation of HCl, H_2O, CO and CO_2 are in this case very important for the results. The thermodynamic data for these substances have been determined with very high accuracy and an estimation of the quality of the data is available in JANAF.[12] Provided equilibrium is attained the calculations are expected to give very precise results.

EXPERIMENTAL

Gravimetric procedure

Permeation tubes, FEP (fluorinated ethylene propylene), were prepared according to the procedure proposed by O'Keeffe and Ortman.[13] The tubes (0·25 cm i.d., 0·40 cm o.d., 3–5 cm in length) were sealed with steel balls. The tubes were stored in test-tubes and a low flow of nitrogen was flushed through the test-tubes, which were connected in series. The effluent nitrogen was passed through a bottle of paraffin oil to absorb the entrained vinyl chloride. The test-tubes, each containing one permeation tube, were immersed in a thermostat. The temperature constancy was 25·0 ± 0·1° during a period of three months. With careful

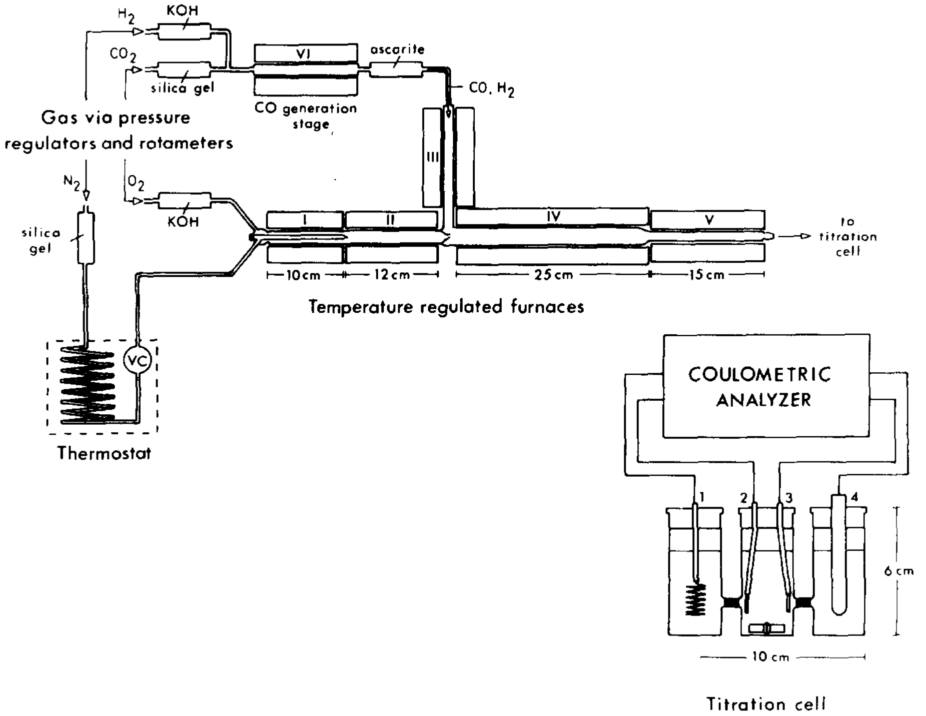

Fig. 1. Experimental arrangement. (1) Auxiliary electrode, (2) working electrode, (3) indicating electrode, (4) reference electrode, (VC) the vinyl chloride permeation tube.

adjustment of the heating and cooling, the temperature constancy within over an 8-hr period was 25·0 ± 0·02. The permeation tubes were normally weighed once a week.

Coulometric procedure

Six electrically heated ovens were arranged as shown in Fig. 1. The ovens I–V were provided with thermoelements connected to thermoregulators which kept the temperature constant within 10°. The combustion tube was made from quartz and its outlet tube was provided with a ground joint. The coulometric cell was placed very close to the outlet tube in order to eliminate the need for a heater. All gases were taken from high-pressure cylinders *via* reduction-valves, needle-valves and rotameters. The purity of the gases with respect to HCl and chlorinated hydrocarbons was examined. HCl was easily removed by absorption on solid potassium hydroxide and chlorinated hydrocarbons were pyrolysed to form HCl which was then absorbed on solid potassium hydroxide or "Ascarite". Normally this pyrolysis step was not needed. CO was produced at 1300 K by reaction between CO_2 and graphite according to the reaction $CO_2 + C \rightleftharpoons 2\,CO$. At 1300 K more than 99·9% of the CO_2 was transformed into CO. The amount of water in the gases as well as the water formed in the combustion was determined coulometrically according to a method developed earlier.[14] The rotameters were calibrated with soap-bubble flowmeters. The flow of hydrogen was also determined by coulometric determination of the amount of water formed. The agreement between these two methods was about 5% for a hydrogen flow of 1 ml/min.

A coulometric cell was made from glass with Teflon caps as shown in Fig. 1. It consisted of three chambers, one for the platinum auxiliary electrode, one for the generating silver wire (1 cm^2) electrode and the silver indicating electrode (diam. 1 mm, length 5 mm) and one for the Radiometer K 601 mercury–mercurous sulphate reference electrode. All compartments were filled with 15 ml of 70% (v/v) acetic acid (*p.a.*). Electrolytic contacts were made *via* asbestos-filled liquid junctions. Asbestos (Hopkin & Williams) was plugged tightly with a hard tool into the connecting glass tubes. The electrodes were cleaned once a day in concentrated nitric acid and rinsed carefully with distilled water. The generating electrode was placed close to the junction of the auxiliary electrode and the indicating electrode close to the reference electrode junction in order to minimize the interference from the generating electrode system with the indicating system. Further, the three compartments were arranged in line so that there should be geometric symmetry in the sample compartment. The sample compartment was provided with a gas-inlet tube and a magnetically-driven stirrer bar. The influence of light was minimized by wrapping the sample compartment with aluminium foil. The titration procedure was started by addition of at least 50×10^{-9} mole of chloride to ensure that solid silver chloride was always present in the sample compartment electrolyte.

The electrodes were connected to an LKB 16300 Coulometric Analyzer. This instrument contains a high-impedance voltmeter which measures the voltage between the indicator and the reference electrodes. This voltage is compared with a preset voltage and any deviation is amplified and used to control the current through the generating-electrode system. The gain and preselected indicator-electrode potential can be used to choose a suitable silver ion concentration during a continuous titration of chloride. A difference of 5–10 mV between the preselected potential and the indicator-electrode potential was found to be suitable. Normally the preselected potential was chosen to be −100 mV which corresponds to a potential value in the neighbourhood of the equivalence point of the titration. The amount of electricity required to titrate the chloride was recorded by an electronic integrator which could be read to 1×10^{-11} mole.

RESULTS

Gravimetric determinations

Weight losses for six permeation tubes are plotted *vs.* time in Fig. 2. The mean values and the standard deviations of the permeation rates during three months are given in Table 1 for 6 tubes. Only weight changes of more than 5 mg have been included in the calculations. A variation of 1% in the permeation rate corresponds to a temperature variation of 0·1°, which means that the temperature variation is the main factor influencing the standard deviations presented in the Table 1. The steel balls used to seal the permeation tubes were somewhat affected by corrosion. A precipitate, probably PVC, was formed inside the tube. The HCl formed in the polymerization process is known to catalyse the corrosion process. None of these products seemed to affect the permeation process. The assumed polymerization process can probably be reduced in extent by the use of stainless-steel balls.

Theoretical calculations

Case A. Flow of CO is zero. Figure 3 shows the recovery of HCl as a function of temperature and the amounts of H_2 added to 150 ml of air (120 ml of N_2 + 30 ml of O_2) containing 1 ppm (v/v) of vinyl chloride. The total pressure was assumed to be 1 atm. As can be seen in the figure there is a maximum on each curve between 900 and 1000 K. At such low temperatures the equilibrium is not expected

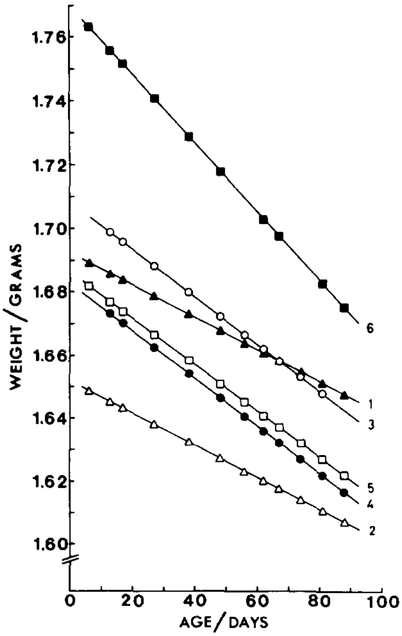

Fig. 2. Weight losses for six permeation tubes as a function of time. The mean value and standard deviation of the weight differences for the respective tube are given in Table 1.

Table 1. Gravimetric determinations of the permeation rate of vinyl chloride during a period of three months

Tube No.	Permeation rate mean value, *μg/min*	Number of determinations	Std. devn., *μg/min*	Rel. std. devn., %
1	0·352	11	0·0040	1·1
2	0·352	11	0·0085	2·4
3	0·514	10	0·0065	1·3
4	0·524	10	0·0075	1·4
5	0·509	11	0·0075	1·5
6	0·744	9	0·0079	1·1

to be reached rapidly enough, so it is perhaps more realistic to comment on this diagram for temperatures of the order of 1200 K. At this temperature about 50 ml of H_2 are needed to obtain 100·0% recovery of HCl: 50 ml of H_2 will, after reaction with O_2, give rise to about 37 mg of water, which causes a very unfavourable situation with respect to the coulometric detector, as will be shown later. It is thus necessary to add a rather large amount of H_2 to the air sample in order to obtain a high recovery of HCl. It is not necessary, however, to add H_2 in excess of O_2.

Case B. CO present. As is well known, in a combustion of an organic matrix it is not necessary to add H_2 when only traces of chlorine are present. This is so because H_2 is formed in the water-gas equilibrium (3) in sufficient amounts to yield 100% recovery.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad (3)$$

This was explicitly shown in a recent paper by Cedergren.[15]

Consequently, we studied the influence of CO added to the gas mixture. Figure 4 shows the recovery of HCl at 1200 K as a function of H_2 and CO added to 150 ml of air containing 1 ppm (v/v) vinyl chloride.

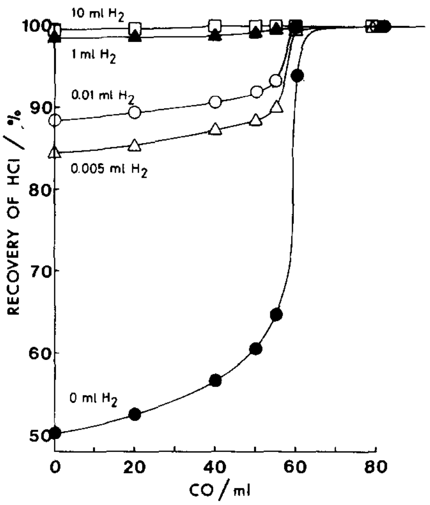

Fig. 4. The theoretical recovery of HCl at 1200 K as a function of H_2 and CO added to 150 ml of air (30 ml of O_2 + 120 ml of N_2) containing 1 ppm (v/v) vinyl chloride. The total pressure was 1 atm.

The smallest amount of H_2 for which a recovery of 100·0% is obtained is about 0·01 ml at CO = 60 ml. This amount of H_2 corresponds to a humidity of the air of about 67 ppm (v/v).

In Fig. 5 the recovery of HCl is given as a function of the amount of CO added to 150 ml of air containing 1 ml of H_2 and 1 ppm (v/v) vinyl chloride. The system was studied at 1100, 1200 and 1300 K. As can be seen, at least 60 ml of CO must be added in order to attain 100·0% recovery.

Figure 6 shows the distribution of other chlorine-containing compounds such as Cl(g), HClO(g), ClO(g), Cl_2(g) as a function of different volumes of CO added to the above-mentioned gas mixture at

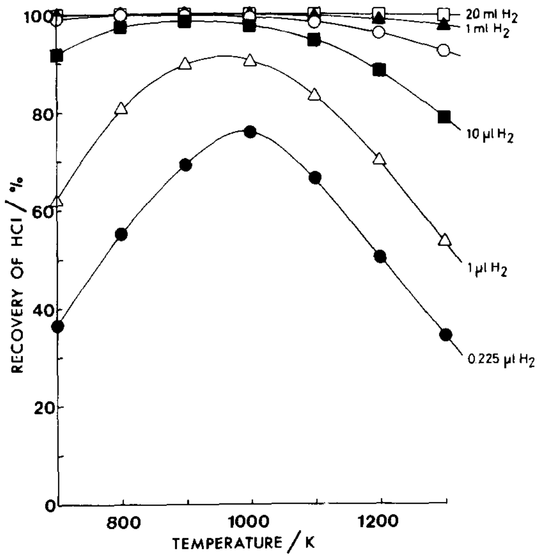

Fig. 3. The theoretical recovery of HCl as a function of temperature and the volume of H_2 added to 150 ml of air (30 ml of O_2 + 120 ml of N_2) containing 1 ppm (v/v) vinyl chloride at a total pressure of 1 atm.

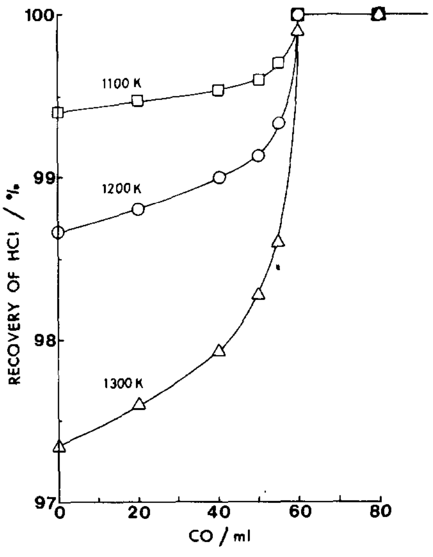

Fig. 5. The theoretical recovery of HCl at 1100 K, 1200 K and 1300 K as a function of CO added to 150 ml of air (30 ml of O_2 + 120 ml of N_2) containing 1 ppm vinyl chloride. The amount of H_2 added was 1 ml.

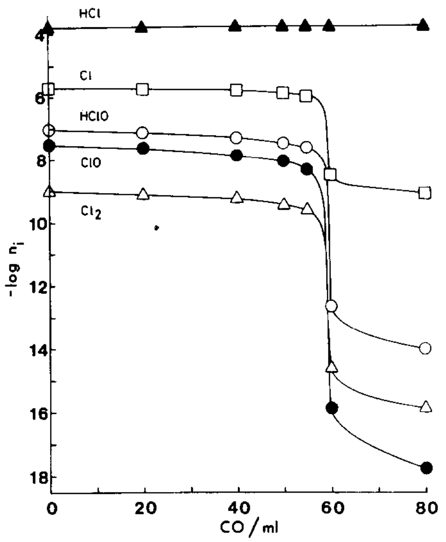

Fig. 6. Distribution of various chlorine-containing compounds at 1200 K as a function of various volumes of CO added to 150 ml of air containing 1 ppm (v/v) vinyl chloride. The amount of H_2 added was 1 ml. n_i is the number of moles of substance at equilibrium.

1200 K (1 ml of H_2 is also added). $COCl_2$, CCl_4, CH_2Cl_2 and $CHCl_3$, which were initially considered, are neglected in Fig. 6 because they were present in very small amounts.

Coulometric determinations

A coulometric determination of the permeation rate was made as shown in Fig. 1. Nitrogen was passed at 120 ml/min over a permeation tube containing vinyl chloride and into the combustion tube where it was mixed with oxygen flowing at a rate of 30 ml/min. The gas mixture was preheated in oven I to 800 K. The combustion occurs in oven II in an excess of oxygen. The temperature was kept between 1100 and 1200 K and was not critical. Dried CO_2 and H_2 were mixed and passed through a quartz tube filled with graphite, in oven VI which was kept at 1300 K. The carbon dioxide was converted into CO with almost 100% efficiency. H_2 passes this reactor unchanged. The gases were dried and preheated in oven III at 1200 K and mixed with the combustion products in oven IV. A preliminary investigation showed that this oven must be kept at 1200 K in order to reach equilibrium sufficiently quickly. If the gas mixture entering the titration cell is too hot, the evaporation will be high. Oven V was therefore kept at 1000 K, which also favours formation of HCl in the gas mixture, see Fig. 3. The gas was bubbled through the sample compartment of the titration cell, where it was titrated continuously with coulometrically generated silver ions.

Table 2 shows the recovery of HCl when the flows of CO and H_2 were varied. The results are also compared with recoveries calculated by the method discussed above and it can be seen that the agreement is good except for the first value. The discrepancy might depend on difficulties in measuring the very low flow of H_2. It should also be noted that the calculations were made for 1200 K in oven IV as the rate was too low at lower temperatures. The equilibria might change somewhat in oven V, resulting in a higher recovery of HCl than that calculated, compare Fig. 3.

Table 2. The recovery of HCl as a function of H_2 and CO at 1200 K. O_2 = 30 ml/min; N_2 = 120 ml/min; $CH_2{=}CHCl$ = 7·42 × 10^{-9} mole/min (mean value of gravimetric results)

H_2*, *ml/min*	CO, *ml/min*	HCl found† mean values, %	Rel. std. devn., %	Number of dtns.§	Theoretical recovery of HCl, %
0·01	0	92	1	3	88·3
0·1	20	97·7	—	2	96·3
1	0	98·6	0·1	3	98·7
1	20	99·0	0·1	10	98·8
1	60	99·9	0·1	10	100·0
0·6	80	99·8	0·2	3	100·0

* Determined as water after reaction with oxygen.

† The values are related to the gravimetric mean value: 7·42 ± 0·04 nmoles of vinyl chloride per min.

§ The time for each determination was 5–10 min.

There are several combinations of H_2 and CO which give high recovery of HCl. At 60 ml/min practically all CO is converted into CO_2 by the oxygen and it is desirable to limit the CO to this value as the excess is emitted to the air. Therefore the selected CO_2 gas flow was 30 ml/min which equals a CO flowrate of 60 ml/min after reaction with the graphite. The flow of H_2 required then becomes 1 ml/min or somewhat less.

By use of the optimum conditions deduced, the permeation rate of a tube was determined and the results are given in Table 3, which also contains the results of gravimetric determinations on the same tube. As can be seen, the coulometric method gives precise results which are in good agreement with the gravimetrically determined values. The coulometric results were corrected for a blank value which was about 1% of the sample value, *i.e.*, less than 10^{-10} mol of chloride per min. The variation in the blank was less

Table 3. Comparison between gravimetric and coulometric determination of the permeation rate

Gravimetric		Coulometric*	
Date	*μg/min*	Date	*μg/min*
10·2	0·464	28·2	0·464
17·2	0·465	4·3	$0{\cdot}462_5$
24·2	0·460	10·3	$0{\cdot}462_5$
3·3	0·464	14·3	0·464
12·3	0·466	17·3	0·461
Mean value: 0·464		Mean value: 0·463	
Std. devn.: $0{\cdot}002_3$		Std. devn.: $0{\cdot}001_2$	

* For the following conditions: N_2 120 ml/min; O_2 30 ml/min; H_2 1 ml/min; CO 60 ml/min. Furnace temperatures T_1 = 800 K, T_2 = 1100 K, T_3 = 1200 K, T_4 = 1200 K and T_5 = 1000 K.

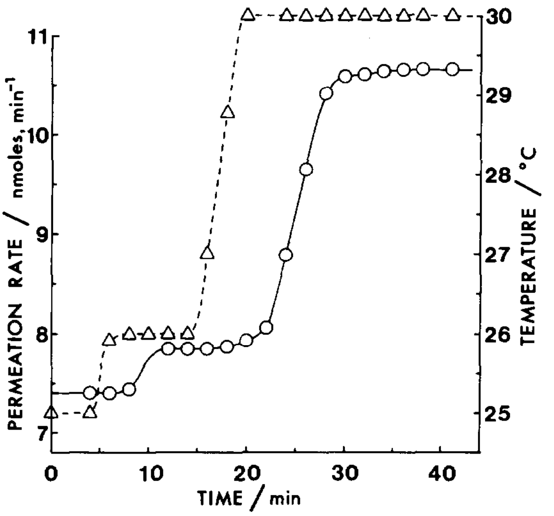

Fig. 7. The temperature response of the permeation tube. The dotted line is to be referred to the right-hand scale and this curve represents the temperature of the thermostat. (△) Temperature curve, (○) permeation-rate curve.

than 10%. The blank can be determined by by-passing the permeation tube.

The temperature-dependence of a permeation tube is represented in Fig. 7. The dotted line in Fig. 7 shows the temperature of the thermostat as a function of time. A change from 25·0 to 26·0° resulted in an increase of the permeation rate from 7·40 × 10^{-9} to 7·85 × 10^{-9} mole/min. About 4 min were needed to obtain a constant permeation rate when the temperature was changed from 25·0 to 26·0°, compared to about 10 min when the temperature was changed from 26·0 to 30·0°. A change in temperature of 0·1° will thus correspond to a change of approximately 1% in the permeation rate and this is about the same as for sulphur dioxide when FEP-tubes are used.[16]

DISCUSSION

The effect of water on the titration system

In a continuous titration using 1 ml of H_2 per min in the combustion there is formation of about 0·7 μl of H_2O per min. In 1 hr this will correspond to 42 μl of H_2O. The error due to the dilution effect of this volume of H_2O on 15 ml of 70% (v/v) acetic acid was negligible. On the contrary if only H_2 (or H_2O) had been used to obtain complete conversion into HCl it would have been necessary to add about 50 ml of H_2 per min. This would have resulted in the formation of 37 μl of H_2O per min or 2 ml in 1 hr. Figure 8 explains the effect of dilution of the titration medium. In this experiment 2 ml of H_2O were added to 15 ml of 70% (v/v) acetic acid. Two titrations were done; one for 15·0 ml of 70% acetic acid and one for 15·0 ml of 70% acetic acid + 2 ml of water. The figure shows explicitly the end-point displacement resulting from dilution of the solvent.

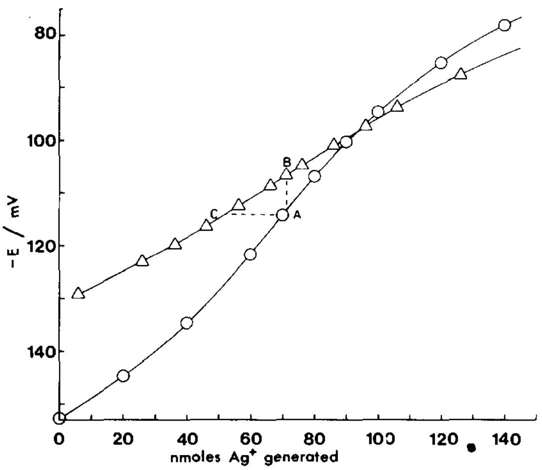

Fig. 8. The effect of diluting the titration medium with water. For the significance of A, B and C, see the text under "Discussion". (○) 15 ml of 70% HAc, (△) 15 ml of 70% HAc + 2 ml of H_2O.

The potential of point A in Fig. 8 is the equivalence point for use of the 70% (v/v) solvent. When this solvent is diluted the potential of the new system corresponds to point B because in both cases there must be equivalence between chloride and silver ions. As the coulometric analyser titrates to a predetermined potential it will titrate to point C. The error, which is negative in this case, will correspond to the marked difference CA on the abscissa. As shown earlier,[17] this water effect can be compensated for either by adding the equivalent of distance CA in Fig. 8 to the result read on the integrator or by selecting an end-point other than the equivalence point. However, the corrected result will be more uncertain than that determined by the present method in which this type of error is eliminated. For this reason conditions corresponding to Case B in the calculations, *i.e.*, addition of CO, were selected.

Comparison between the coulometric and the gravimetric methods

As was shown in Table 3, the results obtained by the coulometric and the gravimetric methods were not significantly different from each other. In fact the mean values of the coulometric results were about 99·9% of the gravimetric mean value. However, it is difficult to prove that the coulometric method is capable of giving a recovery of 100·0%, because of the relatively large standard deviation of the gravimetric method to which the coulometric mean value is referred. In order to obtain a precision of 1% by the use of the gravimetric method about three weeks were needed and during this time three weight differences of about 5 mg each could be obtained provided that the permeation rates were of the order of those presented in this paper. The coulometric method for standardizing the permeation tubes was very rapid. In less than 1 hr the permeation rate could be determined with a precision of about 0·1%. In this time about eight 5-min titrations plus a blank run could be performed.

The relative standard deviation of 0·2% which was obtained for determinations of 1 ppm of vinyl chloride in air on different occasions is equal to an uncertainty of about 0·002 ppm (v/v). This means that the coulometric method is capable of accurate and rapid standardization of test atmospheres in the range 0·1–100 ppm (v/v).

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SIMULTANEOUS DETERMINATION OF TRACE NIOBIUM, TANTALUM AND TUNGSTEN IN FERROUS AND NON-FERROUS ALLOYS

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Summary—A method is presented for the determination of niobium, tantalum and tungsten in steel and non-ferrous alloys, based on hydrolysis with sulphurous acid followed by X-ray fluorescence measurements. The limit of determination is about 0·002% and the standard deviation is 0·002 at the 0·05% level. Results below 0·01% by this method are only semiquantitative.

A rapid chemical X-ray method is proposed for determining trace amounts of niobium, tantalum and tungsten in iron-base and non-ferrous alloys. Standard wet chemical procedures for these elements tend to be time-consuming and lack sufficient sensitivity for accurate analysis at levels less than 0·1%.[1] Direct instrumental methods (X-ray, atomic absorption and optical emission) are severely limited by the number and types of standards available as well as by a general lack of sensitivity at levels below 0·01%. For the method described in this report, the ease and speed of sample preparation together with the demonstrated accuracy and precision render it extremely useful for the determination of these elements at trace levels, a task which is becoming increasingly more important in alloy development programmes and is widely pursued at Crucible's Research Center for a number of traces, already reported.[2,3] The method utilizes the hydrolysis of niobium, tantalum and tungsten in the dissolved sample before their determination by X-ray fluorescence. All three elements are chemically characterized by a strong tendency to hydrolyse, enhanced by the use of sulphurous acid (H_2SO_3).[4,5] X-ray examination of hydrolysed niobium, tantalum and tungsten oxides on the same sample, showed constant and reproducible recoveries of the elements, thus offering a simple method for their determination without tedious separations and with no involved sample preparation.

EXPERIMENTAL

X-Ray apparatus

A Siemens X-ray fluorescence spectrograph, type "Crystalloflex IV", with an X-ray generator and control having a full-wave rectified power-supply voltage and current regulation up to 50 kV and 40 mA in air, and a high-purity gold target, was used.

Materials

Niobium, tantalum and tungsten solutions, 0·10 *mg/ml.* Dissolve 0·10 g of the appropriate metal in 20 ml of hydrofluoric acid–nitric acid mixture (1:1) and dilute with distilled water to 1000 ml.

Procedure

Weigh a sample containing between 0·20 and 1·0 mg of niobium, tantalum and tungsten and transfer it to a 600-ml beaker. Add 50 ml of water followed by 50 ml of concentrated hydrochloric acid. Heat gently and add 10 ml of concentrated nitric acid to complete the dissolution. Add 30 ml of 70% perchloric acid and evaporate to low volume (20–25 ml). Dilute to 200 ml with boiling water and add, while stirring, 30 ml of sulphurous acid (7·3% SO_2). Boil for 10 min and allow to stand for 10 min before filtering off on a 0·22-μm micropore membrane. Wash the precipitate with boiling water, air-dry for 1 min and mount the membrane in a suitable holder for X-ray analysis. Place the mounted membrane in the X-ray spectrograph and determine niobium, tantalum and tungsten sequentially, starting with niobium, according to the following conditions:

Primary voltage	50 kV
Primary current	40 mA
Detector	Scintillator
Detector voltage	500–700 V
Pulse-height analyser base-line	8 V
Pulse-height analyser channel-width	8 V
Preset time	24 sec
Crystal—lithium fluoride 1st order K_α radiation for niobium, 1st order L_β radiation for tantalum, L_α radiation for tungsten	
2θ values	Nb 21·41° Ta 38·47° W 43·00°

Measure the counts accumulated during a fixed time (24 sec), also the number of counts accumulated at a 100 V higher detector voltage for niobium and at 1° above the 2θ values for tantalum and tungsten; take the difference between the two counts for the element sought and divide it by the fixed time to calculate the count-rate.

Plot counts/sec against mg of niobium, tantalum and tungsten to construct calibration graphs, using a set of synthetic standards consisting of 1·0 g of pure iron containing 0·1–1·0 mg of the element of interest and treated according to the procedure. Calibration graphs constructed by the use of electrolytic iron dosed with niobium, tantalum and tungsten are linear over the range from 0·1% down to just below 0·02% of the element (Table 1).

RESULTS AND DISCUSSION

A number of individual samples of ferrous and non-ferrous materials, including certified standards, were analysed in order to evaluate the accuracy, precision and reproducibility of the method.

Table 1 shows that for both niobium and tungsten it appears that at 0·20 mg the method is operating at its limit of detection. For tantalum the detection of levels lower than 0·06 mg seems feasible although the accuracy below 0·20 mg is questionable.

To evaluate the accuracy, NBS stainless and low-alloy steel samples were analysed for the three elements. Results obtained by use of the original calibration graphs used for the data in Table 1 are given in Tables 2 and 3; duplicate results are reported. In general, agreement between duplicate analyses in Tables 2 and 3 is satisfactory. Agreement obtained with the values reported by NBS for niobium and tantalum is good in Table 2 and superior in Table 3. No significant improvement in the accuracy was obtained for tungsten by using either a 0·5 or a 1·0 g sample, while it is evident from Tables 2 and 3 that the use of a 1·0 g sample improves the accuracy and precision for niobium and tantalum by shifting the responses to areas where the method operates at its best. For tungsten our values are consistently lower than those reported by NBS but if corrected by a factor averaged out for NBS 363, NBS 442 and NBS 443 they would read 0·045, 0·070 and

Table 1. Results for 1·0-g samples of NBS 365 electrolytic iron

Element	Added, *mg*	Found, *mg*	Count, *cps*
Niobium	0	0	0
	0·06	0·014	15
	0·09	0·015	41
	0·20	0·023	208
	0·40	0·397	809
	0·80	0·805	2074
	1·00	0·994	2658
Tantalum	0	0	30
	0·03	0·034	74
	0·06	0·039	80
	0·09	0·133	219
	0·20	0·160	254
	0·40	0·405	622
	0·80	0·824	1243
	1·00	1·019	1532
Tungsten	0	0	7
	0·20	0·204	74
	0·40	0·396	504
	0·80	0·805	1420
	1·00	1·003	1863

Table 2. Niobium, tantalum and tungsten results for 0·5-g samples of NBS samples

Sample	Niobium,* %	Niobium,† %	Tantalum,* %	Tantalum,† %	Tungsten,* %	Tungsten,† %
NBS 361	0·029	(0·022)	0·028	(0·021)	—	—
Low Alloy	0·029	—	0·022	—	—	—
NBS 363	0·054	(0·049)	0·051	(0·053)	0·038	(0·04)
Low Alloy	0·054	—	0·059	—	0·041	—
NBS 442	0·035	0·032	—	—	0·046	(0·06)
Cr 16-Ni 10	0·026	—	—	—	0·042	—
NBS 443	0·048	0·056	—	—	0·058	(0·09)
Cr 18-Ni 9·5	0·046	—	—	—	0·061	—

* Values obtained.
† Reported by NBS.

Table 3. Niobium, tantalum and tungsten results for 1·0-g samples of NBS samples

Sample	Niobium,* %	Niobium,† %	Tantalum,* %	Tantalum,† %	Tungsten,* %	Tungsten,† %
NBS 361	0·021	(0·022)	0·022	(0·021)	—	—
Low Alloy	0·023	—	0·023	—	—	—
NBS 363	0·043	(0·049)	0·056	(0·053)	0·029	(0·04)
Low Alloy	0·050	—	0·054	—	0·031	—
NBS 442	0·031	0·032	—	—	0·046	(0·06)
Cr 16-Ni 10	0·031	—	—	—	0·048	—
NBS 443	0·051	0·056	—	—	0·049	(0·09)
Cr 18-Ni 9·5	0·050	—	—	—	0·057	—

* Values obtained.
† Reported by NBS.

Table 4. Tantalum results for 1·0-g samples of rare-earth alloys

Sample	Tantalum added, *mg*	Tantalum found, *mg*	Tantalum, *cps*	Tantalum found, %
6-1 Mischmetal	0			
6-2 Mischmetal	0·055	0·04	20	0·004
6-3 Mischmetal	0·11	0·12	90	0·012
6-4 Mischmetal	0·33	0·32	251	0·032
1-a Mischmetal	—	0·17	128	0·016
1-b Mischmetal	—	0·17	133	0·017
2-a Mischmetal	—	0·16	118	0·015
2-b Mischmetal	—	0·14	105	0·014
3-a Mischmetal Cobalt	—	0·15	115	0·014
3-b Mischmetal Cobalt	—	0·15	110	0·013
4-a Sm-Co$_5$	—	0·16	120	0·015
4-b Sm-Co$_5$	—	0·13	100	0·012
5-a Samarium	—	0·17	131	0·016
5-b Samarium	—	0·15	110	0·014

0·080% respectively, against the 0·047, 0·060 and 0·090% reported by NBS.

Table 4 includes duplicate results obtained for the determination of tantalum in mischmetal, samarium and rare-earth–cobalt alloys.

Tantalum recoveries obtained for samples 6-1 to 6-4, used as background for an addition technique, were quite satisfactory. Again, at 0·055 mg the method is operating below optimum sensitivity levels, which explains the lack of agreement between tantalum found and added.

Tables 5, 6 and 7 include niobium, tantalum and tungsten results for high-temperature alloys. Such an analytical capability was needed because of a lack both of solid standards for direct X-ray techniques and wet chemical methods for the analysis of the desired traces.

The results in Tables 8 and 9 show satisfactory recoveries of all three elements down to the 0·05 mg level. Again, an addition technique was employed whereby the sample to be analysed was used as background for known additions of the three elements sought.

Efforts were made to determine lower levels of the three elements (0·001–0·01%) by the use of an addition technique; 0·40 mg of each element was introduced into a series of electrolytic iron samples which were subsequently dosed with 0·02–0·10 mg of niobium, tantalum and tungsten. The results were corrected for the 0·04% background, and as shown in Table 8 were reasonable for the range up to 0·01%.

Table 5. Niobium results for 0·4-g samples of nickel-base alloys

Sample	Niobium added, *mg*	Count,* *cps*	Niobium found, *mg*	Found, %	Nominal content, %
X-1	0·00				
X-2	0·02	141	0·03	0·007	0·005
X-3	0·04	159	0·04	0·010	0·010
X-4	0·12	254	0·09	0·023	0·030
X-5	0·20	421	0·19	0·047	0·050
X-6	0·40	816	0·40	0·10	0·100

* Corrected for X-1.

Table 6. Tantalum results for 0·4-g samples of nickel-base alloys

Sample	Tantalum added, *mg*	Count,* *cps*	Tantalum found, *mg*	Found %	Nominal content, %
X-1	0·00				
X-2	0·02	58	0·04	0·010	0·005
X-3	0·04	76	0·05	0·013	0·010
X-4	0·12	157	0·10	0·025	0·030
X-5	0·20	329	0·19	0·047	0·050
X-6	0·40	585	0·34	0·085	0·100

* Corrected for X-1.

Table 7. Tungsten results for 0·4-g samples of nickel-base alloys

Sample	Tungsten added, *mg*	Count,* *cps*	Tungsten found, *mg*	Found, %	Nominal content, %
X-1	0·00				
X-2	0·02	Not detected			
X-3	0·04	38	0·05	0·012	0·010
X-4	0·12	99	0·08	0·020	0·030
X-5	0·20	334	0·20	0·050	0·050
X-6	0·40	754	0·42	0·105	0·100

* Corrected for X-1.

Table 8 shows that the addition of 0·40 mg of each element seems beneficial in providing semi-quantitative analytical capability for all three elements below 0·01%. The reproducibility after the addition of 0·40 mg of each element falls within the statistical limits reported in Table 9. Attempts to increase sensitivities by using larger samples (5–10 g) were unsuccessful.

Reproducibility

The reproducibility of the method was evaluated by analysing ten 1-g samples of NBS 363. The results are given in Table 9.

Table 8. Niobium, tantalum and tungsten results obtained by addition method

Sample	Niobium assumed, %	Niobium found, %	Tantalum assumed, %	Tantalum found, %	Tungsten assumed, %	Tungsten found, %
1	0·000	0·000	0·000	0·003	0·000	0·004
2	0·002	0·000	0·002	0·014	0·002	0·000
3	0·004	0·003	0·004	0·000	0·004	0·003
4	0·006	0·005	0·006	0·012	0·006	0·003
5	0·008	0·003	0·008	0·012	0·008	0·004
6	0·010	0·006	0·010	0·008	0.010	0·006

Table 9. Precision for niobium, tantalum and tungsten (ten 1·00 g samples of NBS 363)

Number of determination	Niobium, %	Tantalum, %	Tungsten, %
1	0·053	0·056	0·033
2	0·049	0·053	0·032
3	0·048	0·052	0·035
4	0·051	0·052	0·036
5	0·051	0·057	0·033
6	0·051	0·060	0·037
7	0·051	0·058	0·033
8	0·048	0·056	0·031
9	0·048	0·054	0·035
10	0·045	0·051	0·032
Mean (N)	0·0495	0·055	0·034
Standard deviation (σ)*	0·0023	0·0030	0·0020
% Coefficient of variation (C.V.)†	±4·7	±5·4	±5·8
NBS Value	0·049	0·053	0·04

* $\sigma = \sqrt{\dfrac{\Sigma d^2}{n-1}}$ (d = difference from the mean value, n = number of determinations).

† $\text{C.V.} = \dfrac{100 \times \sigma}{N}$.

X-Ray interferences

The 2θ lines used and background correction applied during the development of the method were chosen after careful testing with available X-ray instrumentation. To confirm the lack of any interference caused by tantalum L_α 44·41°, in the background read for tungsten L_α 43·00° at 1° above 2θ, a study was conducted on synthetic samples with and without tungsten and tantalum, as shown in Table 10.

Table 10. Data to show lack of interference between tantalum and tungsten background

Sample composition	Background for tungsten read at 44·00°, counts/24 sec
Iron + 0·80 mg Ta + 0·80 mg W	1670
Iron + 0·80 mg W	1674
Iron	1530

No other interferences were encountered or needed to be explored.

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USE OF LONG-CHAIN ALKYLAMINES FOR PRECONCENTRATION AND DETERMINATION OF TRACES OF MOLYBDENUM, TUNGSTEN AND RHENIUM BY ATOMIC-ABSORPTION SPECTROSCOPY—II

MOLYBDENUM IN SOILS, SEDIMENTS AND NATURAL WATERS

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Summary—Molybdenum is extracted as the thiocyanate complex with the quaternary long-chain aliphatic amine Aliquat 336 in chloroform, followed by evaporation of the solvent, dissolution in MIBK, and atomic-absorption spectroscopy. The method is simple, rapid and sensitive, with few interference problems for the determination of the Mo content of soils and sediments in the range 0·1–1·0 ppm with a relative standard deviation better than 5% when 1-g samples are used. Quantitative extraction from large volumes of aqueous solution has also been confirmed, allowing the determination of Mo in natural waters in the ppM range.

Methods based on solvent extraction of molybdenum complexes, with either spectrophotometric or atomic-absorption finishes, continue to be popular for the determination of traces of molybdenum in waters and geological, biological and industrial materials. Such methods have the advantages of sensitivity, selectivity and speed. Kim *et al.*[1] used solvent extraction of the molybdenum thiocyanate complex (Mo–SCN) with methyl isobutyl ketone (MIBK) for the determination of molybdenum in the range 1–500 ppm in soils and geological materials by atomic-absorption spectroscopy. The method had few interferences and the detection limit was 0·1 ppm with a relative standard deviation not exceeding 8% at the level of 1 ppm. Kim *et al.*[2] also showed that solvent extraction of the Mo–SCN complex with long chain alkylamines could form the basis of methods for the determination of Mo, W and Re with improved sensitivity. Haddad *et al.*[3] reported a versatile spectrophotometric or fluorometric method using the ternary complex formed by the reaction of the molybdenum oxypentathiocyanate ion with the dyestuff Rhodamine B for the determination of molybdenum in soils and plants with detection limits of 0·1 μg and 0·05 μg respectively for the absorption and fluorescence methods.

Other trace methods for molybdenum recently reported in the literature include: molybdenum in hard dental tissues by using ammonium pyrrolidinedithiocarbamate–MIBK with a detection limit of 0·2 ppm;[4] vanadium and molybdenum in uranium products and uranium minerals in the range from ppm to mg by using anion-exchange;[5] a spectrophotometric method for molybdenum in steels in the range 1–32 μg by using solvent extraction of the thiosulphate complex into isoamyl alcohol;[6] an enthalpimetric method with a sensitivity between 3×10^{-3} and 2×10^{-2} ppm;[7] molybdenum in high-purity tantalum by using proton-activation analysis with a reported detection limit of 0·2 ppm;[8] an automated catalytic method for molybdenum in plants, based on liberation of iodine from potassium iodide and hydrogen peroxide, applicable in the range 0·2–2·0 ppm;[9] a spectrophotometric method using the Mo–SCN complex with two different extractions with different reagents applicable to rocks in the range 0·3–5 μg/g;[10] a modification of the extraction of the dithiol complex of molybdenum with spectrophotometric finish, with sensitivities of 0·05 ppm for biological materials, 0·5 ppm for geological materials and 10 ppm for steels with relative standard deviations of ±7%;[11] and a spectrophotometric method for molybdenum(VI) in the range 0·75–8·5 μg/ml by extraction with 2-mercaptobenzo-γ-thiopyrone.[12] Nearly all of these methods[4–12] suffer from some interferences, time-consuming processing or lack of colour stability or sensitivity in the important range below 1 ppm.

We have developed and applied the procedure using solvent extraction of the Mo–SCN complex with long-chain alkylamines[2] for the determination of traces of molybdenum in soils, sediments and natural waters. The extraction is done with the quaternary long-chain aliphatic amine Aliquat 336 in chloroform followed by evaporation of the solvent, dissolution in MIBK, and atomic-absorption finish. The method offers significant advantages as a simple, rapid, sensitive procedure with very few interferences.

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* Part I—*Talanta*, 1975, **22**, 739.

In addition, similar procedures can be used for the determination of tungsten and rhenium in related materials, with improved sensitivity.

EXPERIMENTAL

Reagents and apparatus

All reagents have been described previously.[2] The atomic-absorption spectrophotometer used was a Varian–Techtron AA5 instrument and instrumental settings have also been reported.[2]

Procedure

The general procedure for determination of molybdenum was extraction from aqueous medium of 1*M* hydrochloric acid, 1% potassium thiocyanate and 1% stannous chloride into a chloroform solution of a long-chain alkylamine, followed by evaporation of the chloroform and dissolution of the residue in MIBK. Molybdenum in the final MIBK solution was determined by atomic absorption. Complete details of this procedure have been published.[2]

This general procedure was modified as follows for determination of molybdenum in natural samples. Soil and sediment samples (1 g) were dissolved by the method of Kim *et al.*,[1] giving a final solution volume of 40 ml in 1*M* hydrochloric acid. To this solution were added 2 ml of 20% potassium thiocyanate solution and 2 ml of 20% stannous chloride solution. If required, more stannous chloride solution was added slowly with stirring until the red colour of ferric thiocyanate disappeared. Molybdenum was extracted with 10 ml of 0·2% Aliquat 336 in chloroform by shaking vigorously for 1 min. After phase separation, the organic phase was drained into a 25-ml weighing bottle. The aqueous phase was extracted with a further 10 ml of the organic solvent, which was separated from the aqueous phase and added to the initial organic solvent. After the chloroform had been evaporated off on a steam-bath, 1–10 ml of MIBK were added to the residue, depending on the quantity of molybdenum present (as judged from the colour of the extract). The residue was dissolved in the MIBK by brief warming in the stoppered bottle and, after cooling, the molybdenum atomic absorbance was determined, with MIBK as the blank.

Equilibration time for the complete reduction of Mo(VI) to Mo(V) by stannous chloride and complexation with thiocyanate in 1*M* hydrochloric acid was of the order of a few min. Tests for equilibration were carried out by measurement of extracted molybdenum at various times after the addition of potassium thiocyanate and stannous chloride solutions to the aqueous phase. After equilibration of the aqueous phase, 1 min of vigorous shaking was sufficient for complete extraction of 10 μg of molybdenum from 50 ml of aqueous solution with 10 ml of the organic extracting agent.

For the analysis of waters, samples were filtered through MA-MF Millipore filter paper (0·45 μm), diameter 47 mm, by use of Millipore all-glass filter apparatus, and stored for a short time in polyethylene containers. A sample volume of 100 ml was treated with 1 g of solid potassium thiocyanate and 10 ml of 10% stannous chloride in 10*M* hydrochloric acid, giving a final 1*M* hydrochloric acid solution. Molybdenum was extracted with 10 ml of 0·2% Aliquat 336 in chloroform followed by a 10-ml chloroform wash. The chloroform was evaporated from the organic extract and as before, MIBK [1·0 ml (or 2·0 ml for sea-water)] was added to the residue before measurement of the molybdenum absorbance.

RESULTS

In the previous work by Kim *et al.*,[2] optimization of reagent conditions and interference studies were carried out with Amberlite LA1 as a general extractant for molybdenum, tungsten and rhenium. However, Aliquat 336 in chloroform was shown to give optimum extraction of molybdenum over a wider range of hydrochloric acid concentration (from 1*M* to 5*M*) and wide range of thiocyanate and stannous chloride concentrations (1–5%). Maximum extractions were obtained from 1*M* or 2*M* hydrochloric acid with slight decreases above 2*M*, and 1*M* hydrochloric acid solution was chosen for routine applications. Aliquat 336 in chloroform was therefore used in this work for extraction of molybdenum from aqueous 1*M* hydrochloric acid solution containing 1% potassium thiocyanate and 1% stannous chloride.

Single extractions were carried out with 10 ml of 0·2% Aliquat 336 in chloroform. In order to recover the incompletely separated portion of organic phase, 10 ml of chloroform were used for washing the aqueous phase in the separating funnel and finally combined with the initial extract. After evaporation of the chloroform, the residue was dissolved in MIBK and made up to a final volume of 1–10 ml.

Effect of Aliquat 336 extraction

Data for the extraction of 10 μg of molybdenum with various concentrations of Aliquat 336 in chloroform are given in Table 1. Single extractions with 10 ml of 0·2% Aliquat 336 in chloroform were quantitative. High concentrations of Aliquat 336 in MIBK, up to 6%, were found to have no effect on the molybdenum absorbance, despite the high viscosity of the solutions. Furthermore, there was no background absorbance by 6% Aliquat 336 solution in MIBK, relative to pure MIBK. Accordingly, pure MIBK was used as a blank for zero absorbance setting. In practice, when 1 ml of MIBK was used for final residue dissolution after double extraction with 10 ml of 0·2% Aliquat 336 in chloroform, the concentration of Aliquat 336 in the final MIBK solution was 4% v/v.

Recovery of molybdenum from large volumes of aqueous phase

To establish the possibility of determining traces of molybdenum in waters, recovery from highly diluted aqueous solutions of large volume was determined, as shown in Table 2. Trace quantities of molybdenum (2·0–0·5 μg) were taken in 50–200 ml of 1*M* hydrochloric acid. For the extraction, the volume

Table 1. Optimum concentration of Aliquat 336 in chloroform for extraction of molybdenum (10·0 μg)

Concentration of Aliquat 336 in $CHCl_3$, % *v/v*	Mo recovery, %
0·05	90
0·1	98
0·2	100
0·5	100
1·0	100
2·0	100

Table 2. Recovery of molybdenum from large volumes of aqueous solution

Volume of aqueous phase *ml*	MIBK *ml*	No. of determinations	Mo taken, *μg*	Recovery, %
50	2	5	2·0	99·0–100
100	2	5	2·0	99·5–100
50	1	5	0·5	98·5–101
100	1	5	0·5	99·0–100
200	1	4	0·5	98·5–103

of 20% potassium thiocyanate and 20% stannous chloride solutions added to the aqueous phase was increased by 0·5 ml for every 50 ml of aqueous solution. Single extractions were carried out with 20 ml of 0·2% Aliquat 336 in chloroform.

The data in Table 2 show excellent recovery of molybdenum at 2·5–10·0 ppM levels from aqueous solutions and indicate the value of the present procedure for trace analysis of waters.

Interference studies

A detailed study of interference effects was made for cations and anions in amounts ranging up to 0·1 and 1 g respectively, with 10 μg of molybdenum. Among the cations tested, the only major interference was from rhenium, which was co-extracted with molybdenum as the thiocyanate complex. However, this element can be neglected in applications to soil analysis because of its rarity. Although some elements such as cobalt and palladium were also extracted with molybdenum as coloured complexes, no effect was observed on the atomic absorbance. Cu(II) was reduced to Cu(I) by stannous chloride and formed a white precipitate of CuSCN in the aqueous phase. Interference from large amounts of iron (up to 500 mg) was eliminated by reduction with an excess of stannous chloride.

Among the anions tested, nitrate was extracted and caused a slight negative error. EDTA complexed molybdenum and prevented complete extraction. Perchlorate gave a precipitate of potassium perchlorate after the addition of potassium thiocyanate. Therefore complete evaporation of perchloric acid was required in the dissolution procedure for geological samples.

Interference data are summarized in Tables 3 and 4.

Table 3. Effect of cations on absorbance of molybdenum (10 μg)

Cation (salt used)	Cation, μg added/μg Mo	Absorbance	Cation (salt used)	Cation, μg added/μg Mo	Absorbance
No addition	—	0·60	Mg ($MgCl_2$)	10^3	0·61
Ag (Ag_2SO_4)	10^2	0·59		10^4	0·61
Al [$Al(NO_3)_3$]	10^3	0·61	Mn ($MnCl_2$)	10^3	0·61
	10^4	0·61		10^4	0·60
Au ($NaAuCl_4$)	10^2	0·60	Na (NaCl)	2×10^4	0·60
Ba ($BaCl_2$)	10^3	0·60	NH_4 (NH_4Cl)	2×10^4	0·60
	10^4	0·59	Ni ($NiCl_2$)	10^3	0·59
Bi ($BiCl_3$)	10^3	0·60		10^4	0·58
	10^4	0·61	Pb [$Pb(NO_3)_2$]	10^3	0·60
Ca ($CaCl_2$)	10^3	0·61		10^4	0·60
	10^4	0·61	Pd (PdI_2)	10^2	0·60
Cd ($CdCl_2$)	10^3	0·61	Pt [Pt(PtO)]	10^2	0·60
	10^4	0·61	Re ($KReO_4$)	10^0	0·59
Ce [$Ce(NH_4)_2(SO_4)_3$]	10^2	0·59		10	0·50
Co ($CoCl_2$)	10^3	0·60		10^2	0·45
	10^4	0·60	Rh (metal)	10^2	0·61
Cr ($CrCl_3$)	10^3	0·60	Sb ($SbCl_3$)	10^3	0·60
	10^4	0·65		10^4	0·60
Cu ($CuCl_2$)	5×10^2	0·60	Th ($ThCl_4$)	10^3	0·60
	10^3	0·56		10^4	0·60
Fe [$FeNH_4(SO_4)_2$]	10^3	0·60	Ti ($TiCl_4$)	10^3	0·61
	10^4*	0·60		10^4	0·60
	2×10^4*	0·60	V (NH_4VO_3)	10^2	0·60
	5×10^4*	0·60	W (Na_2WO_4)	10	0·60
Hg ($HgCl_2$)	10^2	0·58		10^2	0·58
In ($InCl_3$)	10^2	0·60	Zn ($ZnCl_2$)	10^3	0·60
K (KCl)	2×10^4	0·60		10^4	0·62
Li (LiCl)	10^3	0·60	Zr ($ZrOCl_2$)	10^3	0·60
	10^4	0·59		10^4	0·61

* More than 2 ml of 20% stannous chloride solution added.

Table 4. Effect of anions on absorbance of molybdenum (10 μg)

Anion (salt used)	Anion, μg added/μg Mo	Absorbance
No addition	—	0·60
Acetate ($NH_4C_2H_3O_2$)	5×10^4	0·61
	10^5	0·60
L-Ascorbic acid	10^5	0·60
Borate (H_3BO_3)	5×10^4	0·60
	10^5	0·62
Citrate [$C_3H_4(OH)(COOH)_3$]	5×10^4	0·60
	10^5	0·60
EDTA (Na_2EDTA)	2×10^4	0·55
Fluoride (NaF)	5×10^4	0·61
	10^5	0·60
Nitrate ($NaNO_3$)	5×10^4	0·58
	10^5	0·56
Oxalate [$(NH_4)_2C_2O_4$]	5×10^4	0·60
	10^5	0·60
Perchlorate ($NaClO_4$)	5×10^4	0·60
	10^5	0·62
Phosphate (NaH_2PO_4)	5×10^4	0·61
	10^5	0·60
Silicate (Na_2SiO_3)	5×10^4	0·58
	10^5	0·56
Sulphate (Na_2SO_4)	5×10^4	0·60
	10^5	0·58
Tartrate [$(CHOHCOOH)_2$]	5×10^4	0·59
	10^5	0·60
Tetrafluoroborate (KBF_4)	5×10^4	0·60
	10^5	0·60

Table 5. Determination of molybdenum in soils and sediments

Sample location and number	Type	MIBK, *ml*	No. of detns.	Range, *ppm*	Mean, *ppm*	RSD, %	Other method, *ppm*
Soils							
Cooroy, S.E.Qld. (A)	Xanthozem on phyllite	10	5	0·96–1·0	0·97	1·8	1·0, 1·1
Gympie, S.E.Qld. (B)	Red podsolic on phyllite	2	5	0·49–0·53	0·52	3·3	0·2, 0·4
Gympie, S.E.Qld. (C)	Prairie soil on andesite	2	3	0	0·62	0	0·4, 0·5
W. Brisbane, S.E.Qld. (F)	Red-yellow podsolic on granite	1	5	0·35–0·36	0·36	1·5	0·2, 0·2
S.Aust., Site A virgin	—	10	5	3·5–3·6	3·6	1·2	3·5, 3·6
S.Aust., Site B virgin	—	10	5	4·4–4·5	4·4	1·0	4·4, 4·4
S.Aust., Site C virgin	—	10	5	4·2–4·4	4·3	2·0	3·8, 4·0
Sediments							
733469*	—	10	3	0	2·4	0	—
740437†	—	1	3	0·58–0·60	0·59	2·0	—
740438†	—	1	3	0·40–0·42	0·41	2·9	—
740439*	—	10	3	0	1·1	0	—

* Tasmanian Department of Mines, marine sediments from Tomer Estuary.
† From Bass Strait, Australia.

Table 6. Determination of molybdenum in waters

Type	Location in Sydney Area	No. of detns.	Proposed method		Oxine-MIBK method[13]	
			Range, *ppm*	Mean, *ppm*	Range, *ppm*	Mean, *ppm*
Fresh	Cook's River	5	0·0014–0·0015	0·0014	0·0003–0·0008	0·0005
Estuarine	Parramatta River	5	0·0041–0·0043	0·0042	0·0042–0·0050	0·0044
Sea	North Bondi Beach	5	0·0108–0·0110	0·0110	0·0089–0·0120	0·0105

In view of the lack of serious interference, we conclude that the present extraction procedure is superior to direct MIBK extraction of the Mo–SCN complex, which suffered from some interference above the 1000-mg iron level (masking agent ascorbic acid) and above the 3-mg titanium level (masking agent sodium fluoride).[1]

Working curve

A standard solution of 2·5 ppm molybdenum in MIBK was prepared from an aqueous solution containing 250 μg of molybdenum. Three consecutive extractions were carried out with 10 ml of 1% Aliquat 336 in chloroform and, after evaporation, the residue was dissolved in MIBK and diluted to 100 ml. A linear calibration curve was obtained for the range 0·1–1·25 ppm molybdenum after appropriate dilution of the 2·5-ppm standard in MIBK. The absorbance values of the standards remained unchanged over a period of two months.

Analysis of molybdenum-deficient soils and sediments

Soils and sediments containing less than 5 ppm molybdenum were analysed by using the Aliquat 336 extraction procedures (Table 5). A 1-g sample was taken in each case and the results were compared with analytical data obtained previously by the direct MIBK extraction procedure.[1] Acceptable agreement between the two methods was obtained for samples containing above 1·0 ppm molybdenum, but the direct method gave poorer reproducibility and a wider spread of results than the Aliquat 336 method for samples with less than 1·0 ppm.

Analysis of natural waters

Samples of sea-water, fresh water and estuarine water were analysed for molybdenum content by the Aliquat 336 extraction method, using 100-ml samples. The results were compared with data obtained by the oxine–MIBK method,[13] reported recently. As shown in Table 6, the molybdenum content was in the ppM range for each sample. We obtained better precision with the proposed Aliquat 336 extraction method than with the oxine method, which gave inferior reproducibility in this concentration range.

CONCLUSIONS

Determination of molybdenum in the sub-ppm range has been demonstrated on samples of soils, sediments and natural waters at concentration levels difficult to determine by earlier methods. In particular, recently reported colorimetric methods[6,10–12] suffer from lack of sensitivity or from interferences. The proposed method offers significant advantages as a simple, rapid, sensitive procedure with few interferences.

It has been shown that the molybdenum content of soils and sediments can be determined in the range 0·1–1·0 ppm with a relative standard deviation better than ±5%, on 1-g samples. Extraction from large volumes of aqueous solution was found to be quantitative, allowing molybdenum determination in the ppM range in natural waters.

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SHORT COMMUNICATIONS

SEPARATION AND GRAVIMETRIC DETERMINATION OF RARE EARTHS WITH *N*-*m*-TOLYL-*m*-NITROBENZOHYDROXAMIC ACID

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N-*m*-Tolyl-*m*-nitrobenzohydroxamic acid (TNBHA) has been used[1] for the separation and gravimetric estimation of Ce^{4+} and La^{3+}. Its use is now extended to determination of Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+} in presence of several other metal ions. The solid complexes formed are of definite composition $(C_{14}H_{11}N_2O_4)_3M$.

EXPERIMENTAL

Reagents

TNBHA was prepared as described elsewhere[2]. Stock solutions of the rare earths were prepared by dissolving weighed quantities of their nitrates, and standardized volumetrically[3]. Masking agents were used as their 1% aqueous solutions.

Procedure

The procedure was the same as that described for cerium (IV) and lanthanum(III)[1], except that the precipitates were digested for only 30 min instead of 2–3 hr.

RESULTS AND DISCUSSION

The pH of precipitation for tervalent rare-earth metals with TNBHA is given in Table 1.

Ag^{+}, Cu^{2+}, Pb^{2+}, Pd^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Bi^{3+}, Fe^{3+} precipitate at pH $\leqslant$ 6·5; Ce^{4+}, Th^{4+} and U^{6+} precipitate at pH 3·8–4·8; Ga^{3+} gives no precipitate.

Ag^{+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+} can be masked with cyanide; Pb^{2+}, Pd^{2+}, Be^{2+}, Sb^{3+}, Sn^{4+}, Bi^{3+}, Zr^{4+} and Ti^{4+} can be masked with citrate and oxalate; Al^{3+}, V^{5+} and Mo^{6+} with Mg–EDTA.

The precipitates are soluble in benzene, ethanol, dioxan and chloroform, but sparingly soluble in diethyl ether, acetone and carbon tetrachloride, and are decomposed by mineral acids.

Table 1. Optimum pH for the precipitation of rare earths with *N*-*m*-tolyl-*m*-nitrobenzohydroxamic acid

Metal	pH	Colour of precipitate
Ce^{3+}	6·0–6·8	Brownish white
La^{3+}	7·5–8·5	Canary
Pr^{3+}	8·6–9·2	Light green
Nd^{3+}	8·8–9·5	Light grey
Sm^{3+}	9·6–10·2	Light green
Gd^{3+}	10·3–10·5	Yellow

Separations can be achieved by selective precipitation at carefully controlled pH..The maximum error observed in determination of 1–30 mg amounts of the lanthanides tested (in the absence of other metal ions) was 0·03 mg. The maximum error for determination of 5–20 mg amounts of these lanthanides in presence of 60 mg each of silver, titanium and zirconium, 80 mg each of copper(II), zinc, cadmium, palladium(II), antimony(III), bismuth, gallium, arsenic(III) and aluminium, and 100 mg each of manganese(II), metal, mercury(II), vanadium(V), molybdenum(VI), uranium(VI), tin(IV), and other lanthanides, with selective precipitation and masking as outlined above, was 0·04 mg and the general error was 0·01 mg.

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Summary—*N*-*m*-Tolyl-*m*-nitrobenzohydroxamic acid is used as a reagent for separation and gravimetric determination of Ce^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Gd^{3+}. By proper control of pH and use of masking agents these metal ions can be separated from several others and determined gravimetrically. The complexes can be weighed as $(C_{14}H_{11}N_2O_4)_3M$ after drying.

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PROPERTIES OF 4-AMINO-4′-METHYLDIPHENYLAMINE AS A REDOX INDICATOR*

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The properties and structure of 4-amino-4′-methyldiphenylamine suggest its application as a redox indicator. Some preliminary studies of this compound were carried out by Erdey *et al.*,[1] but fuller characterization is desirable.[2] In this study appropriate constants have been measured and the usefulness of the indicator verified experimentally.

EXPERIMENTAL

Reagents

4-Amino-4′-methyldiphenylamine has been synthesized[3] and transformed into its hydrochloride with excess of hydrochloric acid. The compound was purified similarly to Variamine Blue.[4] Its aqueous solution, $5 \times 10^{-3}M$, was kept under nitrogen to prevent oxidation.

The chemicals used were of analytical grade.

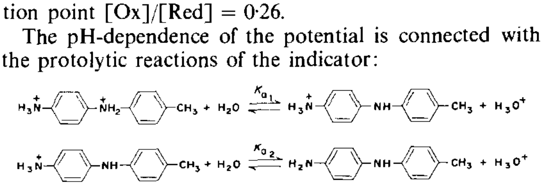
The standard solutions used in this work were prepared by the usual procedures.

RESULTS AND DISCUSSION

When applied in redox titrations in the pH range 1·5–5·5, the indicator exhibits a reversible colour change. In the course of potentiometric redox titrations of the indicator the hysteresis of the titration curve is insignificant, confirming its reversibility (Fig. 1). On the basis of such titrations the formal potentials of the indicator were determined at the half-oxidation point ($f = 0{\cdot}5$) for the pH range 1·5–5·0. The value of this potential may be described by the equation $E = 0{\cdot}735 - 0{\cdot}059\,\mathrm{pH}$. On this basis and from the stoichiometry of the reaction it follows that the oxidation is a two-electron process in which two protons are set free.

The transition potential, determined by titration of iron(II) with standard vanadate solution, is 0·54 V at pH 2·6–2·8. The indicator concentration was $8 \times 10^{-5}M$. This transition potential is about 0·035 V lower than the formal potential, determined above. This means that at the transition point [Ox]/[Red] = 0·26.

The pH-dependence of the potential is connected with the protolytic reactions of the indicator:



The absorbance of the indicator solution depends on pH, thus allowing determination of the dissociation constants. The most significant absorbance change is at $\lambda = 280$ nm (Fig. 2) in the acidity range from $H_0 = -1{\cdot}0$ to pH 6·0 and the constants determined have the values $\mathrm{p}K_{a_1} = -0{\cdot}08 \pm 0{\cdot}04$ and $\mathrm{p}K_{a_2} = 5{\cdot}15 \pm 0{\cdot}09$. The latter value is uncertain because in the pH region 4·5–6·0 the absorbance change is small. However, the potentiometric method[5] has confirmed the result, giving the value $\mathrm{p}K_{a_2} = 5{\cdot}09 \pm 0{\cdot}02$.

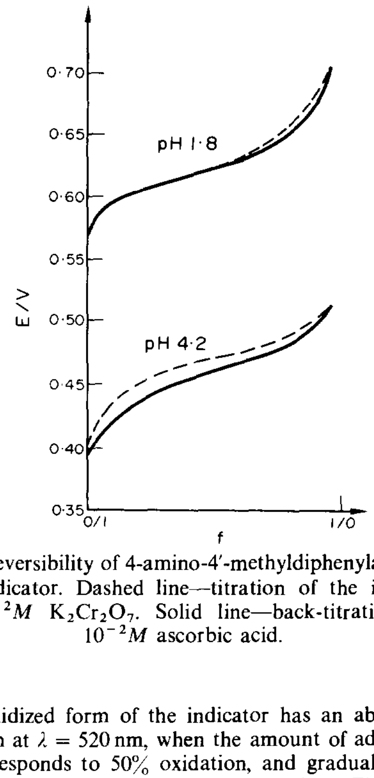
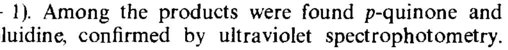


Fig. 1. Reversibility of 4-amino-4′-methyldiphenylamine as redox indicator. Dashed line—titration of the indicator with $10^{-2}M$ $K_2Cr_2O_7$. Solid line—back-titration with $10^{-2}M$ ascorbic acid.

The oxidized form of the indicator has an absorption maximum at $\lambda = 520$ nm, when the amount of added oxidant corresponds to 50% oxidation, and gradually shifts to 510 nm for larger amounts of the oxidant. The molar absorptivity is about 6×10^3 l.mole^{-1}.cm^{-1}, changing less then 10% in the pH range from 1·95 to 5·20. When the pH is greater that 5·5 the oxidized indicator turns from red-violet to yellow, as a result of deprotonation of the oxidized form. This limits the applicability of the indicator to use in the pH range below 5·5.

The oxidized form is not very stable in solution and decomposes at a rate depending on the acidity. The half-life ($\tau_{1/2}$), *i.e.*, the period necessary for decrease of the absorbance to half its initial value, for $10^{-4}M$ indicator solution is 15 min at pH 1·95, 21 min at pH 2·38, 40 min at pH 3·12, 90 min at pH 4·20 and 130 min at pH 5·10.

Thus, it can be concluded that the oxidation of the indicator proceeds according to the equation:



The change of the absorption spectrum in the absence of excess of oxidant probably indicates that in the one-electron process a radical may be formed.

The decomposition products of the oxidized form have been identified by using TLC on Silicagel $HF_{256-366}$, the developing medium being chloroform + diethyl ether (9 + 1). Among the products were found *p*-quinone and *p*-toluidine, confirmed by ultraviolet spectrophotometry. Thus the decomposition of the oxidized indicator should

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* Presented at the IVth Polish Conference on Analytical Chemistry in Warsaw, 26–31 August 1974.

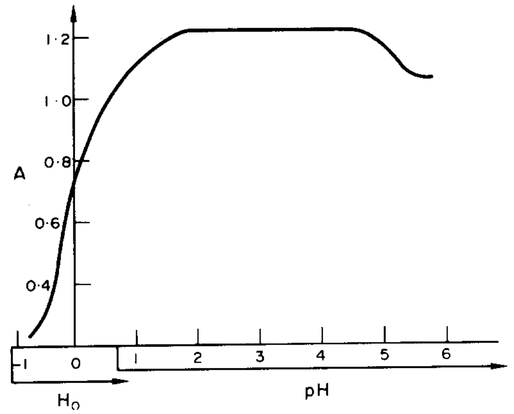
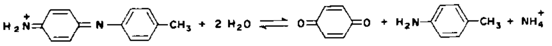


Fig. 2. Absorbance dependence on acidity of the solution for 4-amino-4′-methyldiphenylamine. $\lambda = 280$ nm. Acidity function H_0 determined in H_2SO_4 solutions.[6]

follow the reaction:



The p-toluidine formed may be further oxidized by a strong oxidant, *e.g.*, bromine.

The use of the indicator in titrations

The practical application of the indicator in titration has been confirmed in a standard system with suitable potential, *i.e.*, the titration of Fe(II) with vanadate in the presence of phosphoric acid. For this purpose to 10 ml of 0·1*M* Fe(II) solution, 14 g of sodium acetate and 15 ml of phosphoric acid were added and the sample was diluted to about 100 ml; 1·5 ml of 0·005*M* indicator were added, and the titration was carried out until a red-violet colour persisted. The results obtained, compared with those of potentiometric titrations, indicate that the error is not greater than 0·2%.

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Summary—The properties of 4-amino-4′-methyldiphenylamine as a redox indicator have been studied. The compound acts as a reversible, one-colour indicator, the oxidized form being red-violet, with molar absorptivity 6×10^3 l.mole^{-1}.cm^{-1} at $\lambda_{max} = 510$ nm. The formal potential is described by the equation $E = 0{\cdot}735 - 0{\cdot}059$ pH. The two dissociation constants are p$K_1 = -0{\cdot}08 \pm 0{\cdot}09$ and p$K_2 = 5{\cdot}09 \pm 0{\cdot}02$. The relative error of titration of iron(II) with vanadium(V) is not larger than 0·2%.

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DETERMINATION OF VICINAL HYDROXYL GROUPS IN POLY(VINYL ALCOHOL) (PVA)*

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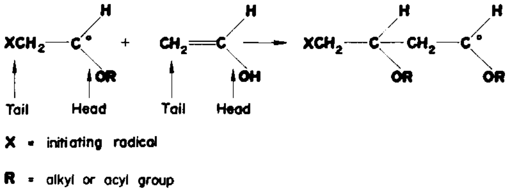
The proportion of vicinal hydroxyl groups in PVA polymers and copolymers is one of the characteristics of molecular structure which can contribute to the physical properties of the material in bulk. In this paper we review an application of the Fleury–Lange periodate–arsenite method[1] for the determination of 1,2-diol groups in PVA.[2]

The normal 1,3-polyol structure of PVA arises from "head-to-tail" free-radical-initiated polymerization of vinyl ester or vinyl ether monomer:



However, the occurrence of the energetically unfavoured head-to-head mode of polymerization produces a polymer

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* Based on part of the report by Miss Y. L. Lan Chun Fung presented in part fulfilment of the requirements for the M.Sc. degree of the University of London in analytical chemistry, 1974.

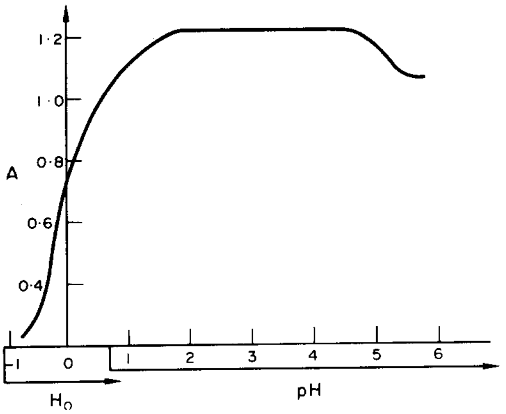
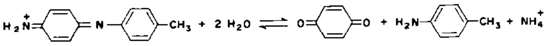


Fig. 2. Absorbance dependence on acidity of the solution for 4-amino-4'-methyldiphenylamine. $\lambda = 280$ nm. Acidity function H_0 determined in H_2SO_4 solutions.[6]

follow the reaction:



The *p*-toluidine formed may be further oxidized by a strong oxidant, *e.g.*, bromine.

The use of the indicator in titrations

The practical application of the indicator in titration has been confirmed in a standard system with suitable potential, *i.e.*, the titration of Fe(II) with vanadate in the presence of phosphoric acid. For this purpose to 10 ml of 0·1*M* Fe(II) solution, 14 g of sodium acetate and 15 ml of phosphoric acid were added and the sample was diluted to about 100 ml; 1·5 ml of 0·005*M* indicator were added, and the titration was carried out until a red-violet colour persisted. The results obtained, compared with those of potentiometric titrations, indicate that the error is not greater than 0·2%.

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Summary—The properties of 4-amino-4'-methyldiphenylamine as a redox indicator have been studied. The compound acts as a reversible, one-colour indicator, the oxidized form being red-violet, with molar absorptivity 6×10^3 l.mole^{-1}.cm^{-1} at $\lambda_{max} = 510$ nm. The formal potential is described by the equation $E = 0{\cdot}735 - 0{\cdot}059$ pH. The two dissociation constants are p$K_1 = -0{\cdot}08 \pm 0{\cdot}09$ and p$K_2 = 5{\cdot}09 \pm 0{\cdot}02$. The relative error of titration of iron(II) with vanadium(V) is not larger than 0·2%.

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DETERMINATION OF VICINAL HYDROXYL GROUPS IN POLY(VINYL ALCOHOL) (PVA)*

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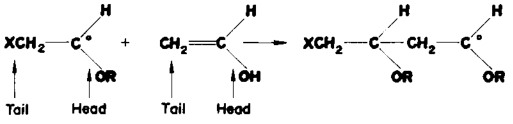
The proportion of vicinal hydroxyl groups in PVA polymers and copolymers is one of the characteristics of molecular structure which can contribute to the physical properties of the material in bulk. In this paper we review an application of the Fleury–Lange periodate–arsenite method[1] for the determination of 1,2-diol groups in PVA.[2]

The normal 1,3-polyol structure of PVA arises from "head-to-tail" free-radical-initiated polymerization of vinyl ester or vinyl ether monomer:



X = initiating radical

R = alkyl or acyl group

However, the occurrence of the energetically unfavoured head-to-head mode of polymerization produces a polymer

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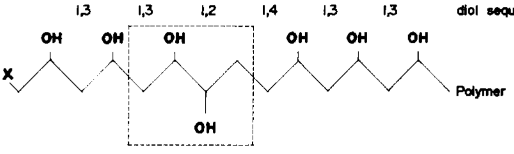
[*] Based on part of the report by Miss Y. L. Lan Chun Fung presented in part fulfilment of the requirements for the M.Sc. degree of the University of London in analytical chemistry, 1974.

with the occasional 1,2 and 1,4 sequences:[3]



I

The fraction of 1,2-diol units can be measured by two methods based on specific cleavage of the 1,2-diol by periodate. In the first, due to Flory and Leutner, the number of 1,2-diol two-carbon units is measured with respect to the total number of two-carbon units condensed in the polymer.[4] The increase in the number of molecules on cleavage is equal to the number of 1,2-diol units and is given by $(w/M_f) - (w/M_i)$ where M_i and M_f refer to the initial and final gram molecular weights and w is the weight of polymer. The total number of vinyl alcohol units condensed is $w/44{\cdot}05$ (atomic weight scale $0 = 16{\cdot}00$), so the fraction of 1,2-diol two-carbon units is $44{\cdot}05\ (1/M_f - 1/M_i)$. The fraction thus determined is about 0·013 for common PVA.[3]

In the titrimetric method, the weight of 1,2-diol units present in the polymer is referred to standard iodine solution through the following reactions:

$$IO_4^- + HAsO_3^{2-} \xrightarrow[\text{(Catalyst)}]{I^-} IO_3^- + HAsO_4^{2-}$$

$$HAsO_3^{2-} + I_2 + H_2O \longrightarrow HAsO_4^{2-} + 2HI$$

R and R′ are organic radicals or H in the case of a standard substance, or macromolecular chains in the case of polymer. The excess of periodate, or all of it in the absence of 1,2-diol, reacts with an excess of arsenious oxide, and the excess of this is titrated with standard iodine solution. The volumes (in litres) of xM I_2 solution consumed in the absence and presence of 1,2-diol can be termed V_0 and V, respectively. When the procedure refers to a pure, low-molecular-weight standard compound, *e.g.*, R = H, R′ = $C_6H_5CH_2$, the weight of standard present (in grams) is $(V - V_0)xW$, where W is the gram molecular weight of the standard, *e.g.*, 138·17. The purity of the standard is then $100\ (V - V_0)xW/$(weight of standard taken). In the case of the polymer, the number of moles of 1,2-diol segments present is $(V - V_0)x$, and the weight of 1,2-diol functional groups would be $(V - V_0)x \times 60{\cdot}05$, because the formula weight of CHOHCHOH is 60·05. However, in order to be consistent with the Flory and Leutner method, the weight must be referred to one-half of the formula weight of the four-carbon segment outlined in I. Thus, the weight of vinyl alcohol segments polymerized head-to-head to generate 1,2-diol groups is $(V - V_0)x \times 44{\cdot}05$, and the fraction of such two-carbon segments present is $100\ (V - V_0)x \times 44.05/$(weight of polymer taken)*.

EXPERIMENTAL

Materials

The PVA was a sample of Gelvatol 1–30, weight-average molecular weight $1{\cdot}40 \times 10^4$, degree of hydrolysis 98·5–100%. It was dissolved in water at 70–80°.

Styrene glycol (1,2-dihydroxy-2-phenylethane) was prepared by the hydration of styrene oxide (Merck). A solution of the oxide (10 g) in iso-octane (200 ml) was stirred vigorously with water (100 ml), at pH *ca.* 5, for 2 hr at *ca.* 50°. The crude product (9 g, m.p. 65–66°) was obtained by crystallization from water. Double sublimation gave an analytical sample of styrene glycol, m.p. 66–67° (m.p. 67–68° when recrystallized from ligroin[5]).

Table 1. Standardization check on periodate cleavage method with styrene glycol, and determination of fraction of 1,2-diol units in PVA

Substance	Weight, *g*	*V*, *ml*	1,2-Diol, %
Styrene glycol	0·0911	24·18*	100·0
Styrene glycol	0·0944	24·62*	99·7
Polyvinyl alcohol	2·4328	24·92†	1·28
Polyvinyl alcohol	2·4354	24·81†	1·27

* Iodine concentration $0{\cdot}04964M$; $V_0 = 10{\cdot}90$ ml.
† Iodine concentration $0{\cdot}05014M$; $V_0 = 10{\cdot}78$ ml.

Analytical-reagent grade arsenious oxide (primary standard, 2·4746 g) was dissolved in 40 ml of 10% w/v aqueous sodium hydroxide solution; the solution was neutralized and made up to give 500·0 ml of $0{\cdot}05005M$ arsenious acid solution. Starch (1 g) was boiled with water (100 ml) for 1 min, and 3 g of potassium iodide were added to the cooled solution to complete the indicator. Resublimed iodine (*ca.* 6 g) was dissolved in 20 ml of 50% w/v potassium iodide solution and made up to give 500 ml of approximately $0{\cdot}05M$ I_2 solution. This was standardized by using it to titrate, to a faint permanent blue colour, aliquots of the arsenious oxide solution (25·00 ml) plus water (15 ml), sodium bicarbonate (2 g) and starch solution (2 ml). A $0{\cdot}071M$ sodium periodate solution was made from the analytical-reagent grade reagent.

1,2-Diol cleavage reaction

A slight excess of the sodium periodate solution (10 ml) was added to the diol solution (*ca.* 2·5 g/350 ml) at room temperature, and the mixture was allowed to stand for 30 min to ensure completion of the cleavage reaction. Sodium bicarbonate (2 g) was added, followed by 25·00 ml of the standard arsenious oxide solution and 0·1 g of solid potassium iodide. The resulting solution was titrated with standard iodine solution (after addition of 2 ml of the starch indicator) to give the results (V) listed in Table 1.

RESULTS AND DISCUSSIONS

Table 1 gives typical results. The styrene glycol is close to 100% pure. It is crystalline and non-deliquescent at room temperature and serves to check our whole procedure. The cumulative (maximum) random errors in V_0 and V are 0·24% and 0·18%, respectively, which yields 0·46% for $(V - V_0)$, if the random error in each volume measurement is estimated as ±0·01 ml (a plausible minimum value for very careful work). There is an error of about ±0·1% in the weighing of the styrene glycol. The estimated maximum scatter in the results for the diol purity in this case could therefore be as large as ±0·6%. Some of the errors would usually cancel, but determinations should clearly be at least duplicated to guard against a freak result. When a much larger weight of PVA is substituted for the styrene glycol (Table 1) the estimated possible scatter is reduced to ±0·5% because the weighing error is no longer significant. Harris and Pritchard reported root-mean-square deviations in the range 2–4% for specimens of PVA from various sources.[2] However, in their work $(V - V_0)$ was less than 2 ml, which introduces a maximum scatter of ±5% on the basis of our estimate above. We therefore suggest the use of a value of $(V - V_0)$ in the range 15–20 ml to keep the error in this quantity to less than ±0·5%. We note that heterogeneity of the 1,2-diol content and gel-forming properties of the PVA could lead to a greater scatter of results.

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* We note that the expression given by Harris and Pritchard[2] is in error by a statistical factor of 2, and by an additional factor of 1000 due to the expression of volume in ml.

The periodate method is reported to give results ranging in accuracy from 99 to 101% for the determination of several 1,2-glycols related to glycerol,[6] and we have found the procedure above useful for the estimation of glycerol α-monochlorohydrin (1-chloro-2,3-dihydroxypropane) in the commercial "monochlorohydrin", which also contains the β-isomer, 2-chloro-1,3-dihydroxypropane. More generally, the method should be used with caution: we have shown, for example, that dimethyl tartrate cannot be estimated, owing to slow non-stoichiometric oxidation by the periodate. Weiss gives a list of substances which do not contain the 1,2-diol group but react with periodate and can interfere if present.[6] The periodate–arsenate method has been applied with 95–98% accuracy to the determination of sugars[7] and is the generally preferred method in this field.[8]

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NEW REDOX TITRANTS IN NON-AQUEOUS OR PARTIALLY AQUEOUS MEDIA—VI*

POTENTIOMETRIC DETERMINATIONS USING DIBROMAMINE-T AND SOME FURTHER APPLICATIONS OF DICHLORAMINE-T

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Despite a recent renewal of interest in non-aqueous redox titrimetry, the number of good oxidants available in this field continues to be very limited. As part of our programme for the development of new redox titrants in non-aqueous media,[1–5] we are introducing *N,N'*-dibromo-*p*-toluenesulphonamide ("Dibromamine-T", hereafter abbreviated as DBT) as an ideal oxidimetric titrant in acetic acid medium. This compound is closely related to Dichloramine-T, developed as an oxidimetric titrant by us earlier[1–3] and can be considered complementary to it in some ways. The results of the individual determinations of typical, yet diverse, reductants such as antimony(III), arsenic (III), thallium(I), ferrocyanide, iodide, ascorbic acid, hydroquinone, iron(II), hydrazine, aniline, phenol and oxine with this new redox titrant are presented in this communication.

In view of our observation that oxine may be readily determined by *direct* potentiometric titration with both DBT and DCT in partially non-aqueous media containing excess of bromide, it was considered worthwhile to examine whether metal oxinates could be similarly determined. The results of such a study proved to be most promising. Procedures for the *direct* potentiometric titrations, with DBT as well as DCT, of oxinates of six typical 3*d*-transition metals, [Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)] are also described in this communication. These direct titration procedures are faster than the usual back-titration and have the further advantage that errors due to loss of bromine are eliminated.

EXPERIMENTAL

Apparatus

The apparatus and electrode assemblies described earlier[2] were used.

Reagents

Dibromamine-T. Prepared by the bromination of chloramine-T. Recrystallized chloramine-T (10 g) was dissolved in water (200 ml) and liquid bromine (2 ml) was added dropwise from a burette with constant stirring of the solution. The golden yellow precipitate of DBT was thoroughly washed with water, filtered under suction and dried in a vacuum desiccator for 24 hr. The dry sample was found to melt at 92–93° with decomposition. The purity of the sample was checked by elemental analysis for N, S and

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POTENTIOMETRIC DETERMINATIONS USING DIBROMAMINE-T AND SOME FURTHER APPLICATIONS OF DICHLORAMINE-T

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Despite a recent renewal of interest in non-aqueous redox titrimetry, the number of good oxidants available in this field continues to be very limited. As part of our programme for the development of new redox titrants in non-aqueous media,[1–5] we are introducing *N,N'*-dibromo-*p*-toluenesulphonamide ("Dibromamine-T", hereafter abbreviated as DBT) as an ideal oxidimetric titrant in acetic acid medium. This compound is closely related to Dichloramine-T, developed as an oxidimetric titrant by us earlier[1–3] and can be considered complementary to it in some ways. The results of the individual determinations of typical, yet diverse, reductants such as antimony(III), arsenic (III), thallium(I), ferrocyanide, iodide, ascorbic acid, hydroquinone, iron(II), hydrazine, aniline, phenol and oxine with this new redox titrant are presented in this communication.

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Br (found: N, = 4·3%, S = 9·6%, Br = 48·5%; required: N = 4·26%, S = 9·73%, Br = 48·56%).

Dichloramine-T. Prepared as described earlier.[2]

Preparation and standardization of stock solutions

The solubility of DBT in acetic acid was determined and was found to be 38 g/l. at 30°. Approximately 0·05*M* (~ 0·2 *N*) solutions of DBT were prepared by dissolving 8·2 g of the sample in 500 ml of water-free acetic acid and were kept in amber-coloured bottles fitted with automatic microburettes and guard-tubes for the exclusion of moisture. These solutions were standardized by adding aqueous potassium iodide solution to aliquots and titrating the liberated iodine with thiosulphate as usual.[2] The stock solutions were found to be reasonably stable. The normality of a typical stock solution (kept as described above) over a period of 15 days is given below.

No. of days	0	1	2	3	5	9	15
Normality	0·2388	0·2388	0·2379	0·2362	0·2345	0·2328	0·2305

Stock solutions of DCT were prepared, stored and standardized as described earlier.[2]

Reductant solutions. Solutions of antimony(III), iodide, ferrocyanide, hydrazine, ascorbic acid, hydroquinone, aniline and phenol were prepared in distilled water. Arsenic(III) solutions were prepared by dissolving weighed quantities of As_2O_3 in 1*M* sodium hydroxide, neutralizing with 1*N* sulphuric acid and making up to a definite volume with distilled water. Solutions of iron(II) were prepared in 2*N* sulphuric acid. Solutions of thallium(I) and oxine were prepared in 50% aqueous acetic acid. The strengths of these solutions were all checked by standard methods.[7]

The oxinates of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by standard procedures.[6] Standard solutions of these oxinates were prepared in 4*N* sulphuric acid and the strengths were checked by the bromate–bromide method.[6] All the reagents used were of analytical reagent quality.

Procedures for titrations

The potentiometric titrations were carried out as described earlier.[5] All the titrations were done at room temperature (28 ± 2°).

Normal, first derivative and second derivative curves were drawn. The equivalence points were obtained both graphically and numerically (employing the Hostetter–Roberts equation[8] or the Yan equation[9]).

RESULTS AND DISCUSSION

A statistical evaluation of results (standard deviations and coefficients of variance) is given in Tables 1 and 2.

Table 1. Potentiometric titrations of some common reductants with Dibromamine-T (6 replicates).

Reductant	Reductant taken, *mmole*	Standard deviation *μmole*	Coefficient of variance, %
Antimony(III)	0·3084	0·10	0·03
Arsenic(III) (As_2O_3)	0·2517	0·55	0·22
Thallium(I)	0·3445	0·18	0·05
Ferrocyanide	0·5442	0·99	0·18
Iodide	0·5331	0·88	0·17
Ascorbic acid	0·7379	1·62	0·22
Hydroquinone	0·5499	1·23	0·22
Iron(II)	0·5037	2·07	0·41
Hydrazine	0·1596	0·10	0·06
Aniline	0·2217	0·15	0·07
Phenol	0·1489	0·12	0·08
Oxine	0·2275	0·06	0·03

Table 2. Potentiometric titrations of metal oxinates with Dibromamine-T and Dichloramine-T (6 replicates)

Reductant	Reductant taken, *mmole*	Standard deviation, *μmole*	Coefficient of variance, %
	Dibromamine-T		
$Mn(C_9H_6ON)_2\ 2H_2O$	0·0875	0·37	0·42
$Fe(C_9H_6ON)_3$	0·0950	0·50	0·52
$Co(C_9H_6ON)_2\ 2H_2O$	0·1127	0·13	0·12
$Ni(C_9H_6ON)_2\ 2H_2O$	0·1120	0·24	0·21
$Cu(C_9H_6ON)_2\ 2H_2O$	0·1244	0·10	0·08
$Zn(C_9H_6ON)_2\ 2H_2O$	0·0966	0·62	0·64
	Dichloramine-T		
$Mn(C_9H_6ON)_2\ 2H_2O$	0·1602	0·04	0·04
$Fe(C_9H_6ON)_3$	0·1095	0·08	0·07
$Co(C_9H_6ON)_2\ 2H_2O$	0·1277	0·06	0·05
$Ni(C_9H_6ON)_2\ 2H_2O$	0·1345	0·15	0·12
$Cu(C_9H_6ON)_2\ 2H_2O$	0·1148	0·01	0·10
$Zn(C_9H_6ON)_2\ 2H_2O$	0·1287	0·13	0·10

In the case of antimony(III), arsenic(III), thallium(I), ferrocyanide, iodide, ascorbic acid and hydroquinone, simple direct titration against DBT was successful; there was no need to add potassium bromide or hydrochloric acid. [It may be noted that Tl(I) and ferrocyanide could be successfully titrated with DCT only in presence of added bromide.] For iron(II), addition of phosphoric acid was necessary to get a clear-cut potential break, by complexing the Fe^{3+} formed. Addition of hydrochloric acid was found to be necessary in the case of hydrazine; otherwise somewhat premature end-points were obtained. Addition of bromide (KBr) was essential in the case of aniline, phenol, oxine and the metal oxinates. The approximate potential jumps (in mV) at the equivalence points for the addition of 0·1 ml of 0·05*M* DBT were as follows: for antimony(III), 200; arsenic(III), 300; thallium(I), 200; ferrocyanide, 500; iodide, 100; ascorbic acid, 400; hydroquinone, 300; iron(II), 400; hydrazine, 250; aniline, 100; phenol, 150; oxine, 350. The potential breaks for the metal oxinates were ~ 300 mV for the addition of 0·1 ml of 0·05*M* solution of either DBT or DCT. In DBT titrations, the time required to attain the steady potentials near the end-point was in general small (< 1 min); in this respect, DBT has a clear advantage over DCT in many cases.

The oxidation half-reactions undergone by the different reductants are the same as those in the case of oxidation by iodobenzene diacetate.[5] In the case of aniline, phenol, oxine and the metal oxinates the actual oxidant is bromine produced *in situ* by the reaction of bromide with the oxidant. In all these cases, DBT is reduced to *p*-toluenesulphonamide in accordance with the half-reaction

$$RNBr_2 + 2H^+ + 4e^- \rightarrow RNH_2 + 2Br^-$$

(where R = $CH_3–C_6H_4–SO_2$).

The formal potential of the DBT–sulphonamide couple was determined at 25 ± 0·02° and found to be +1·28 V (mean of 9 experiments).

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Summary—A new redox titrant, Dibromamine-T (*N,N'*-dibromo-*p*-toluenesulphonamide) is introduced for use in acetic acid media. Potentiometric titrations of Sb(III), As(III), Tl(I), Fe(II), ferrocyanide, iodide, ascorbic acid, hydroquinone, hydrazine, aniline, phenol and oxine are described. Direct potentiometric titrations of oxinates of Mn, Fe, Co, Ni, Cu and Zn with Dibromamine-T as well as with Dichloramine-T are also described.

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INDICATORS IN NON-AQUEOUS CERIMETRIC TITRATIONS OF THIOUREAS AND XANTHATES

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Non-aqueous solvents are important for redox determinations, especially of those compounds which are slightly soluble in water or react with it through hydrolysis or oxidation. However there is a lack of redox reagents of suitable stability for use in non-aqueous media. Acetonitrile, because of its high dielectric constant and resistance to oxidation or reduction has proved quite promising as a solvent[1] especially with stronger oxidants such as ammonium hexanitratocerate(IV). Rao and Murthy have used this oxidant in acetonitrile for the determination of hydroquinone,[2] potassium ethyl xanthate,[3] iron(II),[4] oxalic acid,[5] ascorbic acid[6] and potassium iodide.[7] Verma and Kumar[8] have recently described its use in the determination of thiourea and its derivatives.

The only attempt to use visual indicators in titrations with Ce(IV) in a non-aqueous medium appears to be due to Rao and Murthy[2] who used diphenylamine, ferroin, Methyl Red and Janus Green as indicators in titrations of hydroquinone. The present communication reports the use of some chemical indicators in titrations of thioureas and xanthates with ammonium hexanitratocerate in acetonitrile.

EXPERIMENTAL

Reagents

Acetonitrile. Distilled twice from phosphorus pentoxide (5 g/l.).

Ammonium hexanitratocerate, 0·05N *in acetonitrile.* Prepared by dissolving a little more than the calculated amount of dried analytical-grade oxidant in acetonitrile, and standardized by titration with ferrous ammonium sulphate in the presence of dilute sulphuric acid, with ferroin as indicator. The solution was stored in coloured glass-stoppered bottles and kept in a dry chamber.

Xanthates. Prepared by mixing equimolar quantities of the corresponding alcohols, potassium hydroxide (dissolved in minimum quantity of water) and carbon disulphide, at temperatures below 10°. The compounds were crystallized twice by dissolving in acetone and precipitating with petroleum ether (60–80°). The purity was checked by known methods.

Thiourea. Recrystallized from alcohol. The alkyl derivatives of thiourea were prepared from the corresponding isothiocyanates[9] by condensation with ammonia.

Indicator solutions. Fuchsin, Gentian Violet, Light Green, Methyl Red and quinalizarin indicators were prepared as 0·1% solutions in acetonitrile. Ferroin solution (0·025 *M*) was prepared by dissolving 1·485 g of *o*-phenanthroline and 0·695 g of analytical grade ferrous sulphate heptahydrate in 100 ml of acetonitrile. Diphenylamine was used as a 0·25% solution in acetonitrile.

Procedure

Aliquots of solutions of thiourea or potassium ethyl xanthate in acetonitrile were taken in dry conical flasks, and made up to 20 ml with acetonitrile; indicator solution (2 or 3 drops) was added. Each solution was cooled to room temperature (25°) and titrated with 0·05*M* ammonium hexanitratocerate from a microburette provided with guard-tube for the protection of oxidant solution from atmospheric moisture. During the titration, white cerous nitrate was precipitated. The titrations were repeated with substituted thioureas and xanthates. The results of titrations of thiourea and potassium ethyl xanthate, as representatives of substituted thioureas and xanthates with use of various indicators, are given in Table 1. The colour changes observed during the end-points are also given.

RESULTS AND DISCUSSION

Acetic acid and acetonitrile have been most used as media for non-aqueous redox titrations and electro-

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[*] To whom correspondence should be addressed.

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Summary—A new redox titrant, Dibromamine-T (*N*,*N*′-dibromo-*p*-toluenesulphonamide) is introduced for use in acetic acid media. Potentiometric titrations of Sb(III), As(III), Tl(I), Fe(II), ferrocyanide, iodide, ascorbic acid, hydroquinone, hydrazine, aniline, phenol and oxine are described. Direct potentiometric titrations of oxinates of Mn, Fe, Co, Ni, Cu and Zn with Dibromamine-T as well as with Dichloramine-T are also described.

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INDICATORS IN NON-AQUEOUS CERIMETRIC TITRATIONS OF THIOUREAS AND XANTHATES

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(*Received* 12 *June* 1975. *Accepted* 28 *August* 1975)

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	pot. ethyl xanthate	violet → blue → green	1·3
Light Green‡	thiourea	light green → yellow	1·0
	pot. ethyl xanthate	light green → yellow	0·9
Quinalizarin	thiourea	not sharp	—
	pot. ethyl xanthate	orange red → violet → orange red → yellow	1·0
Ferroin	thiourea	red → yellow	0·9
	pot. ethyl xanthate	not sharp	—
Methyl Red	thiourea	rose red → yellow	1·3
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Diphenylamine	thiourea	not sharp	—
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* Amount of thiourea or potassium ethyl xanthate taken for each titration, 40 mg.
† Ten determinations.
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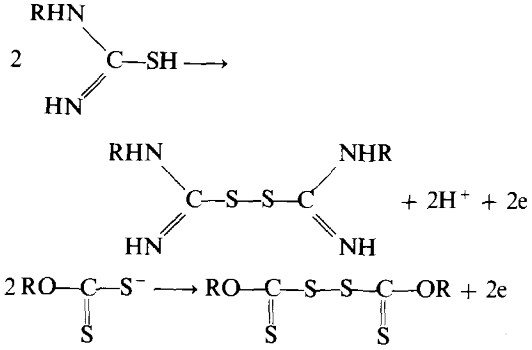
chemical methods (mostly potentiometric) have been used to detect the end-point. Only limited efforts have been made to use visual indicators in non-aqueous redox titrations. This appears to be because the scale of potentials of different redox systems in various solvents, similar to those known in water, has not been developed. Verma and Bose[10] have described the use of quinalizarin as an indicator in the redox determination of phenyl thioureas with lead tetra-acetate in glacial acetic acid. Recently Braun and Stock[11] have employed some indicators in redox titrations in dimethylformamide medium.

The results of titrations of substituted thioureas and xanthates, performed similarly, agree closely with those listed in the table. The results indicate that thioureas and xanthates react with Ce(IV) in a 1 : 1 molar ratio. This corresponds to the oxidation of thioureas and xanthates to the corresponding disulphides and dixanthogens respectively.



The solutions of these indicators may also be prepared in acetic acid or acetic acid–acetonitrile mixtures, but these solutions are not recommended for use in the titrations of xanthates because of the risk of their decomposition with acetic acid.

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Summary—The use of some chemical indicators in the non-aqueous cerimetric determination of thioureas and xanthates in acetonitrile medium is described.

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DETERMINATION OF PEROXYDIPHOSPHATE IN ACID MEDIUM WITH OXALATE (*i*) WITH SILVER(I) AS CATALYST AND (*ii*) IN THE PRESENCE OF EXCESS OF MANGANESE(II)

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Department of Chemistry, University of Rajasthan, Jaipur, India

(*Received* 11 *June* 1975. *Accepted* 19 *June* 1975)

A study in this laboratory of the kinetics and mechanism of oxidations with peroxydiphosphate necessitated the development of titrimetric methods for determination of peroxydiphosphate suitable to a particular kinetics study. So far only two titrimetric methods for its determination have been reported, indirect cerimetric[1] and direct iodometric.[2] The interest in the present work arose on account of a well-known method for determination[3]

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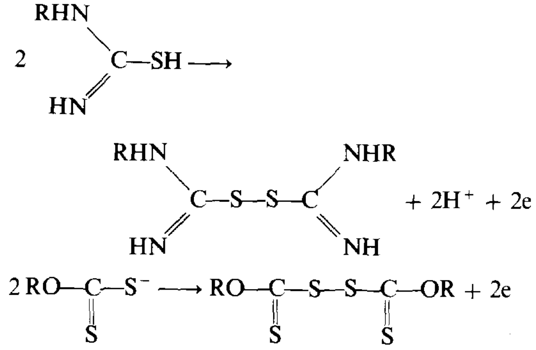

$$2\,\mathrm{RO{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}S^-} \longrightarrow \mathrm{RO{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}S{-}S{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}OR} + 2e$$

The solutions of these indicators may also be prepared in acetic acid or acetic acid–acetonitrile mixtures, but these solutions are not recommended for use in the titrations of xanthates because of the risk of their decomposition with acetic acid.

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EXPERIMENTAL

Reagents

The potassium peroxydiphosphate was a gift sample from FMC corporation, New York, U.S.A. The solution of peroxydiphosphate was prepared by direct weighing and standardized[1] cerimetrically, with *N*-phenylanthranilic acid as indicator. A standard solution of oxalic acid was prepared by direct weighing. All solutions were made in doubly distilled water, permanganate being added before the second distillation.

Procedures

Silver(I) as catalyst. The sample of peroxydiphosphate, a known excess of oxalic acid solution, enough sulphuric acid to give a 2·5*N* solution, and silver nitrate to yield at least a $4 \times 10^{-3}M$ solution, were mixed and heated just to boiling. The unreacted oxalic acid was determined with standard permanganate solution

With excess of manganese(II). The sample of peroxydiphosphate, enough sulphuric or perchloric acid to yield a 0·25–1·0*N* solution and at least a 500% excess of manganese sulphate were mixed and boiled for about 2 min. The manganese dioxide produced was titrated with a standard solution of oxalic acid to a colourless end-point.

RESULTS AND DISCUSSION

Titration of 7–350 mg of peroxydiphosphate by the silver(I) method and of 3–70 mg by the manganese(II) method gave results within ± 0·3% of the cerimetric assay with only one exception (+ 0·9%). The methods are quick but have the drawback that heating is required.

The catalysis of peroxydiphosphate oxidations was recently found[4] in this laboratory during one of the kinetics studies. However, the reaction still does not become instantaneous at room temperature and heating is necessary to complete the reaction. The overall stoichiometry is given by equation (1)

$$H_4P_2O_8 + H_2C_2O_4 \rightarrow 2H_3PO_4 + 2CO_2 \qquad (1)$$

The catalysis by silver(I) probably operates through an Ag(I)/Ag(II) or Ag(I)/Ag(III) cycle as found in the silver(I)-catalysed oxidations by peroxydisulphate[5] and given below.

$$P_2O_8^{4-} + Ag^+ \rightarrow 2PO_4^{3-} + Ag^{3+} \qquad (2)$$

$$Ag^{3+} + C_2O_4^{2-} \rightarrow Ag^+ + 2CO_2 \qquad (3)$$

There is no definite view yet whether Ag(II) or Ag(III) is formed. There is still another view that probably both the higher oxidation states of silver exist in the system in equilibrium.[6]

The determination in the presence of manganese(II) depends on the fact that this is oxidized to MnO_2 or permanganate depending on the concentration of Mn(II) and the acidity of the medium. The Mn(II) is oxidized to Mn^{3+} which in the absence of complexing agents[8–10] and at low acidity disproportionates,[11] yielding MnO_2 and Mn(II).

$$P_2O_8^{4-} + 2\,Mn^{2+} \rightarrow 2PO_4^{3-} + 2Mn^{3+} \qquad (4)$$

$$2\,Mn^{3+} \rightleftharpoons Mn^{4+} + Mn^{2+};\ 2\,Mn^{3+} + 2H_2O = MnO_2 + Mn^{2+} + 4H^+ \qquad (5)$$

A large concentration of Mn(II) is employed to make the reaction of peroxydiphosphate and Mn(II) fast and to inhibit[10] the formation of MnO_2 as far as possible so that there is no difficulty in titration with oxalic acid. Reactions of oxalic acid with Mn^{3+} and MnO_2 are well known.[13,14]

Oxidation of Mn(II) to permanganate by peroxydiphosphate is also possible and thus a colorimetric determination can be made. However, for this the concentration of Mn(II) has to be sufficiently low (but larger than that of the peroxydiphosphate) and the acidity high, or otherwise permanganate will react[15,16] with Mn(II) yielding MnO_2 as in the present method.

Acknowledgements—We are thankful to FMC Corporation, New York, U.S.A., for the generous gift of a sample of potassium peroxydiphosphate. One of us (LMB) is thankful to C.S.I.R., India, for a research fellowship and a grant.

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Summary—Peroxydiphosphate can be determined with oxalate in acid medium in the presence of silver(I). Excess of oxalic acid along with the sample and silver(I) is heated to boiling and the excess of oxalic acid is titrated against standard permanganate. Another method involves boiling for 2 min a mixture consisting of the sample and excess of manganese(II), followed by titration of the resulting Mn(III) or MnO_2 with standard oxalic acid solution.

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SIMPLE SEMIQUANTITATIVE DETERMINATION OF TRACE METAL IONS BY USE OF REAGENT GEL COLUMNS—II

DETERMINATION OF ZINC WITH DITHIZONE GEL*

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(*Received* 3 *June* 1975. *Accepted* 20 *June* 1975)

By use of the principle previously described,[1] zinc(II) at the sub-ppm level in environmental water has been determined with an analytical column packed with dithizone gel beads. As zinc reacts with dithizone at pH 6–7, where many other heavy metal ions are similarly complexed, interfering cations have to be masked.

EXPERIMENTAL

Reagents

All reagents were of analytical grade. Dithizone was recrystallized from chloroform. Buffers, masking reagents and distilled water were treated beforehand with a 0·05% dithizone gel column[2] or shaken with 0·05% dithizone solution in chlorobenzene to remove traces of heavy metal ions. *N,N*-Bis(β-hydroxyethyl)dithiocarbamate[3] and β-dithiocarbaminopropionic acid[4] were prepared according to the literature.

Preparation of dithiozone gel beads

Styrene–divinylbenzene copolymer beads (2% divinylbenzene, particle size 70–100 mesh) were treated successively with 3% hydrochloric acid, distilled water and acetone, dried at 95–97°, then soaked in 0·01% dithizone solution in chlorobenzene for 15–17 hr at 5° in a dark place. The beads were separated by centrifugation, and immediately transferred into 0·1*M* acetate buffer solution (pH 5·6) containing sodium thiosulphate (0·1*M*) as a stabilizer. One gram of dry polymer accepted about 2·9 ml of chlorobenzene.

Preparation of analytical gel bead column

The column and packing procedure were essentially as before,[1] the downward packing being preferred, with the acetate buffer containing sodium thiosulphate as the suspension medium. The column was sealed, wrapped and stored as before.[1]

Procedure

A known amount of sample was placed in a 25-ml volumetric flask, to which acetate buffer solution (pH 6·2) and sodium thiosulphate solution were added to give a final 0·1*M* concentration of both. If interfering cations were present, appropriate masking agents were also added. Finally the whole was made up to volume.

A bead column was connected to a sample reservoir and the flow-rate was adjusted to 0·2 ml/min. As the sample solution flowed through the column, the green gel turned to pink from the upper end when zinc was complexed with dithizone. After passage of a measured volume of sample, the length of pink zone was measured and the amount of zinc was calculated from a (linear) calibration curve. A correction was necessary for the dilution of sample with reagent solutions.

RESULTS AND DISCUSSION

Gel beads and analytical column

Since the concentration of dithizone in the gel beads is directly related to the zone length of the zinc complex, stability of the dithizone is essential for an accurate result. However, dithizone decomposes so easily that gel beads of 0·01% or lower dithizone concentration could not be stored satisfactorily for more than 24 hr even in a dark cool place.

Dithizone gel beads stabilized by means of the zinc chelate, which were successfully used in mercury determination,[1] could not be used, because the regeneration of free dithizone by preliminary acid treatment always suffered interference from the trace of zinc which remained in the inner core of the gel beads. Thus, the green gel turned back to greenish pink when the pH was raised to 6·2.

Free dithizone gel beads were best stored in the 0·1*M* acetate buffer–0·1*M* sodium thiosulphate medium, the latter being added as a stabilizer for dithizone and also as a masking agent for interfering cations.[5] Columns filled with this medium could be stored in aluminium foil for 2·5 month at 5°.

The reaction of dithizone with heavy metal ions is so sensitive that even a slight touch of a metal surface such as a stainless-steel spatula to the green gel beads immediately causes the colour change to pink. Such coloured species tend to be localized in the gel beads, and the gel column gives a very sensitive colour spot-test for trace metal contamination. Incomplete pretreatment of polymer beads, porous plugs and other materials for the preparation of analytical columns with 3% hydrochloric acid often resulted in the appearance of pink spots on the gel column or on the interface between the gel and plugs.

Analytical procedure and colour reaction

The complexation of dithizone with zinc can be expressed as follows:

$$\underset{\text{green}}{2(\mathrm{H_2Dz})_o} + (\mathrm{Zn}^{2+})_w = \underset{\text{pink}}{(\mathrm{Zn(HDz)_2})_o} + 2(\mathrm{H}^+)_w$$

where o and w indicate the organic and aqueous phases respectively. The pH profile of the extraction of zinc dithizonate into chlorobenzene is shifted to slightly higher pH range than that for solvents such as chloroform,[6] reaching 100% extraction at around pH 6·0. On the other hand, free dithizone tends to distribute into the aqueous phase as

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the dithizonate anion at above pH 7. Accordingly, the pH of the sample solution was adjusted to 6·2 with acetate buffer.

As dithizone complexes many heavy metal ions in the neutral pH range, all reagent solutions and the distilled water used have to be completely free from such ions. Therefore, all reagent solutions were previously shaken repeatedly with 0·05% dithizone solution in chlorobenzene until the organic layer remained clear green, or more conveniently were treated with a 0·05% dithizone gel column (11·3 mm bore and 250 mm long).[2]

Various masking agents were evaluated, in order to make the analytical column highly selective for zinc at the pH used. Poisonous reagents such as cyanide should be avoided, because the procedure may be used by non-chemists. Although sodium thiosulphate has been recommended for masking copper, bismuth, lead, cadmium and other interfering cations at pH 4–5·5,[5] this reagent alone was not so effective for moderate amounts of these ions at pH 6·2. *N,N*-Bis(β-hydroxyethyl)dithiocarbamate[3] effectively masked moderate amounts of metal ions such as silver, cadmium, cobalt(II), copper(II), lead and nickel. β-Dithiocarbaminopropionic acid[4] was effective for masking mercury(II) up to an amount equal to that of the zinc. Iron(III) could be masked as the non-extractable ferrous bipyridyl complex with α,α'-bipyridyl and hydroxylamine hydrochloride. With the combined use of these masking agents, the above-mentioned interfering cations could be masked. Tolerances and the amounts of masking agents necessary are summarized in Table 1.

Anions, with the exception of strong complexing agents such as EDTA or cyanide, did not interfere.

The rate of extraction of zinc into dithizone gel at pH 6·2 was found to be much slower than that of mercury(II) at pH 1. Accordingly, the flow-rate was kept at 0·2 ml/min in order to obtain a sharp colour boundary.

The sensitivity can be expressed by the weight of metal ion needed to give unit length of coloured zone. In the present procedure, with 0·01% dithizone gel, a 10-mm length of pink zone corresponded to 0·2 μg of zinc. Therefore, it was possible to determine down to 0·01 ppm of zinc with a 10-ml sample.

The accuracy of the results depends upon the sharpness of zone boundary, as well as the dithizone concentration in the gel beads. With a freshly prepared analytical column of 0·01% dithizone gel and at a flow-rate of 0·2 ml/min, the error is about ±10% at the 0·2–0·4 μg level and ±3% at the 2 μg level.

Under these conditions, the relation between the zone length and the volume of sample solution containing a given amount of zinc was linear, with slope dependent on the zinc concentration. Accordingly, the zinc concentration can be determined either by observing the zone length after passage of a known amount of sample solution, or by measuring the volume of sample solution needed for the coloured zone to reach a given point.

Table 1. Determination of zinc in the presence of some foreign metals (0·1 ppm zinc was taken in each determination)

Foreign metal added,* *ppm*	Zn found, *ppm*	Masking conditions†
Ag(I) 6	0·1	A 0·75 ml
Cd(II) 0·2	0·1	A 0·75 ml
Cu(II) 1	0·1	A 0·75 ml
Co(II) 0·7	0·1	A 0·75 ml
Pb(II) 1	0·1	A 0·75 ml
Ni(II) 0·5	0·1	A 3 ml‡
Hg(II) 0·1	0·11	B 2 ml‡
Fe(III) 7	0·1	C 0·1 ml D 0·5 ml‡
Cd 0·2, Cu 1, Pb 1	0·1	A′ 5 ml
Cd 0·2, Cu 1, Pb 1, Fe 5	0·1	A′ 5ml C 0·5 ml D 0·5 ml‡

* Sample solutions were prepared by diluting the mixture of metal ion solution, 5 ml of 0·5*M* sodium thiosulphate solution, 2·5 ml of 2*M* acetate buffer solution (pH 6·2) and appropriate amount of masking agent solution, to 25 ml.

† Masking agent solutions: A. Ammonium bis(β-hydroxyethyl)dithiocarbamate aqueous solution, 0·04*M*. A′. Same reagent, 0·16*M*. B. Ammonium β-dithiocarbaminopropionate aqueous solution, 0·04*M*. C. Hydroxylamine hydrochloride aqueous solution, 10%. D. α,α'-Bipyridyl aqueous solution, 0·02*M*.

‡ Amount of acetate buffer solution was increased from 2·5 ml to 6·3 ml.

Table 2 summarizes some results obtained by applying this method to the analysis of practical samples with or without a known amount of zinc.

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Table 2. Determination of zinc in practical samples

Sample	Zn found, *ppm*		Recovery of Zn, *ppm*		
	This method	Instrumental*	Added	Found	Expected
Sea-water (Inchon, Songdo, Korea)	0·07–0·08	0·08	0·05	0·14–0·15	0·13
			0·10	0·19–0·20	0·18
			0·15	0·24–0·26	0·23
Mine-water (S. Mine)†	0·11–0·12	0·11	0·05	0·17–0·18	0·16
			0·10	0·20–0·21	0·21
			0·15	0·27–0·29	0·26
River-water (Sangri R.)‡	0·11–0·12	0·13	0·05	0·17–0·18	0·18
			0·10	0·21–0·22	0·23
			0·15	0·26–0·29	0·28

* Absorption spectrophotometric method using dithizone.

† Sample diluted 5-fold.

‡ Sample diluted 2·5-fold.

by the Graduate School of Yonsei University, to whom the authors are thankful.

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Summary—Zinc(II) at the sub-ppm level was determined by using a column, packed with gel beads containing dithizone. The beads turned from green to pink when the sample solution containing zinc was passed through the column at pH 6·2. Various interfering cations were masked by the combined use of sodium thiosulphate, α'α-bipyridyl, hydroxylamine hydrochloride, *N,N'*-bis(β-hydroxyethyl) dithiocarbamate and β-dithiocarbaminopropionic acid. The length of the pink zone was proportional to the amount of zinc in the sample. With 0·01% dithizone gel, as little as 0·01 ppm of zinc could be determined in a 10-ml sample at a flow rate of 0·2 ml/min.

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(*Received* 16 *May* 1975. *Accepted* 10 *June* 1975)

Thiobenzoylacetone (3-mercapto-1-phenylbut-2-en-1-one) has been used for the extractive photometric determination of nickel.[1] Further studies have revealed that cobalt can also be extracted as the orange–yellow complex at pH 8·4–9·1 and measured spectrophotometrically at 640 nm.

No systematic studies have been made on the solvent extraction of cobalt with benzoylacetone, dibenzoylmethane or furoyltrifluoroacetone.[2] Extraction with acetylacetone is generally incomplete[2] whereas extraction with 2-thenoyltrifluoroacetone in acetone–xylene mixture is quantitative. Thiothenoyltrifluoroacetone[3] has also been used but nickel shows strong interference. Thiodibenzoylmethane[4] has been used for the simultaneous spectrophotometric determination of cobalt and nickel with some advantage.

The method proposed in this paper is simple, rapid, selective and sensitive. It not only permits extractive spectrophotometric determination of cobalt at microgram concentrations but also makes it possible to determine cobalt and nickel simultaneously.

EXPERIMENTAL

Reagents

Thiobenzoylacetone (*SBA*). Synthesized from benzoyl acetone by the procedure described earlier.[1] An approximately 0·001*M* SBA solution in benzene was used. The reagent was preferably preserved in the refrigerator.

Cobalt nitrate solution. The hexahydrate (1·2 g) was dissolved in 250 ml of distilled water containing 1% nitric acid. The solution was standardized complexometrically[5] with EDTA, with Pyrocatechol Violet as indicator. The stock solution was diluted 100-fold (cobalt concentration 9·16 μg/ml).

General procedure

A 2-ml aliquot of the diluted cobalt nitrate solution (18·32 μg of Co) was diluted and its pH was adjusted to 8·4–9·1 with 0·01*M* nitric acid and 0·01*M* ammonia solution, in a total volume of 25 ml. It was then shaken for about 10 min with 10 ml of 0·001*M* thiobenzoylacetone in benzene. The layers were allowed to separate. The orange–yellow complex of cobalt(II) was measured spectrophotometrically at 460 nm against a reagent blank.

RESULTS AND DISCUSSION

Spectral properties

The absorption spectrum of the complex measured against a reagent blank had a maximum at 460 nm (Fig. 1). The reagent had an absorption maximum at 400 nm and the difference in absorbance between the complex and the excess of the reagent used was maximal at 460 nm. The molar absorptivity of the complex at 460 nm was $12{\cdot}7 \times 10^3$ $\text{l.mole}^{-1}.\text{cm}^{-1}$. The sensitivity of the method as defined by Sandell was 0·0046 μg/cm^2. Beer's law was obeyed at 460 nm in the concentration range 0·22–4·58 μg/ml in the extract. The absorbance of the complex remained constant for up to 144 hr.

Effect of pH

The extraction was studied over the pH range from 1·00 to 12·00 (Fig. 2). There was no extraction at pH < 6·0. The optimum pH was 8·4–9·1 and pH 8·8 was selected as being about in the middle of the range.

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The method proposed in this paper is simple, rapid, selective and sensitive. It not only permits extractive spectrophotometric determination of cobalt at microgram concentrations but also makes it possible to determine cobalt and nickel simultaneously.

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Effect of pH

The extraction was studied over the pH range from 1·00 to 12·00 (Fig. 2). There was no extraction at pH < 6·0. The optimum pH was 8·4–9·1 and pH 8·8 was selected as being about in the middle of the range.

Table 1. Effect of diverse ions

Foreign ions	Added as	Tolerance limit, *mg*	Foreign ions	Added as	Tolerance limit, *mg*
Ag^+	$AgNO_3$	0·75[a]	Li^+	$Li_2SO_4.H_2O$	20·00
Pb^{2+}	$Pb(NO_3)_2.2H_2O$	0·50[a]	Rb^+	$RbCl$	20·00
Tl^+	Tl_2SO_4	0·80	Cs^+	$CsCl$	20·00
Cu^{2+}	$CuSO_4.5H_2O$	2·00[c]	WO_4^{2-}	Na_2WO_4	0·50
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0·40	$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}4H_2O$	10·00
Sb^{3+}	$SbCl_3.3H_2O$	1·00[b]	AsO_3^{3-}	Na_2AsO_3	5·00
Bi^{3+}	$Bi(NO_3)_2.5H_2O$	1·00[d]	ReO_4^-	$KReO_4$	5·00
Os^{6+}	Na_2OsO_4	1·00	VO_3^-	$NaVO_3$	10·00
Pt^{4+}	$H_2PtCl_6.4H_2O$	0·30	SeO_3^{2-}	Na_2SeO_3	2·00
Ir^{3+}	$IrCl_3$	2·00	TeO_3^{2-}	Na_2TeO_3	2·00
Pd^{2+}	$PdCl_2.2H_2O$	0·40[c]	Cl^-	$NaCl$	20·00
Ru^{3+}	$RuCl_3$	0·50	Br^-	KBr	10·00
Rh^{3+}	$RhCl_3$	0·10	I^-	KI	10·00
Au^{3+}	$HAuCl_4.xH_2O$	0·05	NO_3^-	$NaNO_3$	20·00
Fe^{3+}	$Fe_2(SO_4)_3.7H_2O$	4·5[b]	NO_2^-	KNO_2	10·00
Cr^{3+}	$CrCl_3.6H_2O$	0·5[b]	SO_3^{2-}	Na_2SO_3	10·00
Al^{3+}	$Al(NO_3)_3.9H_2O$	0·6[e]	SO_4^{2-}	Na_2SO_4	20·00
Th^{4+}	$Th(NO_3)_4.4H_2O$	0·76[e]	PO_4^{3-}	$Na_2HPO_4.7H_2O$	10·00
U^{6+}	$UO_2(NO_3)_2.6H_2O$	0·50	$S_2O_3^{2-}$	$Na_2S_2O_3.5H_2O$	20·00
Ce^{4+}	$Ce(SO_4)_2.(NH_4)_2SO_4.2H_2O$	0·50	SCN^-	$KCNS$	10·00
Zr^{4+}	$Zr(NO_3)_4.4H_2O$	0·35	F^-	NaF	4·00
Be^{2+}	$Be(NO_3)_2.4H_2O$	0·35[e]	$tart^{3-}$	tartaric acid	2·50
Zn^{2+}	$ZnSO_4.7H_2O$	0·10	cit^{3-}	citric acid	0·05
Mn^{2+}	$MnSO_4.7H_2O$	1·00	$malonate^{2-}$	malonic acid	4·00
Ca^{2+}	$CaCl_2.6H_2O$	20·00	$ascorbate^-$	ascorbic acid	10·00
Sr^{2+}	$Sr(NO_3)_2.2H_2O$	15·00	CH_3COO^-	CH_3COONa	20·00
Ba^{2+}	$Ba(NO_3)_2.4H_2O$	15·00	tu	thiourea	5·00
Mg^{2+}	$MgSO_4.7H_2O$	20·00			

Selective extraction with (a) tributyl phosphate, (b) mesityloxide, (c) acetylacetone. Interference eliminated by masking with (d) thiourea, (e) fluoride.

Effect of reagent concentration

All other factors being kept constant, the concentration and volume of the reagent were varied. It was observed that the extraction of cobalt was complete with 10 ml of 0·001*M* SBA in benzene. The studies with 0·00025–0·002*M* reagent showed that the extraction was incomplete at lower concentration of the reagent, and no substantial increase in the extraction at higher reagent concentration. Varying the volume of 0·001*M* reagent from 2·5 to 20 ml showed that the extraction was quantitative even with 6 ml of reagent, but throughout 10 ml of reagent were used for the purpose of extraction.

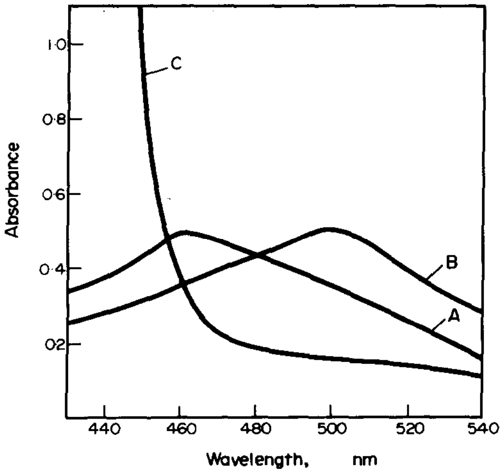

Fig. 1. Absorption spectra. A = Co(II)–SBA complex against reagent blank; B = Ni(II)–SBA complex against reagent blank; C = reagent blank against benzene. Co(II) = $3·886 \times 10^{-5}M$; Ni(II) = $8·396 \times 10^{-5}M$; SBA = 0·001*M* in benzene.

Period of equilibration

The period of equilibration was varied from 2 to 20 min. A wrist-action flask-shaker was used. The extraction was quantitative after 5 min of equilibration. It is therefore recommended to shake the mixture for at least 8–10 min.

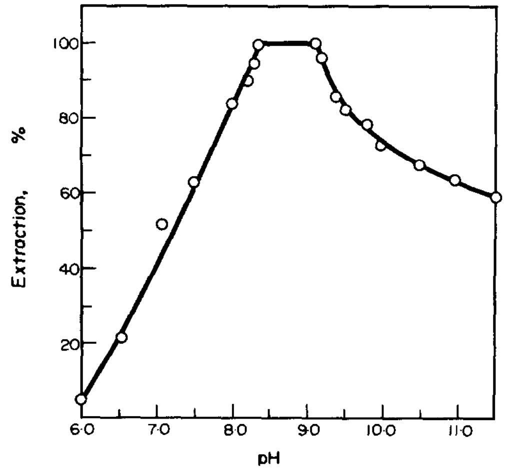

Fig. 2. Extraction of Co(II) as a function of pH. Co(II) = $3·109 \times 10^{-5}M$, 0·001*M* SBA in benzene.

Effect of salting-out agents

Ammonium, sodium, potassium, magnesium and calcium nitrates were tested as salting-out agents in the concentration range 1–4*M* but none enhanced the extraction.

Effect of diverse ions

Several ions were examined for their effect on the extraction of cobalt(II). The tolerance limit was taken as the amount of foreign ion required to cause ±2% error in the cobalt(II) recovery (Table 1). It was observed that many ions were tolerated in weight ratios (relative to cobalt) of 200:1 and 50:1. The ions showing interference were mercury(II), cyanide and EDTA. Several sequestering agents were tolerated at higher levels and hence they were used to eliminate the interference of some ions by forming negatively charged complexes which were not extracted along with cobalt(II), *e.g.*, silver and bismuth with thiourea, and aluminium, thorium and beryllium with fluoride. Mesityl oxide[2,6] was used to extract antimony, iron and chromium; tributylphosphate[2] was used for extraction of lead; acetylacetone[2] was used for copper and palladium. At the acidity used for the extraction of these ions cobalt(II) remained unextracted in the aqueous phase and could subsequently be extracted and determined with 0·001*M* SBA in benzene.

SIMULTANEOUS DETERMINATION OF COBALT AND NICKEL

Since the absorption maxima of the cobalt and nickel complexes are widely separated, these two metals were determined simultaneously by measurements at 460 and 500 nm (Fig. 1) and suitable spectrophotometric equations were applied.[7] Two conditions for use of these equations were satisfied, *viz.*, the absorbances of the complexes were additive at the wavelengths studied and Beer's law was obeyed by the complexes at both wavelengths. In Table 2 are given the molar absorptivities of the complexes for use in the calculations.[7]

$$C_{\text{Co}}(a_{\text{Co}})_{460} + C_{\text{Ni}}(a_{\text{Ni}})_{460} = A_{460} \qquad (1)$$

$$C_{\text{Co}}(a_{\text{Co}})_{500} + C_{\text{Ni}}(a_{\text{Ni}})_{500} = A_{500} \qquad (2)$$

where a = molar absorptivity and C = concentration of metal ion.

Table 2. Molar absorptivities of cobalt and nickel complexes, $l.mole^{-1}.cm^{-1}$

	460 *nm*	500 *nm*
Co(II)	$1{\cdot}27 \times 10^4$	$8{\cdot}84 \times 10^3$
Ni(II)	$4{\cdot}42 \times 10^3$	$5{\cdot}46 \times 10^3$

Table 3. Simultaneous determination of cobalt and nickel

Taken, μg $Co^{2+} + Ni^{2+}$	Found, μg $Co^{2+} + Ni^{2+}$	Error, % Co	 Ni
9·16 + 39·44	9·46 + 38·7	3·3	1·8
18·32 + 29·58	18·21 + 30·2	0·6	2·2
4·58 + 49·30	4·76 + 48·7	3·8	1·3
18·32 + 39·44	18·16 + 39·6	0·9	0·5
9·16 + 19·72	9·39 + 19·6	2·6	0·6
22·90 + 9·86	23·03 + 10·2	0·6	3·6

Procedure for simultaneous spectrophotometry

The mixture of cobalt and nickel was adjusted to pH 9·0 with 0·01*M* nitric acid and 0·01*M* ammonia solution. It was then extracted for 10 min with 10 ml of 0·001*M* SBA in benzene. The organic layer was separated and measured at 460 and 500 nm. The concentrations of cobalt and nickel were calculated by using the equations above. Results for various concentrations of cobalt and nickel are shown in Table 3.

Accuracy and precision

The proposed method possesses several advantages. The method is simple, selective, sensitive and applicable at tracer quantities. It is possible to extract quantitatively and determine spectrophotometrically cobalt and nickel in 30 min. As little as 0·2 μg/ml can be determined and the results are reproducible. The average recovery of cobalt in the absence of nickel is 99·9 ± 1%, relative standard deviation ±0·85%. The simultaneous determination of cobalt and nickel gives somewhat poorer accuracy (Table 3).

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Summary—Thiobenzoylacetone in benzene is used for the extraction and spectrophotometric determination of cobalt at pH 8·4–9·1. The orange–yellow complex is measured at 460 nm. The system conforms to Beer's law over the range 0·20–4·58 μg/ml of extract. The colour of the complex is stable for at least 144 hr. Cobalt(II) is quantitatively extracted and determined in the presence of 200:1 (w/w ratios) of various ions. The method is made selective by using common sequestering agents such as thiourea or fluoride or by selective extraction with mesityl oxide, tributylphosphate and acetylacetone. It is possible to determine cobalt in the presence of nickel by simultaneous spectrophotometry. The method is rapid, simple, selective and sensitive.

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OXIDATION WITH PERMANGANATE IN ACID MEDIUM CONTAINING FLUORIDE: DETERMINATION OF BISULPHITE

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The reaction with alkaline permanganate has been applied by Issa *et al.*[1] for the determination of sulphite. The estimation of bisulphite has been the subject of a few investigations.[2–5] The reaction between HSO_3^- and MnO_4^- in acid medium is usually beset with difficulties owing to the precipitation of oxides of manganese. In the present method, this difficulty is overcome by oxidizing HSO_3^- with MnO_4^- in acid medium in the presence of fluoride.

EXPERIMENTAL

Solutions

Potassium permanganate solutions were prepared by a method similar to that of Stamm[6] and standardized with sodium oxalate.[7] Sodium bisulphite solutions were prepared and standardized according to a recommended procedure.[2] Other solutions included 2% sodium fluoride, 1*M* sulphuric acid and 0·25*M* copper sulphate. All solutions were prepared from analytical-grade reagents and twice-distilled water.

Apparatus

The emf of the titration cell was measured with a Radiometer millivoltmeter (Model pH M28 b). The cell used consisted of the titration half-cell and a calomel reference electrode. The platinum rod indicator electrode was always abraded with emery paper, etched with *aqua regia* and rinsed with twice-distilled water before use in each titration.

RESULTS AND DISCUSSION

The reaction proceeds rapidly but as the end-point is approached the electrode equilibration becomes rather sluggish, needing 5 min between additions of titrant. The potentiometric titration is not affected by addition of Cu(II), but this is essential for detection of the end-point in the visual titration (to mask the pink colour of the MnF_4^- complex).[8,9]

Titration of bisulphite with permanganate

From Tables 1 and 2, the reaction appears to proceed quantitatively in accordance with the equation

$$MnO_4^- + H^+ + 2HF_2^- + 3HSO_3^- \rightleftharpoons MnF_4^- + SO_4^{2-} + S_2O_6^{2-} + 3H_2O \quad (1)$$

The potentiometric titration curves have two inflections, the first due to formation of Mn(II) and the second to formation of Mn(III) (Fig. 1). This is confirmed by the absence of any absorption band for Mn(III)[10] in the spectrum of the reaction mixture at the first inflection and its presence in the spectrum of the solution at the second inflection.

The first inflection corresponds to:

$$4MnO_4^- + 7H^+ + 15HSO_3^- \rightleftharpoons 4Mn^{2+} + 5S_2O_6^{2-} + 5SO_4^{2-} + 11H_2O \quad (2)$$

and the second to the reaction

$$MnO_4^- + 10HF_2^- + 4Mn^{2+} \rightleftharpoons 5MnF_4^- + 2H^+ + 4H_2O \quad (3)$$

giving (1) as the overall reaction.

The formation of dithionate is confirmed by an absorption band at 242 nm, and by analysis by the method of Murthy.[12]

Table 1. Potentiometric titration of 6 ml of 0·047*M* HSO_3^- with 0·0189*M* $KMnO_4$, whole volume made up to 100 ml with water

Composition of the reaction mixture	Measured pH	Theoretical end-point, *ml*		Experimental end-point, *ml*		Error, %		Max. $\Delta E/\Delta V$, *mV*/0·1 *ml*	
		(*i*)	(*ii*)	(*i*)	(*ii*)	(*i*)	(*ii*)	(*i*)	(*ii*)
(*a*) In presence of 50 ml of 2% NaF and varying amounts of 1*M* H_2SO_4 (*x* ml)									
x									
0·0 0·024*M* NaF				Yellowish turbidity					
0·5 0·01*M* HF + 0·23*M* NaF	5·5	3·97	4·98	3·95					
0·5 0·02*M* HF + 0·22*M* NaF	5·2	3·97	4·98	3·95	5·00	−0·5	+0·4	45	85
2·0 0·04*M* HF + 0·20*M* NaF	4·9	3·97	4·98	3·94	4·96	−0·8	−0·4	50	80
4·0 0·08*M* HF + 0·16*M* NaF	4·7	3·97	4·98	3·9	4·95	−1·8	−0·6	53	78
6·0 0·12*M* HF + 0·12*M* NaF	4·5	3·97	4·98	3·9	4·92	−1·8	−1·1	60	75
9·0 0·18*M* HF + 0·06*M* NaF	3·5	3·97	4·98	3·88	4·82	−2·3	−3·2	65	70
(*b*) In presence of 2·0 ml of 1*M* H_2SO_4 and varying amounts of 2% NaF (*y* ml)									
y									
0·0 0·02*M* H_2SO_4				Slow reaction					
25 0·04*M* HF + 0·08*M* NaF	3·8	3·97	4·98	3·85	4·92	−3·0	−1·2	40	79
50 0·04*M* HF + 0·20*M* NaF	5·1	3·97	4·98	3·94	4·98	−0·8	nil	50	80
60 0·04*M* HF + 0·25*M* NaF	5·2	3·97	4·98	3·98	4·98	+0·2	nil	52	82
80 0·04*M* HF + 0·35*M* NaF	5·5	3·97	4·98	4·02	5·00	+1·2	+0·4	55	82

(*i*) Mn(VII) → Mn(II); (*ii*) Mn(II) → Mn(III).

Table 2. Visual titration of 5 ml of 0·047*M* HSO_3^- with 0·01496*M* $KMnO_4$ in presence of 5 ml of 0·25*M* $CuSO_4$ [Mn(VII) → Mn(III)]

Composition of the reaction mixture	Theoretical end-point, *ml*	Experimental end-point, *ml*	Error, %
(*a*) In presence of 10 ml of 2% NaF and varying amounts of 1*M* H_2SO_4 (*x* ml)			
x			
0·0 0·24*M* NaF		Yellowish turbidity	
1·0 0·02*M* HF + 0·22*M* NaF	5·23	5·20	−0·6
2·0 0·04*M* HF + 0·20*M* NaF	5·23	5·20	−0·6
4·0 0·08*M* HF + 0·16*M* NaF	5·23	5·18	−1·0
5·0 0·10*M* HF + 0·14*M* NaF	5·23	5·15	−1·5
(*b*) In presence of 2 ml of 1*M* H_2SO_4 and varying amounts of 2% NaF (*y* ml)			
y			
0·0 0·02*M* H_2SO_4		Slow reaction	
25 0·04*M* HF + 0·08*M* NaF	5·23	5·00	−0·4
50 0·04*M* HF + 0·20*M* NaF	5·23	5·20	−0·6
60 0·04*M* HF + 0·25*M* NaF	5·23	5·20	−0·6
80 0·04*M* HF + 0·34*M* NaF	5·23	5·25	+0·4

Effect of acidity. Tables 1 and 2 show that reasonable accuracy is obtained at acidities ranging from 0·01 to 0·02*M* sulphuric acid in presence of 0·24*M* sodium fluoride. At lower acidities the solution becomes yellowish brown owing to partial production of Mn(IV). At higher acidities the end-point occurs too early owing to the instability of bisulphite solution under such conditions.

Effect of fluoride concentration. Tables 1 and 2 indicate that the fluoride concentration can be varied from 0·24 to 0·38*M* at constant concentration of 0·02*M* sulphuric acid, without causing appreciable error. Although 0·12*M* sodium fluoride is sufficient for complexation of Mn(III),[9,11] a higher concentration is needed because of protonation of fluoride by the strong acid added, and for stabilization of the MnF_4^- complex.

Effect of $NaHSO_3$ concentration. The visual end-point method is suitable for 10–60 mg of bisulphite, and the potentiometric titration for amounts up to 100 mg (Table 3). With higher bisulphite concentrations the reaction becomes slow and the titration medium slightly turbid owing to hydrolysis of Mn(III) to Mn_2O_3.[9,11] The error is generally < 0·7%.

Titration of permanganate with bisulphite

The results indicate that the reaction proceeds quantitatively according to the equation

$$MnO_4^- + 2HF_2^- + 2HSO_3^- \rightleftharpoons MnF_4^- + 2SO_4^{2-} + 2H_2O \quad (4)$$

The titration curves have a single sharp inflection at the Mn(III) step, varying in height with acidity. Since all manganese(III) salts are strong oxidizing agents, a further reaction between the Mn(III) formed and more HSO_3^- to produce Mn(II) and SO_4^{2-} would be expected to occur, but it was found difficult to continue the titration to the Mn(II) reduction step owing to the sluggishness of the reaction.

Effect of acidity. Table 4 shows that good results are obtained at acidities ranging from 0·02 to 0·05*M* sulphuric acid, both in the visual and potentiometric titrations with use of 50 ml of 2% sodium fluoride solution but at the higher acidities, the end-point occurs later than expected, probably because of partial production of Mn(II).

Effect of fluoride concentration. In 0·24–0·38*M* sodium fluoride at the optimum acidity, the titration yields good results in both the visual and potentiometric methods (Table 4). With lower concentrations of sodium fluoride, late end-points were obtained [production of Mn(II)].

Amounts of permanganate corresponding to 3–16 mg of manganese could be titrated successfully under the optimum conditions (Table 5), the error being generally < 0·7%.

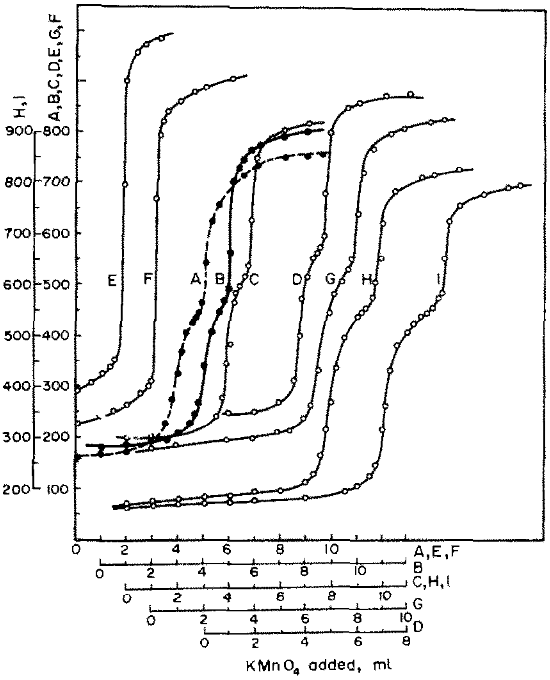

Fig. 1. Titration of 0·047*M* bisulphite with 0·0189*M* MnO_4^-. (A) 6 ml of HSO_3^-, 50 ml of 2% NaF and 1·0 ml of 1*M* H_2SO_4; (B) 6 ml HSO_3^-, 50 ml of 2% NaF and 2·0 ml of 1*M* H_2SO_4; (C) 6 ml of HSO_3^-, 50 ml of 2% NaF and 4·0 ml of 1*M* H_2SO_4; (D) 6 ml of HSO_3^-, 50 ml of 2% NaF and 9·0 ml of 1*M* H_2SO_4; (E) 6 ml of HSO_3^-, no sodium fluoride, 2·0 ml of 1*M* H_2SO_4; (F) 6 ml of HSO_3^-, 10 ml of 2% NaF and 2·0 ml of 1*M* H_2SO_4; (G) 10 ml of HSO_3^-, 50 ml of 2% NaF and 2·0 ml of 1*M* H_2SO_4; (H) 12 ml of HSO_3^-, 50 ml of 2% NaF and 2·0 ml of 1*M* H_2SO_4; (I) 15 ml of HSO_3^-, 50 ml of 2% NaF and 2·0 ml of 1*M* H_2SO_4.

General discussion

Oxidation of sulphur compounds with permanganate usually produces sulphate, especially when performed in

Table 3. Titration of $NaHSO_3$ with 0·01894*M* $KMnO_4$, using 50 ml of 2% NaF and 2 ml of 1*M* H_2SO_4

HSO_3^- (0·047*M*) *ml*	*mg*	Theoretical end-point, *ml* (*i*)	(*ii*)	Experimental end-point, *ml* (*i*)	(*ii*)	Error, % (*i*)	(*ii*)
(*a*) Potentiometric titration							
2	9·78	1·32	1·57	1·25	1·58	−5·3	+0·6
4	19·56	2·65	3·31	2·55	3·33	−3·3	+0·6
6	29·34	3·97	4·97	3·94	4·98	−0·8	+0·2
8	39·12	5·30	6·62	5·26	6·58	−0·8	−0·6
10	48·90	6·62	8·28	6·60	8·22	−0·3	−0·7
12	58·68	7·94	9·94	8·00	9·88	+0·8	−0·6
15	73·35	9·93	12·42	10·12	12·45	+0·9	+0·2
20	97·80	13·24	16·56	13·38	16·65	+1·1	+0·6
(*b*) Visual titration, in presence of 5 ml of 0·25*M* $CuSO_4$							
2	2·78		2·09		2·02		−3·4
5	24·45		5·23		5·20		−0·6
8	39·12		8·36		8·32		−0·5
10	48·90		10·46		10·38		−0·8
12	58·58		12·54		12·44		−0·8
5*	24·45		5·23		5·20		−0·6
5†	24·45		5·23		5·00		−4·4

(*i*) Mn(VII) → Mn(II); (*ii*) Mn(VII) → Mn(II).

* 10 ml of 0·25*M* $CuSO_4$.

† No Cu(II).

Table 4. Potentiometric titration of 8·0 ml of 0·01894*M* $KMnO_4$ with 0·046*M* HSO_3^- [Mn(VII) → Mn(III)]

Composition of the reaction mixture	Theoretical end-point, *ml*	Experimental end-point, *ml*	Error, %
(*a*) In presence of 50 ml of 2% NaF and varying amounts of 1*M* H_2SO_4 (*x* ml)			
x			
0·0 0·24*M* NaF		Slow reaction	
1·0 0·02*M* HF + 0·22*M* NaF	6·59	6·62	+0·5
2·5 0·05*M* HF + 0·19*M* NaF	6·59	6·64	+0·8
5·0 0·10*M* HF + 0·14*M* NaF	6·59	6·65	+0·9
8·0 0·16*M* HF + 0·08*M* NaF	6·59	6·68	+0·4
(*b*) In presence of 2·5 ml of 1*M* H_2SO_4 and varying amounts of 2% NaF (*y* ml)			
y			
0·0 0·025*M* H_2SO_4		Reaction slow and brown ppte formed	
25 0·05*M* HF + 0·07*M* NaF	6·59	6·70	+1·7
50 0·05*M* HF + 0·19*M* NaF	6·59	6·64	+0·8
75 0·05*M* HF + 0·31*M* NaF	6·59	6·64	+0·8
80 0·05*M* HF + 0·33*M* NaF	6·59	6·62	+0·5

Table 5. Titration of various amounts of 0·0189*M* $KMnO_4$ with 0·046*M* $NaHSO_3$, using 50 ml of 2% NaF and 2·5 ml of 1*M* H_2SO_4 [Mn(VII) → Mn(III)]

$KMnO_4$, *ml*	Mn *mg*	Theoretical end-point, *ml*	Experimental end-point, *ml*	Error, %
(*a*) Potentiometric titration				
3	3·07	2·47	2·51	+1·6
5	5·11	4·12	4·15	+0·7
10	10·33	8·23	8·22	−0·1
15	15·34	12·35	12·4	+0·4
(*b*) Visual titration in presence of 5 ml of 0·25*M* $CuSO_4$				
3	3·03	2·45	2·44	−0·4
5	5·05	4·07	4·10	+0·7
7	7·07	5·71	5·75	+0·7
10	10·11	8·15	8·15	nil
12	12·13	9·78	9·84	+0·6

(*a*) Using 0·0189*M* $KMnO_4$.
(*b*) Using 0·0187*M* $KMnO_4$.

alkaline medium.[1,13,14] An exception is the oxidation of sulphide in presence of telluric acid which yields dithionate.[15] In acid medium, dithionate is often an intermediate stage in the oxidation of sulphide, sulphite and thiosulphate,[16] and this is apparently also the case when bisulphite is titrated with permanganate in presence of fluoride, though the reverse titration gives sulphate because the oxidant is always present in excess.

The pH of the reaction mixture under optimum conditions is 4–5·5. Since pK_1 for H_2SO_3 is 1·92 then practically no H_2SO_3 should be present and hence decomposition to yield SO_2 is not probable. This was confirmed experimentally by doing the titration with a closed system and testing the atmosphere above the titrated solution for SO_2; none was found.

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Summary—The factors affecting the success of both visual and potentiometric end-point detection in titration of bisulphite with permanganate in the presence of fluoride are examined. The optimum conditions are 0·02*M* H_2SO_4 and 0·24–0·38*M* NaF. The oxidation product comprises dithionate and sulphate according to the overall reaction $MnO_4^- + H^+ + 2HF_2^- + 3HSO_3^- \rightleftharpoons MnF_4^- + S_2O_6^{2-} + SO_4^{2-} + 3H_2O$. The reverse titration is also satisfactory, but proceeds quantitatively according to $MnO_4^- + 2HF_2^- + 2HSO_3^- \rightleftharpoons MnF_4^- + 2SO_4^{2-} + 2H_2O$.

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ANALYTICAL DATA

COMPLEXES OF Cu(II) WITH 2,2′-BIPYRIDYL AND MALEIC OR PHTHALIC ACID

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INTRODUCTION

The increased stability of mixed complexes of Cu(II), 2,2′-bipyridyl and ligands which have oxygen donor atoms[1] has been attributed to the entropy effect, π-bond formation between copper(II) and the bipyridyl, and, in minor measure, to the effect of the oxygen-donor ligand.[2] To test this hypothesis further, we decided to study a series of dicarboxylic acids in this reaction, first those which form six-membered chelate rings,[3–5] and now those which form seven-membered rings.

EXPERIMENTAL

Reagents

Maleic acid (MALE) and phthalic acid (PHT) were recrystallized several times; their purity was found to be >99·8% by potentiometric titration. Disodium maleate was obtained by adding a slight excess of sodium hydroxide to maleic acid, evaporating the solution to dryness, shaking the residue for 1–2 hr with ethanol to dissolve out the surplus alkali, filtering and drying. Other reagents were prepared as described earlier.[3,4] The copper perchlorate solutions contained a small amount of perchloric acid; this was allowed for in the calculations. All solutions were prepared with twice-distilled CO_2-free water.

Apparatus

The potentiometric equipment was that used earlier.[3] The cells were equipped with a capillary tube for deaeration of the solutions during measurement. All solutions were maintained at 25 ± 0·1° and constant ionic strength 0·1M ± 5% (perchlorate acid and sodium perchlorate).

Procedures

Determination of the ligand protonation constants. Solutions containing the ligand in concentrations from 10 to 1mM were titrated potentiometrically with sodium hydroxide. For maleic acid, which has a very low first pK_a, it was necessary to add an excess of protons (perchloric acid) to the initial solution so that $\bar{n}_H$ was significantly greater than 1.

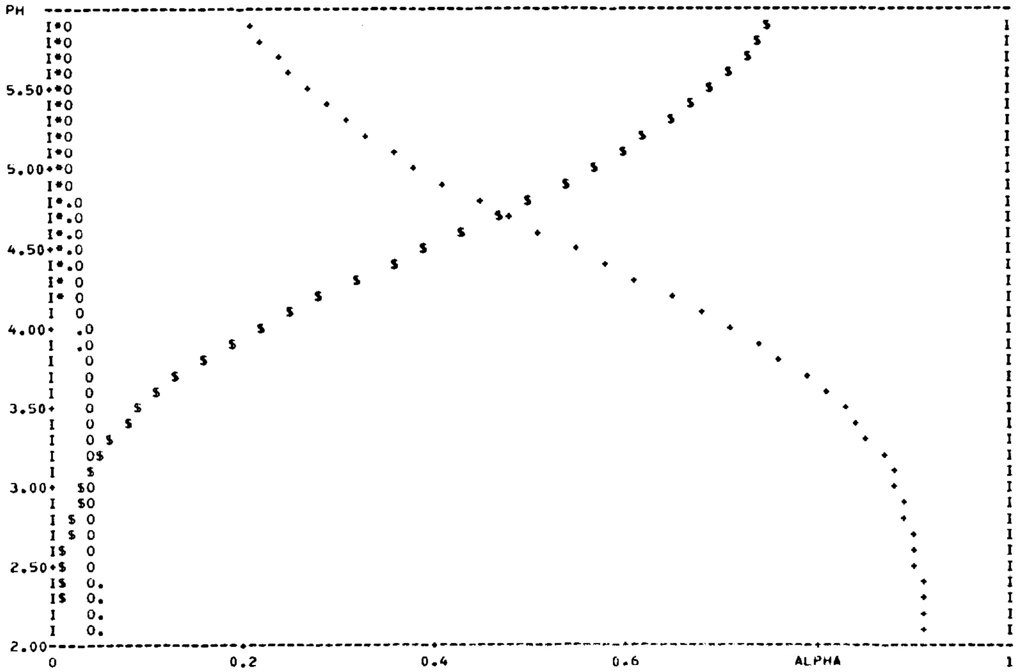

Fig. 1. Distribution diagram of the species present in aqueous solutions of Cu(II), 2,2′-bipyridyl and maleic acid (each 1 mM), calculated by the program DISDI.[7] \$—CubipMALE; +—Cubip; ○—Cubip$_2$; *—CuMALE; ·—Cu; ALPHA = degree of formation.

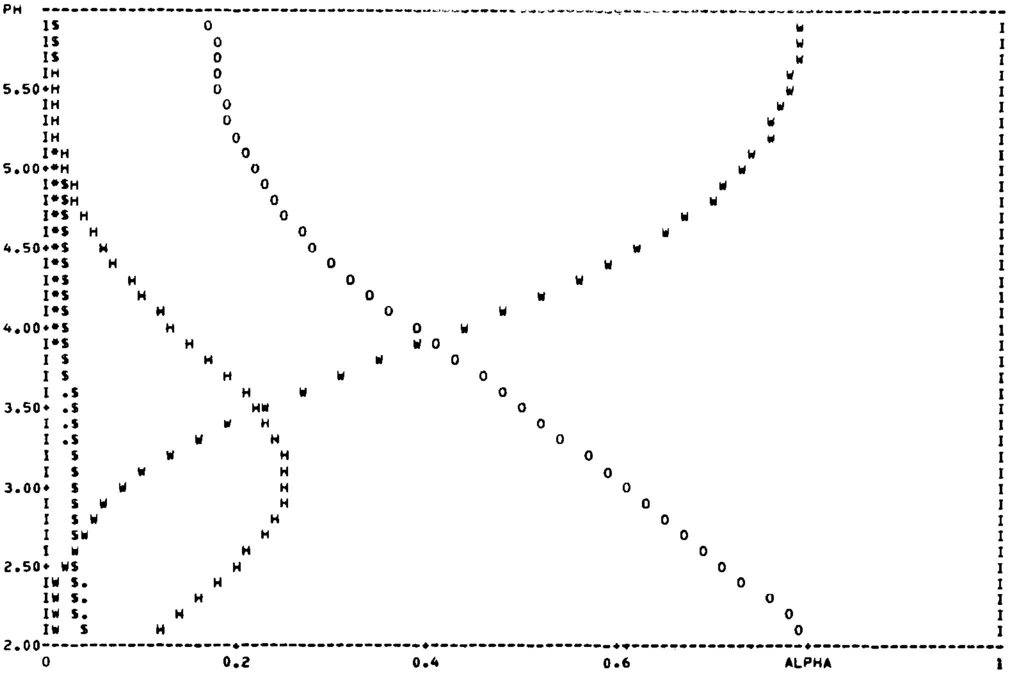

Fig. 2. Distribution diagram of the species present in aqueous solutions of Cu(II), 2,2′-bipyridyl and phthalic acid (each 1 mM), calculated by the program DISDI.[7] W—CubipPHT; O—Cubip; H—CubipHPHT; \$—Cubip$_2$; *—CuPHT; ·—Cu; ALPHA = degree of formation.

Determination of the formation constants of the Cu(II)–maleate and Cu(II)–phthalate complexes. Cupric perchlorate (*ca.* 1mM) solutions containing ligand in up to 6-fold ratio to copper were titrated with sodium hydroxide to a pH equal to pK_2 + 0·2. Solutions containing cupric perchlorate and perchloric acid were also titrated with disodium maleate.

Determination of the formation constants of the mixed complexes. Solutions containing copper, bipyridyl and phthalic acid in the ratios 1:1:1, 1:1:2, 1:1:3, 2:1:1, 3:1:1 (1mM bipyridyl) were titrated to pH 5·3 in the first three cases, and pH 4 in the last two. Solutions containing copper, bipyridyl and maleic acid in the ratios 1:1:1, 1:1:2, 1:1:3 (1mM bipyridyl) were titrated up to pH 6·1, and solutions containing copper and bipyridyl (1:1) and perchloric acid (1mM) were titrated with disodium maleate.

CALCULATIONS

The values of the protonation and formation constants[4,6] of the copper(II) with 2,2′-bipyridyl, for calculation of the constants relative to the ternary systems, were taken from the literature. The calculations were performed by means of the programs PMGZ and SCOGSB, as described earlier.[3,4]

RESULTS AND DISCUSSION

The values of the protonation constants of the acids and their formation constants with copper(II) are listed in Table 1. The stability constants of the ternary complexes are reported in Table 2. Distribution diagrams of the species present in solution are reported in Figs. 1 and 2, as they were printed by the computer.[7] By using the values listed in Tables 1 and 2, we calculated the data relative to the parameters log K_r and Δlog K,[8] defined as before.[3] The results are reported in Table 3, together with those for similar systems already studied, the log $\beta^{\mathrm{Cu}}_{\mathrm{CubipL}}$ values, and the differences between the first and the second stability constants of the complexes CuL and CuL$_2$ (Δ'log K = log $K^{\mathrm{Cu}}_{\mathrm{CuL}}$ − log $K^{\mathrm{Cu}}_{\mathrm{CuL_2}}$). From these values we can say that

Table 1. Protonation constants of maleic and phthalic acids, 2,2′-bipyridyl, and formation constants of the copper(II) complexes at 25 ± 0·1° and 0·1M (H,Na)ClO$_4$

Ligand	log $K^{\mathrm{H}}_{\mathrm{HL}}$	log $K^{\mathrm{HL}}_{\mathrm{H_2L}}$	log $K^{\mathrm{Cu}}_{\mathrm{CuL}}$	log $\beta^{\mathrm{Cu}}_{\mathrm{CuL_2}}$	log $\beta^{\mathrm{Cu}}_{\mathrm{CuHL}}$
MALE	5·848(3)	7·543(9)	3·40(2)	5·48(6)	—
PHT	4·920(1)	7·665(2)	3·251(3)	5·46(7)	6·25(2)
bip[5,6]	4·461(5)	—	8·14(3)	13·64(5)	—

The figures in brackets are the standard deviations of the last decimal figure.

Table 2. Stability constants* of ternary complexes of copper(II), 2,2′-bipyridyl and maleic or phthalic acid, at 25 ± 0·1° and 0·1M (H,Na)ClO$_4$

System	log $\beta^{\mathrm{Cu}}_{\mathrm{CubipL}}$	log $\beta^{\mathrm{Cu}}_{\mathrm{CubipHL}}$	log $K^{\mathrm{Cubip}}_{\mathrm{CubipL}}$	log $K^{\mathrm{CuL}}_{\mathrm{CuLbip}}$
CubipMALE	11·89(3)	—	3·75(4)	8·49(4)
CubipPHT	11·86(3)	15·35(9)	3·72(4)	8·61(3)

* $\beta^{\mathrm{Cu}}_{\mathrm{CubipL}}$ = [CubipL]/[Cu][bip][L]; $\beta^{\mathrm{Cu}}_{\mathrm{CubipHL}}$ = [CubipHL]/[Cu][bip][H][L]; $K^{\mathrm{Cubip}}_{\mathrm{CubipL}}$ = [CubipL]/[Cubip][L]; $K^{\mathrm{CuL}}_{\mathrm{CuLbip}}$ = [CuLbip]/[CuL][bip].
The figures in brackets are the standard deviations of the last decimal figure.

Table 3. Stabilization parameters and stability constants for the ternary complexes of copper(II) and 2,2′-bipyridyl with maleic and phthalic acids, and for other systems already studied

Acid	log $\beta^{Cu}_{Cubipl.}$	Δlog K	log K_r	Δ′log K	Ref.
Ox	13·50	0·70	4·90	1·24	11
MAL	13·44	0·26	5·65	2·50	3
Suc	11·10	0·30	—	—	(9)
CPRD	15·52	1·38	7·78	2·37	4
PHT	11·86	0·49	4·60	0·94	this work
MALE	11·89	0·36	4·52	1·32	" "

Ox, MAL, Suc and CPRD are abbreviations for oxalic, malonic, succinic and cyclopropane-1,1-dicarboxylic acids.

these complexes are more stable than would be expected on statistical grounds (log $K_r > 0·6$) and show good discriminating properties (namely the complex Cubip^{2+} prefers to give the species CubipL rather than the cation Cubip$_2^{2+}$, in fact[1,2] Δlog $K > 0$). Because these systems have the same co-ordination number and type,[11] they can be used to assess the influence of the chelate-ring size and the ligand characteristics on the stability of the mixed complexes. Thus the complexes with five-membered rings are more stable than those with six-membered rings, which, in turn, are more stable than those with seven-membered ones; in contrast, the system CubipCPRD showed a different behaviour, as the conjugating effect of the alicyclic ligand[10,11] increased the chelation effect. Recently, Sigel and co-workers,[12] examining ternary complexes with five- or six-membered rings, and also with one five- and one six-membered ring, pointed out that great care is necessary in choosing the parameters for correct comparison of systems. In particular, the mixing constant log K_r, because it is strongly influenced by Δ′log K, can be used as a stabilization index only for series of systems in which Δ′log K is of the same order of magnitude. As in our systems Δ′log K ranges from 0·9 to 2·5, the use of Δlog K is a more realiable means of evaluating the stabilization of ternary complexes. This agrees with the opinion of others.[13] The final conclusions are: (*a*) ternary complexes with five-membered chelate rings are stabilized more than those with six- and seven-membered rings which have similar stabilizing power; (*b*) a ligand with conjugating and delocalizing properties increases the chelating effect, both with six- and seven-membered rings.

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Summary—The stability constants of ternary copper(II) complexes with 2,2′-bipyridyl and a dicarboxylic acid (maleic and phthalic) have been determined by means of pH-titrations at 25 ± 0·1° and an ionic strength of $0·1M$ (Na,H)ClO$_4$. The stabilities of ternary complexes are compared with those of similar complexes and related to the size of the chelate rings and the nature of the dicarboxylic ligands.

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THERMODYNAMIC STABILITY CONSTANTS OF BERYLLIUM(II) AND *p*-SUBSTITUTED *N*-PHENYL BENZOHYDROXAMIC ACID COMPLEXES*

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(*Received* 19 *February* 1975. *Accepted* 10 *June* 1975)

The thermodynamic stepwise formation constants of beryllium(II) complexes with *p*-substituted *N*-phenylbenzohydroxamic acids have been determined at 35° by titrations in 50% v/v aqueous dioxan (as the ligands and complexes are insoluble in water).

EXPERIMENTAL

The procedure was essentially that of Bjerrum and Calvin[1,2] and Block and McIntyre[3] as modified by Goldberg.[4,5] The thermodynamic protonation constants of the acids were determined by pH-titrations in the same medium at 35°.[6]

The acids were synthesized by the method reported earlier,[7] recrystallized from benzene/petroleum ether and dried under vacuum over phosphorus pentoxide. Their

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* From the Ph.D. thesis of K. R. Gupta, Ravishankar University, Raipur, 1975.

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Table 3. Stabilization parameters and stability constants for the ternary complexes of copper(II) and 2,2′-bipyridyl with maleic and phthalic acids, and for other systems already studied

Acid	log $\beta^{Cu}_{Cubipl.}$	Δlog K	log K_r	Δ′log K	Ref.
Ox	13·50	0·70	4·90	1·24	11
MAL	13·44	0·26	5·65	2·50	3
Suc	11·10	0·30	—	—	(9)
CPRD	15·52	1·38	7·78	2·37	4
PHT	11·86	0·49	4·60	0·94	this work
MALE	11·89	0·36	4·52	1·32	" "

Ox, MAL, Suc and CPRD are abbreviations for oxalic, malonic, succinic and cyclopropane-1,1-dicarboxylic acids.

these complexes are more stable than would be expected on statistical grounds (log $K_r > 0{\cdot}6$) and show good discriminating properties (namely the complex Cubip^{2+} prefers to give the species CubipL rather than the cation Cubip$_2^{2+}$, in fact[1,2] Δlog $K > 0$). Because these systems have the same co-ordination number and type,[11] they can be used to assess the influence of the chelate-ring size and the ligand characteristics on the stability of the mixed complexes. Thus the complexes with five-membered rings are more stable than those with six-membered rings, which, in turn, are more stable than those with seven-membered ones; in contrast, the system CubipCPRD showed a different behaviour, as the conjugating effect of the alicyclic ligand[10,11] increased the chelation effect. Recently, Sigel and co-workers,[12] examining ternary complexes with five- or six-membered rings, and also with one five- and one six-membered ring, pointed out that great care is necessary in choosing the parameters for correct comparison of systems. In particular, the mixing constant log K_r, because it is strongly influenced by Δ′log K, can be used as a stabilization index only for series of systems in which Δ′log K is of the same order of magnitude. As in our systems Δ′log K ranges from 0·9 to 2·5, the use of Δlog K is a more realiable means of evaluating the stabilization of ternary complexes. This agrees with the opinion of others.[13] The final conclusions are: (*a*) ternary complexes with five-membered chelate rings are stabilized more than those with six- and seven-membered rings which have similar stabilizing power; (*b*) a ligand with conjugating and delocalizing properties increases the chelating effect, both with six- and seven-membered rings.

Acknowledgements—We thank the "Consiglio Nazionale delle Ricerche" for financial support.

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Summary—The stability constants of ternary copper(II) complexes with 2,2′-bipyridyl and a dicarboxylic acid (maleic and phthalic) have been determined by means of pH-titrations at 25 ± 0·1° and an ionic strength of 0·1M (Na,H)ClO$_4$. The stabilities of ternary complexes are compared with those of similar complexes and related to the size of the chelate rings and the nature of the dicarboxylic ligands.

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(*Received* 19 *February* 1975. *Accepted* 10 *June* 1975)

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EXPERIMENTAL

The procedure was essentially that of Bjerrum and Calvin[1,2] and Block and McIntyre[3] as modified by Goldberg.[4,5] The thermodynamic protonation constants of the acids were determined by pH-titrations in the same medium at 35°.[6]

The acids were synthesized by the method reported earlier,[7] recrystallized from benzene/petroleum ether and dried under vacuum over phosphorus pentoxide. Their

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purity was confirmed by elemental analysis, m.p., and spectroscopy.

The stability constants were calculated as described earlier, and activity coefficient corrections were applied.

The concentrations of beryllium(II), ligand and nitric acid in the titration vessel were generally around 0·001, 0·01 and 0·001 M respectively. The nitric acid was added in the preparation of the beryllium nitrate solutions, to minimize hydrolysis.

RESULTS AND DISCUSSION

The thermodynamic stability constants are summarized in Table 1. The maximum scatter in log K_1 was ±0·15. The hydroxamic acids used are bidentate ligands. Beryllium(II) has a co-ordination number of 4 in its hydroxamic acid complexes.[8,9] The nature of the metal–ligand bond can be assessed from comparison of the pK_a of closely related ligands and log K_1 for the corresponding 1:1 beryllium complexes. Correlations between pK_a and log K_2 are less exact because other factors influence the complex formation.[10] This is in agreement with the values given in Table 1.

A graph of log K_1 *vs.* pK_a is linear; least squares calculations give the relation log K_1 = 1·44 pK_a − 6·99. Since the slope is greater than unity the nuclear substitution affects the stability of the complex more than that of the free acid.[11–13]

Table 1. Stability constants of beryllium(II) complexes

X	pK_a	log K_1	log K_2
OCH_3	11·13	9·05	8·03
CH_3	10·98*	8·85	7·46
H	10·96*	8·68	7·15
Cl	10·68	8·41	6·98
Br	10·65	8·24	6·89
NO_2	10·15	7·76	6·48

* Ref. 15.

Table 2. Comparison of log K_1 with ionization potential for bivalent metal complexes of *N*-phenylbenzohydroxamic acid

Ion	I.P., *eV*	log K_1[15]
Cu^{2+}	27·92	10·36
Be^{2+}	27·46	8·68*
Zn^{2+}	27·28	7·51
Ni^{2+}	25·76	7·00
Mn^{2+}	23·13	6·02

* This work.

It was found that the Hammett equation is applicable to the K_1 values for the beryllium complexes; a plot of log K_1 *vs.* σ being linear: log K_1 = 8·66 − 1·225 σ. The values of log K_1, log K_2, and pK_a decrease when the substituted acids are arranged in the order

$$CH_3OR > CH_3R > HR > ClR > BrR > NO_2R$$

where R represents $-C_6H_4.CO.NOH.C_6H_5$.

Comparison of the metal ionization potentials and K_1 *values*

It is observed that log K_1 of *N*-phenylbenzohydroxamic acid is linearly related to the ionization potential for Mn, Ni and Zn (Table 2) but the beryllium and copper complexes have higher stability. In the case of copper this may be attributed to the Jahn–Teller effect, and in that of beryllium to the small radius of the beryllium ion.

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Summary—The thermodynamic stability constants of beryllium(II) complexes of *p*-substituted *N*-phenylbenzohydroxamic acids have been determined in 50% v/v aqueous dioxan at 35°. The effect of methoxy, methyl, chloro, bromo, and nitro groups as substituents is discussed. There is a linear relationship between log K_1 and pK_a, and the Hammett equation is applicable. The beryllium complexes have been compared with those of Cu, Zn, Ni and Mn.

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ANALYTICAL PROPERTIES OF 1,3-CYCLOHEXANEDIONE BISTHIOSEMICARBAZONE MONOHYDROCHLORIDE

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Thiosemicarbazones are interesting as analytical reagents. Monothiosemicarbazones with an electron-donating group in the α-position have been studied the most. In this paper the synthesis, properties and analytical possibilities of a β-thiosemicarbazone, *viz*. 1,3-cyclohexanedione bisthiosemicarbazone monohydrochloride (1,3-CHDT·HCl), are described for the first time.

EXPERIMENTAL

Preparation of the compound

A hot solution of 2·0 g of 1,3-cyclohexanedione in 6 ml of ethanol was added dropwise to a stirred solution of 3·26 g of thiosemicarbazide dissolved in 14 ml of water, 12 ml of ethanol and 3 ml of concentrated hydrochloric acid. A white product separated and was purified by washing with ethanol (m.p. 240–242°; yield, 75%). Found: C 32·7%, H 5·1%, N 28·5%. Calculated for $C_8H_{14}N_6S_2 \cdot HCl$: C 32·60%, H 5·09%, N 28·50%. The purity of the product was found to be 99·2% by direct titration with 0·05*M* sodium hydroxide with phenolphthalein as indicator.

To obtain the 1,3-cyclohexanedione bisthiosemicarbazone a hot saturated solution of 1,3-CHDT·HCl was neutralized with 5*M* sodium hydroxide. As the solution cooled a yellow product crystallized out (m.p. 175–177°, decomp.). The yield was poor. Found: C 37·5%, H 5·6%, N 31·9%, S 24·9%. Calculated for $C_8H_{14}N_6S_2$: C 37·21%, H 5·42%, N 32·55%, S 24·80%.

Properties

Some physicochemical properties of 1,3-CHDT·HCl are summarized in Table 1. The absorption spectra at various pH values are shown in Fig. 1. Dilute aqueous solutions of 1,3-CHDT·HCl ($7{\cdot}75 \times 10^{-5}M$) were not very stable, but 0·1% solutions in hydrochloric acid were stable for more than a month. The p*K* values were calculated from the absorption spectra of solutions of 1,3-CHDT·HCl at different pH values from 0·5 to 13·0.[1] The p*K* values shown in Table 1 are the arithmetic mean of the values obtained from measurements at four different wavelengths. The pK_1 value was also determined by potentiometry.

TGA shows a loss of ammonium chloride from 1,3-CHDT·HCl and loss of ammonia from 1,3-CHDT. As in the solutions, the compound is stabilized by protonation.

A peak at 5·7 ppm in the NMR spectrum of the compound dissolved in deuterium oxide indicates the presence of a vinyl proton.

Table 1. Physicochemical properties of 1,3-cyclohexanedione bisthiosemicarbazone monohydrochloride

Solubility in water, *g/l.*	20·81
Solubility in ethanol, *g/l.*	0·84
Solubility in chloroform, *g/l.*	0·03
Solubility in n-amyl alcohol, *g/l.*	0·09
>C═S frequency, cm^{-1}	845
pK_1 (photometric method)	4·7
pK_1 (potentiometric method)	4·75
pK_2 (photometric method)	10·5

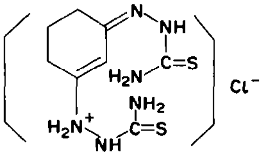
Reactions with cations and anions

The reactions of 40 cations and 13 anions with 1,3-CHDT·HCl were tested at different pH values. The samples were prepared in 50-ml volumetric flasks with 2 or 8 ppm of ion, 10 ml of 0·1% solution of 1,3-CHDT·HCl in 0·01*M* hydrochloric acid, 5 ml of dimethylformamide and 2 ml of 1*M* sodium hydroxide, buffer solution or 1*M* hydrochloric acid, and dilution to 50 ml with distilled water. The absorbance was measured at 350–700 nm against reagent blanks. The most important results are summarized in Table 2.

RESULTS AND DISCUSSION

1,3-Cyclohexanedione bisthiosemicarbazone monohydrochloride is as easily obtained by condensation in hydrochloric acid medium as the α-bis-thiosemicarbazones,[2] probably because it is stabilized as the hydrochloride. In general, the sythesis of β-bisthiosemicarbazones is more complicated[3] and produces thiazoles under the conditions of our synthesis.[4]

The presence of a vinyl proton and the fact that 1,3-CHDT·HCl is obtained as the monohydrochloride shows that there is a quaternary ammonium group. From these results we propose the following structure:



This structure is consistent with the loss (in the TGA) of ammonium chloride from 1,3-CHDT·HCl and ammonia from 1,3-CHDT to give the same product.

The bathochromic shift of a strong absorption band from 309 to 360 nm indicates that in solution, on increasing the pH, the acid is neutralized and the >C═S group is enolized and dissociated.[5]

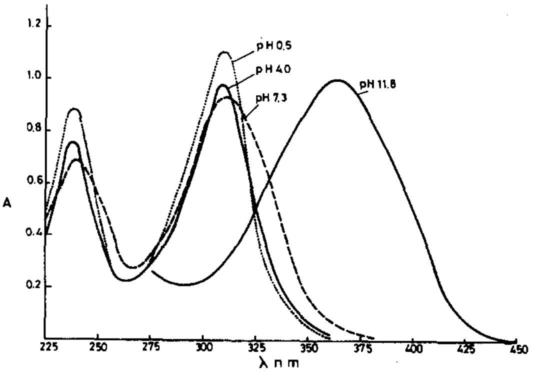


Fig. 1. Absorption spectra of $7{\cdot}75 \times 10^{-5}M$ 1,3-CHDT·HCl in water at different pH-values.

Table 2. Characteristics of 1,3-cyclohexanedione bisthiosemicarbazone compounds

Ion	pH	λ, *nm*	ε, *l. mole*$^{-1}$·*cm*$^{-1}$	p*D**	Observations	
					Ppte.	Soln.
Ag(I)	10			4·7	brown red	
Pb(II)	6·3			5·7	violet red	
Pb(II)	10			5·8	yellow red	
Hg(I)	10			4·6	yellow brown	
Tl(I)	10			4·5	brown red	
Bi(III)	2	540	1·25 × 10^4	4·6		violet red
Cd(II)	6·3	525	1·15 × 10^4	6·5		red
Cd(II)	10			6·0	red	
Hg(II)	10			4·7	yellow	
Au(III)	6·3	360	1·58 × 10^4	—		yellow
Au(III)	10			5·0	yellow	
Pt(IV)	6·3	360	2·27 × 10^4	—		yellow
Se(IV)	5			4·4		brown red
Te(IV)	10			5·0		yellow red
Cu(II)	6·3	350	2·32 × 10^4	6·5		yellow
Cu(II)	10			6·7		yellow
Pd(II)	6·3	370	1·92 × 10^4	4·7		yellow brown
Pd(II)	10			5·2	brown red	
Co(II)	6·3	370	2·80 × 10^4	6·7		yellow brown
Co(II)	10			7·0		yellow brown
Zn(II)	6·3	510	1·42 × 10^4	6·4		red
Zn(II)	10			6·5		red
Ni(II)	6·3	410	1·32 × 10^4	6·4		red
Ni(II)	10			6·5		red
CrO_4^{2-}	5			5·4		yellow
IO_3^-	<3	410	1·23 × 10^4	6·4		yellow
NO_2^-	<2	<350		5·0		yellow
MnO_4^-	<2	<350		5·0		yellow
BrO_3^-	<2	410	1·51 × 10^4	6·2		yellow

* p*D* = logarithm of reciprocal of detection limit concentration.

In general, bisthiosemicarbazones are easily oxidized or reduced and in acid medium are easily hydrolysed. 1,3-CHDT·HCl is unstable towards strong redox agents but is not hydrolysed by acids, and can be used in acidic solutions.

The stability, solubility in water, absence of absorption in the visible region and the sensitive reactions with several ions to form intensely coloured compounds, show that 1,3-CHDT·HCl is an interesting analytical reagent.

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Summary—The synthesis and analytical properties of 1,3-cyclohexanedione bisthiosemicarbazone monohydrochloride are described for the first time. The solubility, spectral characteristics, p*K* values and reactions with 40 cations and 13 anions are reported.

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ANNOTATION

THE EFFECT OF PLATINUM(IV) ON THE COULOMETRIC GENERATION OF TIN(II)

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(*Received* 19 *February* 1975. *Revised* 8 *May* 1975. *Accepted* 4 *July* 1975)

Most titrimetric methods for determination of platinum are based on the preliminary reduction of platinum(IV) to platinum(II); the excess of reducing agent is then determined or is destroyed and the platinum(II) titrated. This is the basis of the biamperometric method of platinum determination, which has been applied to analysis of several technical materials.[1,2] A simpler method would be direct reductometric titration of platinum(IV) but it is difficult to find a convenient titrant. A good reagent of this sort should be tin(II), but its solutions are unstable. Therefore electrogeneration of tin(II) should be considered.

Several authors have investigated electrolytic generation of tin(II) by reduction of tin(IV). Those studies indicate the difficulty of getting 100% current efficiency, which depends on the electrolyte composition and the type of electrode used. Because of competitive reduction of hydrogen ions, the choice is limited to electrodes which have a high overpotential for hydrogen evolution and electrolytes in which the formal potential of the Sn(IV)/Sn(II) system is as positive as possible. However, in some electrolytes tin(II) may be too weak a reducing agent for practical determinations.

Bard[3] has studied titration with electrogenerated tin(II) and its application to the determination of platinum. He used $4M$ NaBr/$0{\cdot}3M$ HCl/$0{\cdot}2M$ $SnCl_4$ as electrolyte with gold or platinum electrodes. In our experiments we failed to obtain satisfactory results by use of those conditions. Ginstrup[4] also used electrogenerated tin(II) for platinum(IV) reduction under those conditions, but the determination was completed by oxidation with bromine. He also mentioned difficulties in obtaining 100% efficiency of tin(II) generation. We have been trying to develop a coulometric titration for platinum and have investigated electrogeneration of tin(II) as the titrant. This paper described the difficulties encountered.

EXPERIMENTAL

Reagents

Platinum(IV) solution was obtained by dissolution of 99·99% pure platinum foil in *aqua regia*, evaporation three times with hydrochloric acid, and dilution to standard volume.

Sodium bromide, $4M$ solution; sodium chloride, $4M$ solution; calcium chloride, $5M$ solution; tin(IV) chloride, $2M$ solution; cadmium chloride, $0{\cdot}5M$ solution: all were prepared from analytical-grade reagents.

Apparatus

Coulometric analyser (Radelkis OH-404), pH-meter (N-512, Elpo-Poland), quartz clock (C-549, Elpo).

All measurements were carried out in a 150-ml cell.

RESULTS AND DISCUSSION

Coulometric generation of tin(II)

Tin(II) was generated in concentrated halide solutions, namely $6M$ hydrochloric acid, $3M$ sodium bromide, $3M$ sodium chloride, or $2M$ calcium chloride, the last three being acidified to be $0{\cdot}2M$ in hydrochloric acid. Gold, platinum, graphite, graphite impregnated with paraffin[5] and glassy carbon (surface area about 1 cm^2) were used as electrodes. A cadmium bar was used as the anode, in $0{\cdot}5M$ cadmium chloride, separated by a sintered-glass disc from the rest of the electrolytic cell.

The efficiency of generation was calculated on the basis of the voltammetric curves obtained for solutions with and without tin(IV) (Figs. 1 and 2). The potential of the electrode was potentiostatically controlled and varied at 0·05 V intervals in the range from 0 to $-1{\cdot}0$ V *vs.* SCE.

In all cases an increase of tin(II) generation was

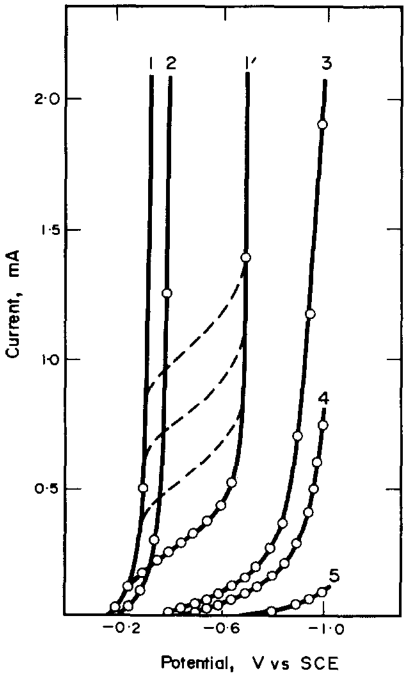

Fig. 1. Voltammetric curves obtained for various electrodes (approx. 1 cm^2 surface area) in $3M$ NaBr/$0{\cdot}2M$ HCl. 1—platinum, 2—gold, 3—graphite, 4—glassy carbon, 5—paraffin-impregnated graphite. The dashed lines indicate results for various degrees of passivation of the platinum electrode.

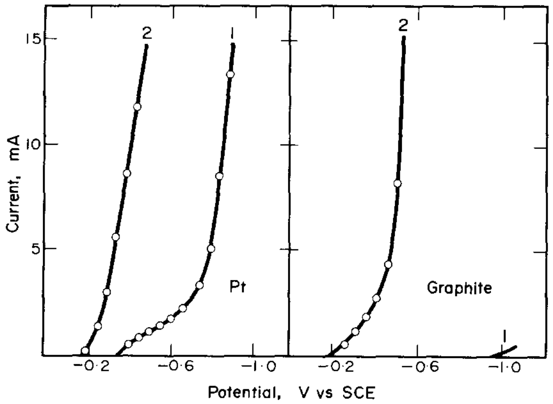

Fig. 2. Voltammetric curves for the platinum and paraffin-impregnated graphite in the following electrolytes: 1—3*M* NaBr/0·2*M* HCl, 2—3*M* NaBr/0·2*M* HCl/0·2*M* $SnCl_4$.

observed for current densities above 10 mA/cm^2, but at 20 mA/cm^2 reduction of tin(IV) to metal was observed (Fig. 3). However, this does not influence the efficiency of generation of the reducing agent, which remains constant at current densities up to 50 mA/cm^2.

The efficiency at metallic electrodes was lower than that at graphite electrodes, the highest being for the paraffin-impregnated graphite. With this electrode, for 0·2*M* tin(IV) chloride, the calculated efficiencies are

3*M* NaCl + 0·2*M* HCl	99·7–99·9%
3*M* NaBr + 0·2*M* HCl	99·7–99·9%
2*M* $CaCl_2$ + 0·2*M* HCl	99·9–99·98%
6*M* HCl	98–99%

In 6*M* hydrochloric acid, generation of tin(II) proceeded satisfactorily only at the graphite electrodes. In the other media the efficiency at the gold electrode was about 0·5% lower that at the impregnated graphite electrode. For the platinum electrode the results were still lower, and significantly dependent on the nature of the platinum surface. The results were especially poorly reproducible in sodium bromide. The passivated platinum electrode was found better than gold, but freshly cleaned platinum has an efficiency lower by several per cent. The current–potential curves for platinum electrodes passivated to various degrees are indicated by dashed lines in Fig. 1. Change of tin(IV) concentration from 0·02 to 4*M* increases the limiting current density at which tin(IV) is reduced to metal, causing the better efficiency of Sn(II) generation only up to 2 mA/cm^2. For greater current densities the concentration of Sn(IV) does not influence the efficiency of Sn(II) generation (Fig. 4).

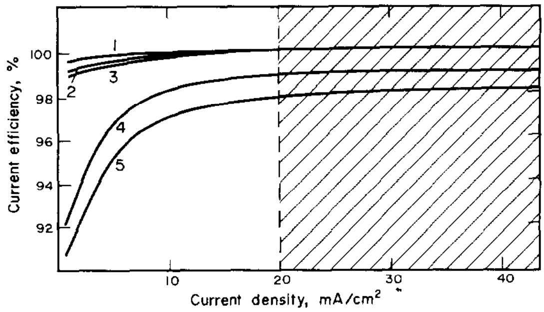

Fig. 3. Current efficiency of tin(II) generation at the various electrodes in 3*M* NaBr/0·2*M* HCl/0·2*M* $SnCl_4$: 1—paraffin-impregnated graphite, 2—graphite, 3—glassy carbon, 4—platinum, 5—gold. The shaded area corresponds to the range of current density where metallic tin is deposited on the electrode.

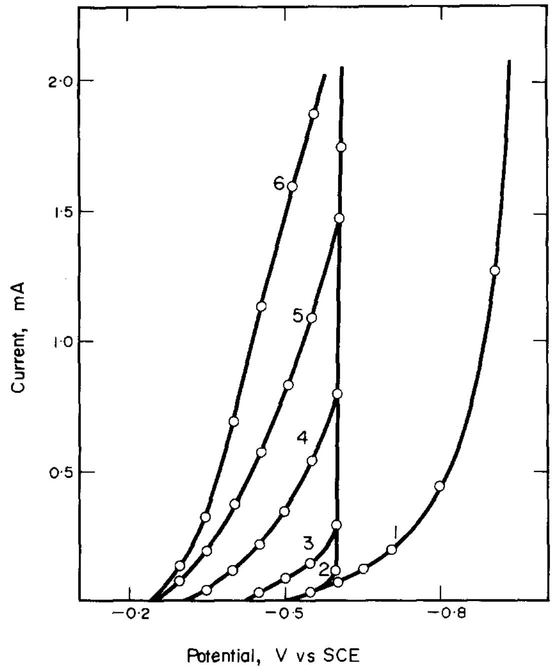

Fig. 4. Voltammetric curves for the paraffin-impregnated graphite electrode in 3*M* NaBr/0·2*M* HCl containing the following concentrations of $SnCl_4$: 1—0, 2—0·02*M*, 3—0·05*M*, 4—0·1*M*, 5—0·2*M*, 6—0·4*M*.

Titration of platinum

To obtain high current efficiency in the generation of tin(II) the current density should be at least 10 mA/cm^2, but too great an increase in current density may favour reduction to the metal, which prolongs the titration. Therefore intermediate current densities were used in the range from 10 to 20 mA/cm^2. Impregnated graphite or platinum were used for the working electrodes. Titrations were done in a nitrogen atmosphere with a working electrolyte volume of 100 ml, 1 ml of platinum solution being added as sample by microburette, thus enabling several titrations to be done in one solution. The end-point was determined potentiometrically, using a platinum indicator electrode. Titration of 1–10 mg of platinum in 3*M* sodium bromide medium proceeds slowly, as the result of a slow redox process as well as slow establishment of the potential of the indicator electrode. These conditions correspond to those used by Bard.[3] In subsequent titrations in the same electrolyte solution the potential end-point break systematically decreases. The results indicate insufficient titration efficiency (Table 1), contrary to the previously obtained efficiency data based on voltammetric curves. When several samples are titrated in the same solution, the titration efficiency systematically decreases, whichever electrode is used. This behaviour is more marked at higher current density.

The same effects were much more obvious in titrations in 3*M* sodium chloride medium. Under those conditions the presence of platinum(IV) has a catalytic effect on the electrolytic reduction of hydrogen ions. For platinum concentrations of 10 μg/ml the efficiency is only about 95%, and decreases with increasing platinum concentration; at the 100 μg/ml level the titration is completely impossible.

These processes can be explained and summarized as follows. In the presence of platinum(IV) the products of

Table 1. Titration of platinum with electrogenerated tin(II) (100 ml of electrolyte)

Electrolyte composition	Current density, mA/cm^2 (electrode)	Platinum, *mg*		Current efficiency, %
		Taken	Found	
$3M$ NaBr $0{\cdot}3M$ HCl $0{\cdot}2M$ $SnCl_4$	10 (paraffin-impregnated graphite)	9·97	10·23	97·7
			10·23	97·7
			10·28	97·3
			10·17	98·2
			10·40	96·0
		5·06	5·06	100·0
			5·13	98·9
			5·13	98·8
			5·18	97·8
	15 (platinum)	5·06	4·88	103·8
			5·13	98·9
			5·21	97·1
			5·25	96·5
			5·30	95·5
$3M$ NaCl $0{\cdot}3M$ HCl $0{\cdot}2M$ $SnCl_4$	10 (paraffin-impregnated graphite)	1·065	1·12	95·5
			1·08	98·5
			1·12	95·0
		5·33	6·01	88·7
			6·54	81·6
			8·12	65·7

Results for each weight of platinum shown as taken were obtained by successive titrations in the same electrolyte solution.

electrolytic reduction of tin(IV) react according to

$$Pt(IV) + Sn(II) \rightarrow Pt(II) + Sn(IV)$$

$$Pt(IV) + Sn(0) \rightarrow Pt(II) + Sn(II)$$

but at low current densities direct reduction of platinum to the metal is also possible:[2]

$$Pt(IV) + 4e \rightarrow Pt(0)$$

At high current densities the contribution of the catalysed hydrogen evolution significantly increases:

$$2H^+ + 2e \xrightarrow{Pt} H_2$$

When an electrode covered with metallic tin is immersed in tin(IV) solution, slow dissolution of the metal proceeds. If this solution also contains platinum(IV), hydrogen is vigorously evolved at the electrode surface immediately. This indicates that the reduction of hydrogen ions by metallic tin proceeds according to the equation:

$$Sn(0) + 2H^+ \xrightarrow{Pt} Sn(II) + H_2$$

The reduction of hydrogen in the absence of platinum compounds in the solution is very slow because of the high overpotential of hydrogen evolution in spite of thermodynamically favourable conditions. The addition of platinum(IV)—and to a smaller extent platinum(II), because of the less favourable kinetics in the latter case—produces platinum black at the electrode surface. This is responsible for the formation of the centres exhibiting a seriously diminished overpotential for hydrogen evolution.

The catalytic effects of platinum(IV), occurring at the electrode as well as in the chemical process, may also have a significant effect in coulometric titrations with reducing agents other than tin(II). The greater stability of the $PtBr_6^{2-}$ complex compared with $PtCl_6^{2-}$ is responsible for the somewhat better results in bromide solutions, where the catalytic activity of platinum is smaller.

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Summary—The current efficiency of tin(II) generation has been measured for various electrolytes and electrodes. The best results (>99·9%) were obtained with the paraffin-impregnated graphite electrode in $2M$ $CaCl_2$ + $0{\cdot}2M$ HCl + $0{\cdot}2M$ $SnCl_4$. In titrations of platinum(IV) with electrogenerated tin(II) in an electrolyte containing chloride or bromide it was found that the presence of platinum(II) or (IV) interferes in the cathodic generation of tin(II). The platinum is reduced to the elemental state at the electrode and causes simultaneous generation of hydrogen which decreases the current efficiency. This effect is more pronounced in chloride media.

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LETTER TO THE EDITOR

DERIVATION OF THE SAMPLING CONSTANT EQUATION

Sir:

In 1972, Ingamells and Switzer[1] published a general equation for the sampling constant of a two-mineral mixture of uniform grain size. Derivation of this equation was not given in detail, and a typographical error, undiscovered in proof, interchanged subscripts on two terms. The correct equation is

$$K_s = \left(\frac{Bd_B - Hd_H}{K}\right)^2 \cdot \frac{p_w q_w u^3 w}{d_B w_H + d_H w_B} \cdot 10^{-8} \text{ grams} \qquad (1)$$

[i.e., with $(d_B w_H + d_H w_B)$ in the denominator, not $(d_B w_B + d_H w_H]$. In this equation, B and H are the X-contents of the two constituent minerals, K is the X-content of the mixture, p_w and q_w are the weight proportions of the two minerals, w is the weight of a sample containing w_H grams of one mineral and w_B grams of the other, u is the linear dimension (grain size) in μm, and K_s is the sampling constant for the constituent of interest, X, (i.e., the weight of the mixture which must be taken to ensure a sampling error of no more than 1% with 68% confidence). This equation may be derived as follows.

If q and p are the volume proportions of the two minerals in the mixture, it is identically true that

$$\frac{q}{p} = \frac{d_H q_w}{d_B p_w}\ , \quad p_w + q_w = 1\ , \quad p + q = 1 \qquad (2)$$

where d_B and d_H are the densities of the two minerals in g/cm^3.

The total relative sampling error, R (%), is related to the relative sampling error R_H incurred in sampling the constituent with X-content H and the relative sampling error R_B incurred in sampling the constituent with X-content B:[2]

$$KR = \left| p_w H R_H - q_w B R_B \right| \qquad (3)$$

From Kleeman,[3] we have the binomial relationships

$$R_H = \frac{100}{\sqrt{n}}\sqrt{\frac{q}{p}} \quad \text{and} \quad R_B = \frac{100}{\sqrt{n}}\sqrt{\frac{p}{q}} \qquad (4)$$

Also, identically,

$$K = p_w H + q_w B \text{ and } q_w = \frac{w_B}{w}\ , \quad p_w = \frac{w_H}{w} \qquad (5)$$

Substituting (4) in (3) and squaring,

$$K^2R^2 = \frac{10^4}{n}\left(p_w H\sqrt{\frac{q}{p}} - q_w B\sqrt{\frac{p}{q}}\right)^2 \qquad (6)$$

Substituting (2) in (6),

$$K^2R^2 = \frac{10^4}{n}\left(H\sqrt{p_w q_w d_H/d_B} - B\sqrt{p_w q_w d_B/d_H}\right)^2 \qquad (7)$$

$$= \frac{10^4\ p_w q_w}{n}\left[\frac{(d_H H)^2 + (d_B B)^2 - 2\ BH d_B d_H}{d_B d_H}\right]$$

whence

$$R^2 = \frac{10^4 p_w q_w}{n d_B d_H}\left(\frac{Bd_B - Hd_H}{K}\right)^2 \qquad (9)$$

By definition,[1]

$$K_s = R^2 w \tag{10}$$

The number of equal-sized cubic grains in a sample of weight $w_H + w_B = w$ is

$$n = \frac{w_H}{d_H(10^{-4}u)^3} + \frac{w_B}{d_B(10^{-4}u)^3} \tag{11}$$

$$= \frac{d_B w_H + d_H w_B}{d_H d_B (10^{-4}u)^3} \tag{12}$$

Substituting (9), then (12), in (10) gives the correct equation (1). This equation may be put in several different forms by substituting the identities (2) and (5) and through the use of appropriate approximations: putting $p_w = w_H/w$, $q_w = w_B/w$, and $K = p_w H + q_w B$,

$$K_s = \left(\frac{Bd_B - Hd_H}{Bw_B + Hw_H}\right)^2 \cdot \frac{w_B w_H u^3 w}{d_B w_H + d_H w_B} \cdot 10^{-8} \text{ grams} \tag{13}$$

or, with $w_H = p_w w$ and $w_B = q_w w$

$$K_s = \left(\frac{Bd_B - Hd_H}{p_w H + q_w B}\right)^2 \cdot \frac{p_w q_w u^3}{p_w d_B + q_w d_H} \cdot 10^{-8} \text{ grams} \tag{14}$$

or, solving (2) and (5) to eliminate p_w and q_w, obtaining
$p_w = (B - K)/(B - H)$ and $q_w = (K - H)/(B - H)$,

$$K_s = \frac{(Bd_B - Hd_H)^2 (B - K)(K - H)u^3}{d_B(B - K)(B - H) + d_H(K - H)(B - H)} \cdot \frac{10^{-8}}{K^2} \text{ grams} \tag{15}$$

These equations involve no approximations. If the densities of the two component minerals are nearly the same,

$$K_{s(d_B \sim d_H)} \sim (B - K)(K - H)u^3 d_B \cdot \frac{10^{-8}}{K^2} \text{ grams} \tag{16}$$

If B is much larger than K (the common case in mineral exploration),

$$K_{s(B \gg K)} \sim (B - H)(K - H)u^3 d_B \cdot \frac{10^{-8}}{K^2} \text{ grams} \tag{17}$$

$$\sim B^2/K^2 \cdot p_w q_w u^3 d_B \cdot 10^{-8} \text{ grams} \tag{18}$$

Other forms are useful, depending on the application. The parameter u, which is rather artificial, may be replaced by an <u>effective</u> grain size, which may be estimated in a number of ways. In many real cases, the linear dimension of the mesh of the screen through which the material is passed is very close to the effective grain size.

Equation (17) may be derived in several ways: this is of interest because of its importance in mineral exploration and mine evaluation.[4] An alternative derivation has been published.[5]

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18 November 1975

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INSTRUMENTS IN ANALYSIS – CRITICAL REVIEWS

THE MASS FILTER

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The analytical function of a mass spectrometer consists in converting atoms or molecules into ions and segregating these ions according to their mass-to-charge ratio (m/e). The mass of the ions is related to the nature of the original atom or molecule and their abundance to the concentration of the atom or molecule in the sample under examination.

The segregation in the past has been most commonly achieved by accelerating the ions in a potential gradient and subjecting them to the influence of a transverse magnetic field. The ions suffer a deflection in their flight path, the extent of this deflection being related to their velocity and their mass-to-charge ratio. Instruments based on this principle have been in an active state of development for the past fifty years and at the present time a considerable number of different designs of magnetic deflection instruments are commercially available.

More recently, however, alternative systems of mass segregation have been developed, the most successful being that embodied in the instrument now known as the mass filter.

Charged particles moving with constant velocity will also suffer a deflection if exposed to a transverse potential gradient. Furthermore, if the potential gradient changes rapidly in strength or direction, the ions are sufficiently light to be able to follow these oscillations with appropriate changes in the extent or direction of their deflections, provided that the mean free path of the ions is sufficiently long, i.e., they make no collisions with gas molecules. The concept of beams of ions oscillating between a pair of electrodes was exploited by Paul and von Zahn who considered the possibility of relating the extent or direction of the oscillations to the nature of the ion, more particularly its mass-to-charge ratio. In the most successful arrangement, beams of ions are allowed to pass along the axis of a field created by four electrodes, disposed symmetrically around the flight path. Theoretically the establishment of an axially symmetrical field requires electrodes of hyperbolic cross-section, but in practice for ease of fabrication, four rods of circular cross section are used. When the rods are connected in opposite pairs to the output of a radio-frequency oscillator, ions have unstable trajectories. If, however, upon the radiofrequency field there is superimposed a d.c. field, the applied voltage (U) being less than one-sixth of the peak amplitude of the RF voltage (V), so that if P_x and P_y are the instantaneous potentials on the opposite rod-pairs and $P_x = -P_y = U + V \cos \omega t$ (where ω is the frequency of oscillation), then some ions have stable trajectories. After injection, ions can traverse the longitudinal space between the rods and emerge from the opposite end in a manner defined by the relationships

$$U = 1.212\, m\, \omega^2 r_0{}^2$$

$$V = 7.219\, m\, \omega^2 r_0{}^2$$

where r_0 is the field radius (in cm), ω is the frequency in MHz and m is the mass of the ion (relative to C = 12). It has been found that for a given RF frequency and a given peak voltage on the rods, only those ions with a closely defined mass-to-charge ratio can escape from the quadrupole rod assembly. The arrangement thus constitutes a mass filter, for an ion-source producing a multi-ionic beam may be coupled to the rod assembly and an ion-detector mounted at the far end. The mass-to-charge ratio of the ion reaching the detector is then selected by adjusting either the frequency, or more conveniently, the amplitude, of the RF voltage applied to the rods. While some of the properties of this quadrupole system are shared by other electrode geometries involving the use of rings or single poles and grounded strips, it is the quadrupole electrode system which has been commercially exploited and forms the basis of a number of recently developed instruments.

The first commercial design was marketed by the Atlas Company in Germany in the early sixties and had a mass resolution of 100. In less than ten years other manufacturers have produced instruments having a performance better by an order of magnitude. Before considering the future possibilities of mass filters it is appropriate to examine the advantages of this type of mass segregation over the more conventional magnetic deflection and to describe how these advantages are embodied in recent commercial designs. The chief advantage which was exploited in the earliest designs was the small size and simplicity of the rod assembly, commonly about 20 cm in length and 5 cm in diameter (the individual rods being less than 1 cm in diameter). Further, the rate at which the spectrum can be scanned is high, scan-time being in the msec range. This is not as fast as the time-of-flight mass spectrometer, but faster than the magnetic deflection instruments and allows the spectrum to be displayed upon an ordinary rather than a long-persistence oscilloscope.

The mass-selection system is not very demanding upon the homogeneity of the ion-beam as regards its direction or its velocity, so that comparatively simple ion-sources may be used, most having only three plates, and finally, the ion-accelerating voltage must not be too high, otherwise the ion cannot undergo sufficient oscillations between the rods to reveal its identity. As a result, most ion-sources operate with accelerating voltages below 100 V and this makes them more accessible to external probes and auxiliary equipment. The problems associated with the high accelerating potentials of magnetic deflection instruments are thus avoided.

The instruments now commercially available may be divided into two classes, those with mass resolutions of 100 or less, which are most commonly designed for the monitoring of residual gases in vacuum systems, and those with resolutions of 250 and above, which are used as low-resolution general purpose mass spectrometers.

RESIDUAL GAS ANALYSERS

The total pressure in vacuum systems is normally measured by means of an ionization gauge which collects and measures the ion-currents produced by ionizing all the constituents of the residual gas in the system. As vacuum systems become more efficient and complex and are applied to a variety of production processes there emerges a demand for a partial-pressure gauge, which not only gives a measurement of the total residual gas pressure, but also provides an indication of the composition of the residual gas by measuring ion-currents representative of each constituent. Because of the comparative ease of manufacture of mass filters with resolutions below 100, quadrupole partial-pressure gauges which can monitor the air, carbon dioxide, water vapour and hydrocarbon constituents of residual gases have been marketed. Their chief defect is their inability, because of low resolution, to distinguish between carbon monoxide and nitrogen. In its simplest form the quadrupole partial-pressure gauge consists merely of an ion-source, an analyser and a detector, bolted directly into the vacuum system to be monitored. Centronics have produced devices of this type, the simplest being a disposable gauge head having multiple filaments and a mass resolution of about 30. A more highly developed version is the model Q806 with a resolution of 100 and a sensitivity of better than 10^{-12} mmHg for nitrogen.

Similar instruments have been marketed by VG-Quadrupoles Ltd. The Q4 provides a measurement of total pressure, or alternatively, a reading of ion-current at any *m/e* value up to 60. It can be used for leak detection with a suitable probe gas, such as helium. Scanning facilities are provided in the more complex model Q7 which has twice the resolution and mass range. It provides a reading of total and partial pressures, but may be combined with a suitable inlet system, enabling it to carry out simple analytical tasks such as the monitoring of respiratory gases.

These devices are in competition with partial-pressure gauges based upon small radius (2 cm) 180° magnetic deflection instruments. These use permanent magnets, and scan by altering the ion-accelerating potential. If the mass filter is pumped separately and provided with an inlet system it can be used for stable-isotope tracing for such isotopes as nitrogen-15, oxygen-18 and carbon-13.

The E.A.I. Company in the U.S.A. were the first to produce a satisfactory instrument with a resolution in excess of 250, but this performance is exceeded by a range of instruments produced by the VG-Quadrupoles Company. Using molybdenum rods of 18 mm diameter, they have produced units with a resolution of 700 and a mass range of 350 (Model Q50). By reduction of the rod diameter to 12 mm the range has been extended to 800 and the resolution to 1200 (Model Q40). The most advanced quadrupole mass filter is that marketed by Finnegan Instruments. This has a mass resolution of 2000 and a mass range of 1000. The model 3300F incorporates a programmable ion-source allowing injection of ions with a velocity appropriate to the mass, thus giving improved sensitivity.

The short mass scan-time (about 0.1 sec) and the ability of the analyser to perform at comparatively high pressures (up to 10^{-4} mmHg) make the mass filter eminently suitable as a monitor for the effluents from gas-chromatography columns. Mass spectra of components of mixtures issuing from the chromatographic column can be recorded on a *U/V* recorder, displayed upon an oscilloscope or processed in a data system using a small computer. In addition, advantage is taken of the fast response-speed and scan-time to allow continuous monitoring of a selected small number of mass peaks. Similar diversity is incorporated into the Dodecapole instrument marketed by Hewlett Packard. In this device advantage is taken of the linear relationship between rod voltages and the masses of the ions transmitted. Mass marking is achieved neatly by matching a mass-peak displayed on an oscilloscope, with a blip on a second trace, the position of which is determined by an adjustable reference voltage. This voltage is indicated on a digital voltmeter directly in terms of mass. The Dodecapole is a more complex instrument in which the shortcomings of the single quadrupole mass analyser are minimized by the use of additional rod systems. The resolution is thereby increased to as high as 3000.

Opponents of the quadrupole system of mass analysis have claimed that it is particularly susceptible to contamination and that rod performance declines with use. The rod alignment is critical and may be disturbed by baking. However, at the present time, the choice between a low-resolution magnetic sector instrument and a quadrupole of comparable performance is difficult to make. It is significant that the Vacuum Generators Group of Companies market both types.

FUTURE PROSPECTS

Today, the mass filter is approximately in the same state of development as the single-focusing magnetic deflection system was in the late fifties, before the advent of the double-focusing mass analyser. While it is not possible to speculate upon the introduction of some similar revolutionary improvements in the case of mass filters, sufficient evidence is forthcoming to provide a guide to the possible ultimate performance of a simple quadrupole analyser. There are three broad areas of improvement: the sensitivity, the mass range and the mass resolution. If we accept that no great change is going to occur in either the efficiency of ionization within the ion-source or the degree of particle multiplication at the detector, then any increase in sensitivity is likely to come from improvements in the transmission of the rod system. The aperture into the rod system is not the physical but the electric aperture imposed by the fields. At present many of the ions produced in the ion-source do not pass through this aperture. Some undergo unstable trajectories under the influence of the fringing fields at the ends of the rods. Marked improvements in sensitivity have been achieved by reducing the effects of these fields with the aid of a second rod assembly which experiences only the RF voltages and guides the ions into the electric aperture. This aperture is reduced by increased resolution so for high-performance instruments the ultimate limitation may be space charge. The mass range of a quadrupole is limited by the voltage which can be applied to the rods to make the ions oscillate. This in turn is limited by the power requirements imposed upon the oscillator as the voltage rises. The power required increases with increase in rod dimensions so that power is saved by smaller rods, but these tend to be less efficient as the ions perform fewer cycles with a small rod assembly. Raising the frequency would correct this, but would once again call for increased RF power. These limitations are summarized in the equation

$$\text{Power (in W)} = 6.5 \times 10^{-4} \frac{Cm^2 \omega^5 r_0{}^4}{Q}$$

where C is the capacity of the rod assembly (in pF) and Q is the figure of merit of the power circuit. Multiple-analyser assemblies will probably permit recording of masses in the 1–2000 region, allowing competition on this score with magnetic deflection instruments.

The resolution obtainable with a quadrupole mass filter depends upon a number of factors. Mass peaks tend to be trapezoid in shape rather than Gaussian and increasing the d.c. to RF voltage ratio (U/V) converts these into triangles before the transmission drops to zero. With a constant U/V ratio the resolution depends not only on the accuracy with which the voltages can be kept constant, but more critically upon the accuracy of alignment of the rods and the quality of their surfaces.

Fyte has calculated that a quadrupole assembly capable of providing a resolution of 5000 would require an accuracy of alignment of 1 part in 4×10^7. This would require prohibitively expensive engineering of the highest precision. Already the rod system in the mass filter marketed by Finnegan instruments involves a precision of 1 part in 10^6. There is, however, one feature of the mass resolution of a quadrupole which is not yet completely exploited and that is the ability to change the U/V ratio during scanning. This changes the resolution and the sensitivity so that low masses are recorded with high sensitivity and low resolution and only the resolution necessary at any point on the mass-scale is actually employed.

We may therefore expect a slow and steady improvement in mass-filter performance over the next decade, allowing the device to compete successfully with other systems of mass analysis. The development of high-resolution instruments capable of comparison with double-focusing mass spectrometers must await the appearance of a new principle.

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TALANTA MINI-REVIEW*

RECENT APPLICATIONS OF QUANTITATIVE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY IN PHARMACEUTICAL RESEARCH

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Summary—Increasing use is being made of N.M.R. spectroscopy as a quantitative analytical tool. Recent developments (1970–mid-1975) in methods and reagents are discussed with special regard to the role of Fourier-transform spectrometers, lanthanide-shift reagents and the choice of standard materials. Applications to quantitative analytical problems in pharmaceutical research are listed together with an indication of the advantages of the N.M.R. method over official analytical procedures.

A previous review written by this author in 1970[1] was concerned with the application of quantitative N.M.R. methods to a range of pharmaceutical materials. This article describes recently developed instruments, accessories, reagents and techniques, together with applications of N.M.R. to the quantitative problems encountered by analysts working in pharmaceutical research and control. It is designed to extend coverage to summer 1975.

BOOKS AND GENERAL REVIEW MATERIAL

A comprehensive book describing the quantitative uses of N.M.R. has appeared.[2] Practical methods are well discussed with a multitude of applications to functional group analysis and to problems in pharmacy and industrial chemistry. Reports have also appeared in French[3] and English[4] concerning quantitative measurement on non-pharmaceutical products and in German[5,6] and English[7] on the general application of the quantitative N.M.R. approach to pharmaceutical[5,6] and forensic[7] chemistry. The importance of peak areas, signal shapes and saturation effects in quantitative N.M.R. is clearly set out in a manufacturer's publication.[8]

EQUIPMENT, REAGENTS AND TECHNIQUES

Instrumentation

A few examples of the use of dedicated computers of average transients (CAT) to enhance the signals from small quantities of material have appeared, *e.g.*, for sub-milligram levels of barbiturates in brain autopsy material,[9] DDT in tissues[10] and 30–40 μg levels of potentially carcinogenic polynuclear hydrocarbons.[11] The disadvantages of CAT accessories lie in baseline instability, resolution limitation and the need for long accumulation times.

The approach to the proton N.M.R. spectra of small quantities and to low abundance nuclei (*e.g.*, ^{13}C) has been revolutionized by the advent of the Fourier-transform spectrometer. The high cost of this equipment has to be offset against the ease of obtaining good proton spectra on μg quantities within a few hours and the excellent resolution which can be achieved. A constant problem with this technique lies in the impurities present in commercial N.M.R. solvents. These may be insignificant when a conventional instrument is used but become very apparent, even at the μg level, on accumulation. It is helpful to store these solvents over a clean molecular sieve in glass- (not plastic-) stoppered bottles to minimize peaks due to water or leached plasticizer. Pre-washing of the N.M.R. tube with D_2O/MeOH-d_4 is also a help in reducing the water peak. Alternatively, and more satisfactorily when solubility permits, one can use capillary microcell inserts (*e.g.*, for the Varian XL-100[12]) with the sample material dissolved in only a few μl of solvent. Fourier-transform spectrometers are unlikely to come within the budget of the smaller control laboratory for several years but the analyst with occasional access to this equipment is in a position to resolve some hitherto insoluble problems.

Lanthanide-shift reagents (*LSR's*)

This family of organometallic reagents has achieved wide popularity amongst chemists and analysts for separating and simplifying the N.M.R. peaks of complicated molecules and of normally unresolved isomeric mixtures. In this respect, a low-cost instrument can sometimes match, or surpass, the performance of the most powerful superconducting-magnet systems. A recent review (1970–1973) lists nearly 500 papers but only a handful exploit the potential of LSR's for

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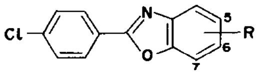
* For reprints of this Mini-Review, see Publisher's announcement near the end of this issue TALMR3.

quantitative analysis.[13] Applications of LSR's to problems in pharmaceutical research and outside N.M.R. (*e.g.*, to gas chromatography[14] and infrared spectrophotometry[15]) are very scarce. The scope of LSR-assisted analysis is indicated below.

Positional isomers and homologous series. The anti-inflammatory compound, "Benoxaprofen" (**I**, R in the 5-position) has been analysed for possible impurities (R in the 6- or 7-positions).[16]



I, R is —CH(Me)CO_2H

All compounds were converted into their methyl esters. No separation of peaks was seen in $CDCl_3$ solution but addition of an LSR resolved the peaks of the methyl esters and the side-chain methyl groups, allowing assay of the impurities. With a 90-MHz Fourier-transform spectrometer, a minimum detection limit of 0·2% for the 6- or 7-isomers was achieved. On conventional instruments the detection limit was 3–4%. It has also been possible to determine the isomeric *o*-, *m*- and *p*-cresols in admixture[17,18] and analyse mixtures of homologous (C_1–C_6) alcohols[19] and carboxylic acids (C_1–C_8).[20]

Optical isomers (enantiometers). Optically active lanthanide-shift reagents form diastereoisomers with mixtures of optical isomers.[13,21] In favourable cases, the N.M.R. signals of the enantiomers are clearly distinguished and the enantiomer ratio can be calculated. This technique can be used[22] for detecting low levels of unwanted L(+) penicillamine in the D(−) enantiomer after a simple derivative-formation step. The limit of detection is 0·4% with a Fourier-transform spectrometer (see Fig. 1).

Separation of enantiomer peaks can sometimes be improved by using an LSR and an optically active solvent.[23] The N.M.R. method yields results which compare very favourably with enantiomer ratios based upon optical activity, but without the need to prepare an optically pure specimen of one enantiomer as calibration standard.[21,24]

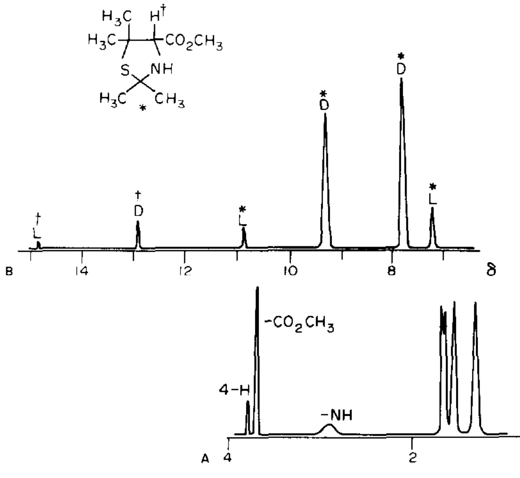


Fig. 1. A. Spectrum of acetone adduct of penicillamine (D : L isomer ratio = 92 : 8). B. Part spectrum of adduct after addition of 0·45 mole equivalents of optically active europium shift reagent.[22] (Reprinted by permission of the copyright owners).

Cis/trans *isomers and diastereoisomers.* The *cis/trans* ratio of oxime isomers can be readily determined with the aid of europium-shift reagents.[25] This method offers advantages over previous N.M.R. techniques using benzene solvent shifts. The same ratio can also be determined for vitamin A isomerization,[26] aminocyclohexylmethanes[27] and oleate/elaidate esters.[28] However, it is known that LSR's can themselves affect the ratio of *cis/trans* isomers in secondary amides[29] and this complication must be eliminated before reliance can be placed on assay figures.

A new isoxazolobenzoxazine anti-inflammatory agent consists of a pair of diastereoisomers, and a convenient method using a europium-shift reagent is available for their assay.[30] Similarly, the N.M.R. peaks for the diastereoisomeric tetrahydropyranyl ethers of cholestanes and cholestenes are clearly resolved when such a reagent is added.[31]

Other quantitative applications of LSR's. These include the analysis of mixtures of tocopheryl acetates,[32] glycerinformals,[33] steroidal enones and polyenones[34] and of polymers derived from chloroprene[35] and polyalkylene glycols.[36,37] Lanthanide reagents closely related to LSR's can also be used to distinguish between substrate molecules which are "inside" and "outside" a model cell membrane system.[38]

Use of nuclei other than the proton

Fourier-transform N.M.R. spectrometers allow one to obtain spectra for ^{13}C nuclei within a few hours (30–50 mg of material). The ^{13}C spectrum is often much simpler to interpret than the corresponding proton spectrum, because of extended chemical shifts. Serious drawbacks to ^{13}C N.M.R. quantitative analysis are the low inherent sensitivity and the lack of correspondence between peak areas and relative numbers of carbon atoms. This is due to unequal peak enhancements, attributable to varying nuclear Overhauser effects and relaxation times. Shoolery[39] has discussed methods of overcoming these problems by using gated decoupling or special shiftless relaxation reagents (preferring the latter for speed). He gives examples of the analysis of acenaphthenes and corn and crude oil samples. Good agreement is found between the ^{13}C and iodine-number assays. Other workers have assumed that chemically similar compounds in mixtures will show approximately the same relaxation and nuclear Overhauser effects and assumed exact equivalence of peak areas and carbon atom content, *e.g.*, for 2,4- and 2,6-isocyanatotoluenes,[40] n- and iso-paraffin oils[41] and *cis/trans* polypentenamers.[42]

N.M.R. spectra obtained for the ^{19}F nucleus are also characterized by larger chemical shift differences (and hence simpler spectra). In contrast to ^{13}C, the nucleus has 100% natural abundance and is of high inherent sensitivity. It is possible to convert μg quantities of hydroxysteroids into their trifluoroacetates and assay them by using the ^{19}F peaks.[43] Other examples include simple aliphatic alcohols[44,45] (with trifluoroacetic acid or hexafluoroacetone), xylenols,[46] terpenols,[47] amino-acids and peptides[48] and hydroxyl groups in polymers.[49]

Bowen and co-workers have reported the only relevant application of the ^{31}P nucleus, *i.e.*, the analysis of a sucrose/aqueous phosphorylcolamine formulation, with sodium triphosphate as added standard.[50]

N.M.R. analysis of liquid/solid components

The analysis of liquids in the presence of solid materials has been further exploited in the last five years. Most applications have been concerned with the liquid contents of fats,[51] meats[52] and cereal and oil seeds.[53] A pulsed N.M.R. spectrometer provides a particularly rapid means of analysing fats and margarines.[54]

Lawrenson has shown that a low-cost permanent-magnet spectrometer can be applied cryoscopically to a variety of problems, including the purity control of phenol, cyclohexanone and a pesticide.[55]

Computer simulation of spectra

This method may be of assistance in cases where the components to be determined possess N.M.R. peaks which overlap seriously (*e.g.*, closely similar aromatic compounds). Although a chromatographic method of analysis may often prove most suitable, it is still possible to proceed by N.M.R. A computer is programmed to accept the individual spectra of the components and an estimated weighting is put on these. The summed spectra are then calculated. The weightings can then be varied by an iterative procedure until the best fit of observed and calculated spectra is obtained. A drawback to this procedure arises from small variations in frequency with concentration and with intermolecular interactions, but a frequency shift of 2–3 times the peak width appears to be tolerable if a suitable line-broadening parameter is included. Quantitative analysis by this procedure has been mentioned briefly[8] and a full paper has recently appeared.[56]

Standards added for quantitative analysis

The criteria for internal standards for quantitative analysis are that they possess a sharp N.M.R. absorption in a clear region of the spectrum and are easily purified materials reacting with neither solvent nor analysed substance. The addition of an unrelated standard to the solution under test is preferred to the use of solutions of the pure material and separate analysis of their spectra. In the former, instrumental conditions (field homogeneity and integral response,) are identical and it is possible to assay without the necessity of preparing a very pure sample of the unknown.

In his book, Kasler[2] presents a comprehensive series of 128 likely internal standards. A choice can be made on the basis of an optimum "window" in the N.M.R. spectrum of the unknown. It is important to remember that some apparently well-suited standards may be precluded because they are unstable when strong acids or bases are to be analysed (*e.g.*, *sym*-tetrachloroethane with base) or because of molecular interactions (*e.g.*, donor–acceptor complexes with polynitrobenzenes) which can cause unacceptably large chemical shifts. Two groups[50,57] give a shorter selection of standards for non-polar solvents, including hexamethylcyclotrisiloxane, hexamethylbenzene, dimethylsulphoxide, t-butanol, methanol, malonic, maleic and succinic acids, *p*-benzoquinone, *p*-dichlorobenzene and 1,2,4,5-tetrachlorobenzene. We have found one of the standards hexamethylcyclotrisiloxane ($\delta = 0{\cdot}15$), trioxan ($\delta = 5{\cdot}10$) or pyrazine ($\delta = 8{\cdot}51$) suitable for any quantitative assay problem when using $CDCl_3$ or $CDCl_3/(CD_3)_2SO$ mixture. It may be advantageous to add two standards to improve the precision of the analysis and to detect any decomposition of one of these.[58] This "dual standard" approach has been used in a reverse manner to analyse mestranol by means of both the ethinyl and the methoxyl protons of the drug and a single added standard. The presence of starting material impurity was indicated by the discrepancy between the assay figures for the chosen mestranol protons[59] as well as by analysis using thin-layer chromatography.

Aqueous solutions are less frequently assayed.[50,57,60] Standards suitable for this medium are sodium acetate, maleic acid, succinic acid, sodium formate and t-butanol.

A Japanese group[61] recommends the use of coaxial N.M.R. tubes for quantitative work, with the standard material in the central tube and the unknown in the outer annulus. These can be particularly useful for containing solutions which are not miscible or are chemically reactive.

QUANTITATIVE PHARMACEUTICAL ANALYSIS

Applications

Within the past five years, more N.M.R. applications have been found for the quantitative analysis of drug formulations and products with a pharmaceutical background. The pioneering work carried out by Turczan and colleagues[57,62–73] represents a major attempt to establish N.M.R. as an alternative to USP and NF official analytical procedures. In Table 1 the compounds and formulations which have been analysed are collected according to their mode of clinical action. Quantitative methods for a further 20 compounds, including amphetamine, antipyrene, aspirin, bemegride, caffeine, mannitol, pentaerythritol tetranitrate and phenobarbital have also been briefly mentioned.[57,68] Collections of reference spectra are also available for sulphonamides,[64] amphetamines[89] and barbiturates.[90,91]

The N.M.R. method

N.M.R. offers a number of advantages over alternative analytical techniques for the analysis of pharmaceutical materials. It is often quicker than official USP or NF procedures and compares very favourably in accuracy (error usually <2%); thus thiotepa[83] involves a lengthy titrimetric or spectrophotometric USP method but can be analysed by N.M.R. in 10 min with a standard deviation of 0·6%. Indeed the first quantitative N.M.R. method in the NF (for amyl nitrite) has recently appeared.[92]

Further, little sample preparation is needed, and the method has been applied to tablets, capsules, syrups, injections, suspensions, creams and aerosol fluids. Interference from excipients (starch, lactose, gelatin and colouring agents) is rare.

Specific structural proof of the identity of the analysed material and of impurities can be obtained.

Table 1. Quantitative N.M.R. analysis of pharmaceuticals

Mode of action and name	Solvent	Standard	Standard deviation (*a*) or average error (*b*)	Ref.
Central Nervous System				
Meprobamate, carisoprodol mebutamate	$(CH_3)_2CO$	Malonic acid	*b*, 0·9%	62, 74
Chloral hydrate	D_2O	Maleic acid	*a*, 0·6%	65
Carbromal, bromural	CCl_4/Py	HMCTS*	*a*, 0·7%, 0·5%	73
Sodium triclofos	D_2O	CH_3CN	*b*, 2·0%	75
Trimethadione	H_2O	t-BuOH	*a*, 0·3%	68
Methsuximide, phensuximide	CCl_4, CH_2Cl_2/CCl_4	HMCTS	*a*, <0·6%	70
Phenacetin, phenazine, aminophenazine, caffeine	TFA	Fumaronitrile	*a*, 5·0%	76
Pentylene tetrazole	CCl_4	HMCTS	*a*, 0·7%	66
Amantadine†	D_2O	Succinimide	*a*, 0·8%	72
Cardiovascular and Respiratory				
Aminophylline	$NH_3/KCN/D_2O$	t-BuOH	*a*, 0·2–0·5%	67
Quinidine, hydroquinidine	$CDCl_3$	2,3,5-Tribromothiophene	*a*, 0·97	77
Amyl nitrite	$CDCl_3$	—	*a*, 1·4%	78
Acetazolamide (and Na salt)	NH_4OH/H_2O	t-BuOH	*a*, 0·7%	71
Anti-Infective Agents				
Methenamine mandelate	DMF $(CH_3)_2CO$ MeCN	Maleic acid	*b*, 1–2%	69
Sulphatriad	D_2O/OH^-	—	—	8
Parabens	PEG/H_2O	Pure compound	—	79
Pyrimethamine	TFA	Caffeine	*a*, 1·96%	80
Steroids				
Corticosteroids	DMSO, H_2O	Fumaric acid or Et_3NHCl	*b*, 0·6%	81
Mestranol	Py	Diphenyl acetic acid	*a*, 0·6%	59
Anti-Histamines and Anti-Eczema				
Dimenhydrinate	$CDCl_3$	Hexamine	—	8
Sodium cacodylate	H_2O	Succinic acid	*a*, 2·3%	82
Oncolytic				
Thiotepa	CCl_4	Benzoic acid	*a*, 0·6%	83
Alcohol Therapy				
Disulfiram	$CDCl_3$	HMCTS	*b*, 1·4%	84
Miscellaneous				
Dimethylsulphoxide	MeOH, $CDCl_3$	MeOH	*a*, 1–5·4%	63
Polysiloxanes	$CCl_4\cdot CDCl_3$	Cyclohexane, *p*-dichlorobenzene	*a*, 0·9%	85, 86
Glucose	DMSO-d_6	—	*b*, 0·11%	87

* HMCTS = hexamethylcyclotrisiloxane

† originally used as an anti-viral agent.

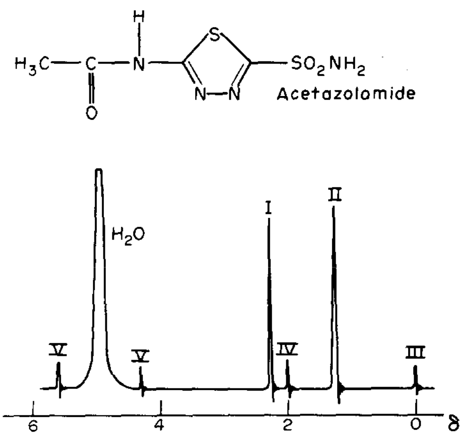


Fig. 2. N.M.R. spectrum of acetazolamide in 25% ammonia solution. (I) Acetazolamide; (II) t-butanol; (III) TMS Na salt; (IV) acetate decomposition product; (V) side-bands. (Reprinted by permission of the copyright owners).

Thus N.M.R. shows a specificity which is often absent in official spectrophotometric or titrimetric procedures. Chloral hydrate[65] can contain impurities, and acetazolamide[71] an acetate degradation product (Fig. 2) which are clearly identified and determined by N.M.R. but not by the official USP methods, where they behave analytically in the same way as the matrix.

Although the method is most suitable for high unit-dosage materials, it can be extended to the analysis of smaller (sub-milligram) quantities by using dedicated computer facilities and micro-sample containers.

Quantitative measurements are carried out by means of relative peak areas (or, rarely, peak heights). Thus an ultrapure sample of the determinand is not needed as a standard.

MISCELLANEOUS QUANTITATIVE ANALYSES USING N.M.R.

The analyst working in the pharmaceutical research laboratories of a multi-operational organization may very often be called upon to examine materials from affiliate disciplines, *e.g.*, biochemical metabolites and agricultural or veterinary formulations. Some applications of the quantitative N.M.R. procedure to such problems are listed below.

Determination of alcohols as their trimethylsilylethers.[93]

Estimation of keto-enol tautomers.[94]

Pesticides.[10,95]

Surfactants.[96,97]

Diglycerides,[98] wax esters and oils.[99]

Polyethylene glycols[100] and cellulose ethers.[101]

Modified starch.[102]

Peroxides[15] and hydroperoxides.[103]

Organo-magnesium, -lithium and -mercury reagents.[104]

Enzymatic dipeptide hydrolysis.[105]

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ADDENDUM

Two brief, general articles have appeared from the Laboratory of the Government Chemist describing some applications of quantitative N.M.R. methods (^{1}H, ^{13}C and ^{31}P).[106,107] N.M.R. methods have also appeared for the following: Oleate/elaidate esters by ^{13}C,[108] lynestrenol/ethinylestradiol methyl ether by a Fourier Transform procedure,[109] chloroform in syrups,[110] tetrazole acetic acids,[111] glutethimide[112] and the thiadiazole impurity in cefazolin.[113]

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SPECTROPHOTOMETRIC AND FLUOROMETRIC DETERMINATION OF COBALT

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Summary—The reaction of Co(II), pyridine-2-aldehyde-2-pyridyl hydrazone (PAPHY) and eosin at pH 5·6 produces the ternary complex $Co(L)(HL)E_2$ (where HL represents the protonated form of the ligand and E represents the eosinate anion). This complex is extracted by a chloroform–acetone mixture to give a strongly coloured and highly fluorescent extract. Spectrophotometric and fluorometric methods for the determination of Co have been developed with detection limits of 0·017 and 0·008 ppm respectively. Cu(II), Ni, Fe(II), Pd(II) and Hg(II) interfere. The spectrophotometric method has been successfully applied to the analysis of steels, following ion-exchange separation of Co.

Ternary complexes, wherein a metal reacts with two separate ligands, have found increasing use over recent years, particularly in spectrophotometric analysis. The most common form of ternary complex is the ion-association type in which a metal ion reacts with a ligand to produce a charged binary complex; this complex then further reacts with an ion of the opposite charge, usually a dyestuff.

Almost all publications in this field relate to reaction of anionic binary complexes with cationic (or basic) dyes. Ion-association ternary complexes containing a cationic binary complex are quite rare and are generally of the type metal–1,10-phenantholine–substituted fluorescein. The element studied most in this way is silver, with selectivity being achieved by using EDTA as a mass masking agent.[1,2] Very little application to fluorometric analysis has been made using this type of ternary complex, although the methods for silver were examined fluorometrically and a brief survey of the fluorescence of other metal–phenanthrotine–eosin complexes has been conducted.[3]

Substituted hydrazones such as pyridine-2-aldehyde-2-pyridyl hydrazone (PAPHY) and pyridine-2-aldehyde-2-quinolyl hydrazone (PAQH) have been extensively investigated as terdentate chelating agents in both acidic and alkaline solution.[4–9] The structures of these compounds are shown in Fig. 1. In acid solution, they react with many metals to form mono or bis complexes which are cationic.[10] Thus, reaction with a bivalent metal M produces the complexes $M(HL)^{2+}$ or $M(HL)_2^{2+}$ where HL represents the protonated form of the ligand.

If the solution is made alkaline, the hydrogen atom marked with the asterisk in Fig. 1 is lost from the molecule. Deprotonation of the complexes above produces $M(L)^+$ for the mono complex and $M(HL)L^+$ or ML_2 for the bis complex. The uncharged complex ML_2 is generally readily extractable, and such behaviour has been observed for predominantly six-coordinate metals such as nickel, zinc, cadmium, iron and manganese.[10] The charged complexes can only be extracted as suitable ion-pairs, *e.g.*, palladium(II) has been extracted as the complex Pd(PAPY)Cl into chloroform.[11]

In this work, the reaction between cobalt(II), PAPHY and the dyestuff eosin at pH 5·6 has been used to form a ternary complex which is then extracted into a chloroform–acetone mixture. Here, a cationic binary complex is formed between cobalt-(II) and PAPHY, and eosinate acts as the counter-anion in the ion-association ternary complex.

EXPERIMENTAL

Apparatus

All absorption measurements were taken on a Perkin–Elmer PE 124 recording spectrophotometer, and fluorescence measurements were taken with a Hitachi Perkin–Elmer MPF-2A fluorescence spectrophotometer. Wavelengths used were 547 nm for absorption and 530 and

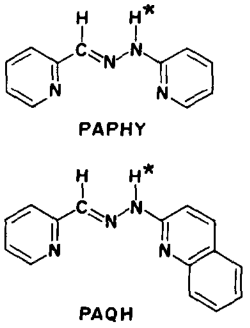

Fig. 1. Substituted hydrazone chelating agents.

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558 nm for fluorescence excitation and emission, respectively.

Reagents

Eosin (*2,4,5,7-tetrabromofluorescein*), 0·1% aqueous solution.

Ion-exchange resin. Amberlite CG. 400 (100–200 mesh) anion-exchanger, prewashed with 10*M* hydrochloric acid and distilled water alternately.

PAPHY. Obtained from Aldrich Laboratories and used as a 0·1% solution prepared by dissolving 0·1 g in the minimum quantity (about 3 or 4 drops) of 5*M* hydrochloric acid and diluting to 100 ml with distilled water. The solution was kept for no more than one week.

Cobalt stock solution. A 1000-ppm Co(II) solution was prepared by dissolving the appropriate amount of analytical grade cobalt nitrate [$Co(NO_3)_2.6H_2O$] in 250 ml of distilled water and diluted as required to make standards of lower concentration.

All other reagents used were analytical grade.

Procedures

The effect of pH on the extraction of cobalt(II)–eosin–PAPHY was studied in the following way. An aliquot of cobalt(II) solution containing 10 μg of Co^{2+} was mixed with 0·5 ml of 0·1% PAPHY solution and 1 ml of 0·1% eosin solution and the pH adjusted to the required value with 0·1 *M* hydrochloric acid and 0·1 *M* ammonia. The final volume was about 20 ml. The solution was then transferred to a 125-ml separating-funnel and 10·0 ml of chloroform were added, after which the flask was shaken for 30 sec. The organic layer was drained off and centrifuged at moderate speed for 1 min before measurement of absorbance.

Calibration curves based on absorbance and fluorescence measurements were obtained by adding 0–4 and 0–2 μg of Co respectively to 125-ml separating-funnels. The following reagents were then added, in turn, 1 ml of citrate buffer (pH 5·6), 0·5 ml of 0·1% PAPHY solution and 0·5 ml of 0·1% eosin solution, before the final volume was made up to about 20 ml. A 30:70 v/v mixture of acetone and chloroform was prepared and 10·0 ml were added to each separating-funnel and shaken for 1 min. After the phases had separated, the organic layer was removed and centrifuged for 1 min at moderate speed. An aliquot of the organic layer was then transferred to a 1-cm quartz fluorometer cell and fluorescence and absorbance measurements taken.

Steel samples were analysed by weighing out an amount of steel containing about 20 μg of cobalt and dissolving it in 5 ml of *aqua regia*. The solution was evaporated to dryness and the residue dissolved in 5 ml of concentrated hydrochloric acid and made up to 50 ml with distilled water. This solution was then electrolysed at 0·5 A for 30 min, in a divided cell (this comprised a fritted glass tube cut just below the frit, containing one electrode and filled with saturated sodium sulphate solution: the second electrode was a platinum mesh electrode inserted in the sample solution in the usual way[12]). The electrolysis step was included to remove copper. Hydrogen peroxide (30%, 2 ml) was added to oxidize all iron(II) to iron(III) and the sample was evaporated to a volume of about 5 ml. This solution was transferred with 9*M* hydrochloric acid to a 15 × 2·5 cm anion-exchange column previously washed with 9*M* hydrochloric acid. The column was then eluted with two bed-volumes (about 80 ml) of 9*M* hydrochloric acid to remove nickel, and the cobalt was eluted with two bed-volumes of 4*M* hydrochloric acid. The cobalt eluate was placed on a hot-plate and evaporated to about 5 ml, then allowed to cool before quantitative transfer to a 25-ml volumetric flask and dilution to the mark with distilled water. If successive samples were to be run through the ion-exchange column, the adsorbed iron was removed by eluting with distilled water and the column rewashed with 9 *M* hydrochloric acid before the next sample was added. An aliquot of the evaporated eluate solution (prepared as above) corresponding to about 4 μg of cobalt was mixed with 0·5 ml of 0·1% PAPHY solution and the pH adjusted to about 5·6 with dilute ammonia solution, after which 1 ml of citrate buffer and 0·5 ml of 0·1% eosin solution were added, the final volume being 20 ml. This solution was then extracted and the fluorescence and absorbance were measured as described in the procedure for construction of a calibration curve. A reagent blank was also run through the entire procedure.

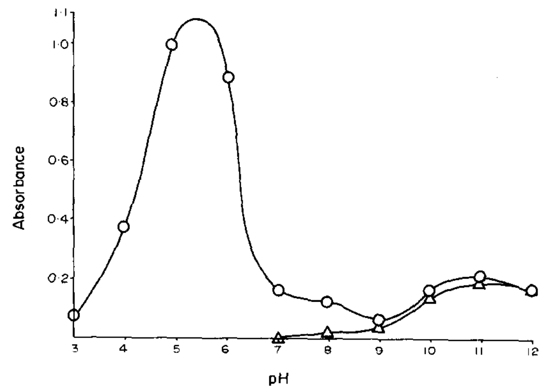

Fig. 2. Extraction of Co–PAPHY (△) and Co–PAPHY–eosin (○) at various pH values ([Co] = 10 μg/10 ml of solvent).

RESULTS

Effect of pH

Figure 2 shows the effect of pH on the extraction of Co-PAPHY into chloroform, in the presence and absence of eosin. The absorbance was used to estimate the degree of extraction since the chloroform extracts exhibited only a weak fluorescence. The absorption spectrum for Ci–PAPHY–eosin in chloroform is shown in Fig. 3.

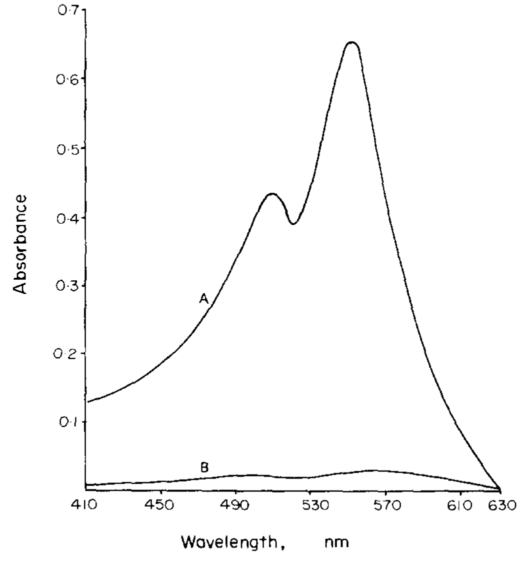

Fig. 3. Absorbance spectrum of Co–PAPHY–eosin ([CO] = 4 μg/10 ml of solvent). A. Co–PAPHY–eosin, B. Blank

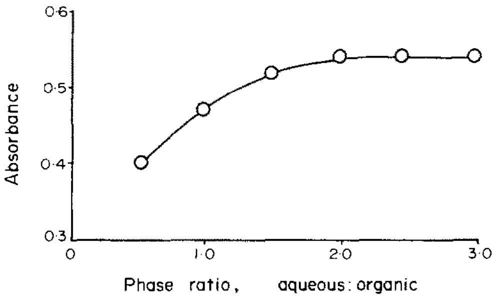

Fig. 4. Effect of phase ratio on extraction of Co–PAPHY–eosin. Conditions: 4 μg of Co/10 ml of solvent, 0·5 ml of 0·1% PAPHY, 1·0 ml of 0·1% eosin, 1 ml of citrate buffer, final volume varied.

The optimum acidity for extraction of the ternary complex was pH 5·4–5·8, and pH 5·6 was selected for further work. It will be noticed from Fig. 2 that this pH corresponds to a region of non-extraction of the Co-PAPHY complex.

In studies on the solvent extraction of complexes containing large organic dye molecules, it has frequently been noted that many buffer systems cause interference by promoting excessive extraction of the dye, presumably as a complex with the buffer components. This leads to unacceptably high blank levels and requires that any buffers used be examined for this type of interference.

Three buffer systems of pH 5·6 were investigated for possible interference; potassium hydrogen phthalate–sodium hydroxide, citric acid–sodium hydroxide and sodium acetate–acetic acid. Of these, the citrate buffer was found to produce the lowest level of extraction of eosin and was therefore used exclusively throughout this work.

Optimization of quantities of reagents

The effects of varying quantities of eosin, PAPHY and citrate buffer on the extraction of 4 μg of cobalt-(II) into 10 ml of chloroform were studied. In each case, the absorbance of the extract increased up to a constant value with increasing reagent concentration. It was observed that extraction of Co–PAPHY–eosin was dependent on the phase-volume ratio. Reduced extraction occurred if the ratio of aqueous:organic phase was less than 2:1. This effect is illustrated in Fig. 4.

The optimum conditions for extraction of Co–PAPHY–eosin into 10 ml of chloroform were found to be 0·5 ml of 0·1% PAPHY solution, 1·0 ml of 0·1% eosin solution, 1·0 ml of citrate buffer and a final aqueous phase volume of 20 ml.

Choice of solvent

Many solvents have been examined[13] for their efficiency in extracting ion-association complexes containing fluorescein derivatives. They are representative of most classes of organic compounds, including alcohols, ketones, esters, ethers, hydrocarbons, chlorinated hydrocarbons and aromatic hydrocarbons. In general, alcohols and ketones have been found to dissolve the dye itself, ethers and esters achieve slight extraction but cause the complexes to float on the interface, and extraction of the complex is only achieved with aromatic or chlorinated hydrocarbons, usually nitrobenzene or chloroform.

These two solvents were examined under conditions of optimum complex formation and extraction. Both extracted the complex, with nitrobenzene being the most efficient, but this solvent produced exceedingly high blank values which rendered it unsuitable. Chloroform gave acceptably low blank values but appeared to concentrate the colour of the complex

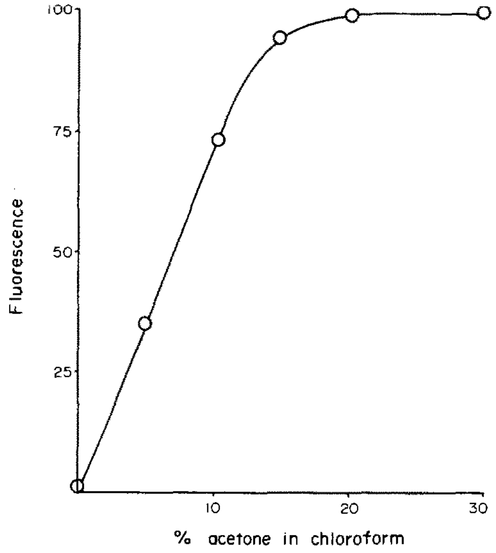

Fig. 5. Effect of solvent composition on the fluorescence of Co–PAPHY–eosin extracts.

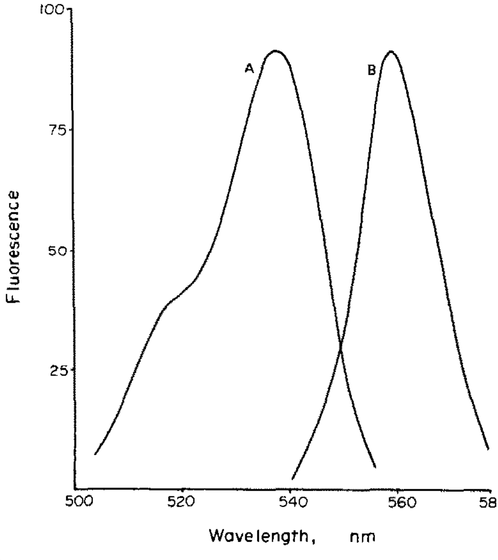

Fig. 6. Fluorescence spectra of Co–PAPHY–eosin in 3:7 acetone/chloroform solvent. A. Excitation spectrum. B. Emission spectrum.

Table 1. Comparison of solvents for extraction of Co(II)–PAPHY–eosin complex

Solvent	Absorbance for 0·4 *ppm* Co soln.	Blank absorbance	Molar absorptivity, *l. mole*$^{-1}$ *cm*$^{-1}$	Remarks
Chloroform	0·612	0·052	$8{\cdot}26 \times 10^4$	Colour collection at interface
Nitrobenzene	1·34	0·560	$1{\cdot}15 \times 10^5$	High blank absorbance
Chloroform–acetone (7:3)	0·595	0·059	$7{\cdot}8 \times 10^{-4}$	Clean phase separation, high fluorescence

at the interface, a uniform colour being assumed only after 10 min standing time or centrifuging. Weak fluorescence was observed from the chloroform extract whereas the nitrobenzene extract showed no fluorescence.

The addition of acetone or alcohol to a chloroform extract of an eosin ion-association complex has been noted to increase fluorescence,[13,14] probably by increasing the solubility of the dye in the organic solvent. Mixed acetone–chloroform solutions* were therefore examined as extractants for the Co–PAPHY–eosin complex, particularly with regard to maximization of fluorescence. Mixtures containing 0–30% acetone were prepared and used to extract 4 μg of Co at optimal reagent concentrations. The results are shown in Fig. 5, and the fluorescence spectra of the complex in the mixed solvent appear in Fig. 6. The fluorescence increased only marginally with more than 15% acetone, but a 30% mixture was chosen as the most suitable because of rapid phase separation and uniform colour distribution of the complex throughout the organic extract. The problem of colour concentration at the interface, mentioned above, was completely eliminated by use of the mixed solvent. In addition, the fluorescence of the extract was increased at least 100-fold. The wavelength of maximum excitation is 537 nm; the proximity of this wavelength to the emission maximum at 558 nm necessitates use of an excitation wavelength of 530 nm, but this reduces the fluorescence emission by only 10%.

The study of solvents can be summarized as in Table 1.

Calibration curves

With the mixed solvent described above, linear calibration curves for both absorbance and fluorescence techniques were obtained in the ranges 0·04–0·4 and 0·02–0·2 ppm Co respectively. The maximum concentrations used in each case were chosen as the points where the calibration curves began to deviate from linearity by more than 5%. That is, beyond the maximum concentration indicated, curvature of the calibration plot occurred, owing either to incomplete extraction, or in the case of fluorescence, to self-absorption effects.

Precision studies

Precision was estimated by taking the standard deviation of the absorbance or fluorescence of seven replicate solutions. Precision of the fluorescence technique was estimated by setting the fluorescence of the first solution to 50 units on the fluorometer scale and comparing the remaining solutions with the first. Values for precision, expressed as the relative standard deviation of the seven replicates were 2·2% (at [Co] 0·4 ppm) for absorbance and 3·5% (at [Co] 0·2 ppm) and 6·1% (at [Co] 0·1 ppm) for fluorescence.

Detection limits were 0·017 and 0·008 ppm Co for absorbance and fluorescence methods, respectively.

Interference studies

The possible interference of a large number of cations and anions in the solvent extraction of 2 μg of Co(II) was examined. This level of cobalt was chosen to enable absorption and fluorescence measurements to be taken on the same sample. The results are summarized in Tables 2 and 3.

Cationic interferences included copper(II), nickel, iron(II), palladium(II) and to a lesser extent, mercury(II); anionic interferences were restricted to thiocyanate and perchlorate and to a very slight extent, silicate. The interference of mercury(II) was the most interesting, with a marked colour change from orange to pink-red occurring when mercury(II) was added to an aqueous solution containing PAPHY, buffer and eosin. This colour was transferred to the organic phase on shaking with the chloroform/acetone mixture, giving rise to positive interferences for fluorescence and absorbance measurements. The colour change observed in aqueous solution could not be detected spectrophotometrically, indicating that it originated from quenching of the orange-yellow fluorescence of eosin. This was confirmed by taking fluorescence spectra for solutions containing 0–150 μg of Hg(II) added to eosin, PAPHY and buffer in the same concentrations as used for formation of the Co–PAPHY–eosin complex, and diluted to 25 ml with distilled water. The fluorescence of these solutions decreased with increasing amounts of Hg(II).

The interference of copper(II), nickel, iron(II) and palladium(II) can be attributed to the fact that these

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* When such mixtures are used in alkaline medium there is said to be a risk of explosion because of a base-catalysed condensation.

Table 2. Effect of cations on determination of cobalt(II)

Cation	(w/w ratio to Co)	Added as	Change in fluorescence, %	Change in absorbance, %
Ag^+	(250)	$AgNO_3$	*	—
Al^{3+}	(500)	$Al(NO_3)_3.9H_2O$	—	—
Cd^{2+}	(500)	$CdCl_2.3H_2O$	—	—
Cr^{3+}	(500)	$Cr(NO_3)_3.9H_2O$	—	—
Cu^{2+}	(500)	$CuSO_4.5H_2O$	−80	7·5
Cu^{2+}	(5)	$CuSO_4.5H_2O$	−8	—
Cu^{2+}	(500)	$CuSO_4.5H_2O$	†	†
Fe^{2+}	(500)	$Fe(NH_4)_2(SO_4)_2.6H_2O$	−100	>1000
Fe^{2+}	(5)	$Fe(NH_4)_2(SO_4)_2.6H_2O$	−26	35
Fe^{2+}	(5)	$Fe(NH_4)_2(SO_4)_2.6H_2O$	−26§	35§
Fe^{3+}	(500)	$FeCl_3.6H_2O$	—	—
Hg^{2+}	(250)	$Hg(NO_3)_2.H_2O$	8	20
Hg^{2+}	(5)	$Hg(NO_3)_2.H_2O$	—	—
Ir^{3+}	(500)	$Na_3IrCl_6.12H_2O$	—	—
K^+	(250)	KNO_3	—	—
Mg^{2+}	(250)	$Mg(NO_3)_2.6H_2O$	—	—
Mn^{2+}	(500)	$MnCl_2.4H_2O$	—	—
Na^+	(250)	$NaNO_3$	—	—
NH_4^+	(250)	NH_4NO_3	—	—
Ni^{2+}	(500)	$Ni(NO_3)_2.6H_2O$	−64	226
Ni^{2+}	(5)	$Ni(NO_3)_2.6H_2O$	−14	—
Pb^{2+}	(250)	$Pb(NO_3)_2$	—	—
Pd^{2+}	(35)	$PdCl_2$	−100	>1000
Pd^{2+}	(5)	$PdCl_2$	−10	34
Rh^{3+}	(500)	$RhCl_3.3H_2O$	—	—
Sr^{2+}	(250)	$Sr(NO_3)_2.4H_2O$	—	—
Th^{4+}	(250)	$Th(NO_3)_4.4H_2O$	—	—
V(V)	(250)	NH_4VO_3	—	—
WO_4^{2-}	(250)	Na_2WO_4	—	—
Zn^{2+}	(250)	$Zn(NO_3)_2.4H_2O$	—	—

* Changes of 5% or less are not listed.

† In the presence of thiourea.

§ In the presence of ascorbic acid.

elements form strong, coloured PAPHY complexes which are extractable at pH 5·6. These species therefore caused increased absorbance of the organic phase and reduced fluorescence through scattering or absorption of fluorescence radiation. The anionic interferences were probably due to the interfering ions causing reduced extraction of the ternary complex, although the mechanism of this interference is not clear.

Thiourea was found to eliminate the interference of copper(II), presumably by its ability to reduce copper(II) to copper(I) under acid conditions. Unfortunately it could not be used in presence of iron(III) (which did not interfere), because it reduced it to iron(II) (which does). It was therefore necessary to remove copper from the solution. The likelihood of palladium being found in significant concentrations in natural samples is low, and because of this, palla-

Table 3. Effect of anions on the determination of cobalt(II)

Anion	(w/w ratio to Co)	Added as	Change in fluorescence, %	Change in absorbance, %
Br^-	(250)	NaBr	*	—
CH_3COO^-	(250)	CH_3COONa	—	—
Cl^-	(250)	NaCl	—	—
ClO^-	(250)	$NaClO_4$	−32	−38
F^-	(250)	NaF	—	—
PO_4^{3-}	(250)	Na_3PO_4	—	—
SCN^-	(250)	KSCN	−8	−9
SeO_4^{2-}	(250)	Na_2SeO_4	—	—
SiO_3^{2-}	(500)	$Na_2SiO_3.5H_2O$	−6	—
SO_4^{2-}	(250)	Na_2SO_4	—	—
Ascorbate	(5000)	Ascorbic acid	—	—
Citrate	(5000)	Sodium citrate	—	—
Tartrate	(5000)	Sodium tartrate	—	—
Thiourea	(5000)	Solid thiourea	—	—

* Changes of 5% or less are not listed.

Table 4. Recovery of added cobalt from 1000 μg of Fe^{2+} + 1000 μg of Ni^{2+} + 1000 μg of Cu^{2+}

Co added, *μg*	Co found, *μg*	Recovery, %
1·0	0.982	98·2
5·0	4·85	97·0
10·0	9·93	99·3
50.0	49·6	99·2

dium can be disregarded as an interferent of major importance. Thus, to eliminate interferences, a method of separation of cobalt from excesses of copper, nickel and iron was required.

Removal of interferences

Of the separation techniques available in analytical chemistry, ion-exchange provided the best possibility for separation of cobalt from copper, nickel and iron. The ion-exchange separation of cobalt from many elements in hydrochloric acid media has been extensively studied,[12,15–17] the results showing that cobalt is adsorbed strongly onto an anion-exchange resin in 9*M* hydrochloric acid. The cobalt can then be eluted from the resin with 4*M* hydrochloric acid, since at this concentration, the distribution coefficient of cobalt is very low. Nickel, which forms no anionic chloride complex, is not adsorbed on the column at any acid concentration. Iron(III), however, is strongly adsorbed at most concentrations of hydrochloric acid and can only be eluted by very dilute acid (0·1*M*). Palladium shows appreciable adsorption at most acid concentrations, with maximal adsorption from 1*M* hydrochloric acid; this element is therefore likely to be retained to a large extent on the anion-exchange column. Copper is difficult to separate from cobalt by ion-exchange, although this can be achieved by use of long columns and judicious choice of flow-rates. It is considerably more expedient to separate the copper first, and this can be readily done by electro-deposition in a divided cell to prevent polarization of the electrodes by the iron in the sample.[11] After the removal of copper, the sample is passed through the anion-exchange column, nickel is eluted with 9*M* hydrochloric acid and then cobalt with 4*M* hydrochloric acid. This process was tested for recovery of cobalt, the results appearing in Table 4.

These recoveries were adequate for determination of cobalt at levels ranging from ppm to percentage levels, provided a suitable sample size was chosen.

Analysis of samples

Ideally, the proposed methods of analysis were suited to samples containing low levels of cobalt in a matrix with favourable ratios of cobalt to copper, iron, nickel and palladium. Samples which met these criteria were plants and some soils, the latter being suitable because of the non-interference of silicate and fluoride (since soil digestion is often done with hydrofluoric acid). Samples of this type were not available, so the determination of cobalt in steels was attempted. The results for four standard steels are shown in Table 5.

Good agreement was obtained for three of the four steels analysed, and no comment can be made on the 221/1 carbon steel result, because of the non-certification of the published analytical result. The highly unfavourable ratio of cobalt to iron necessitated repetition of the ion-exchange separation step to ensure complete removal of traces of iron and nickel remaining after the initial ion-exchange separation. The results shown in Table 5 were obtained by the absorbance method because of the relatively high amounts of cobalt present in the samples. Although lengthy (3 hr), the procedure has the advantage of being applicable to a wide range of cobalt contents, with a very low detection limit.

DISCUSSION

Cobalt(II) complexes of many ligands have shown anomolous extraction behaviour, and this has also been observed for PAPHY and PAQH where the complexes formed have been found to be non-extractable at high pH values.[6,10] It has been demonstrated that PAPHY-type compounds act as oxidizing agents towards cobalt(II),[18] and the Co–PAPHY binary complex has been confirmed to be 2:1 (ligand to metal), diamagnetic and containing cobalt in the +3 oxidation state. Similar properties have been observed for the Co–PAQH complex,[19] in which only one of the ligands in the complex is deprotonated. The reaction between cobalt(II), PAPHY and eosin may be represented by the reaction scheme

(1) $\mathrm{Co(II)} \xrightarrow{\text{PAPHY}} \mathrm{Co(III)}$

(2) $\mathrm{Co^{3+} + 2HL \rightleftharpoons Co(HL)_2^{3+}}$

(3) $\mathrm{Co(HL)_2^{3+} \rightleftharpoons Co(L)(HL)^{2+} + H^+}$

(4) $\mathrm{Co(L)(HL)^{2+} + 2E^- \rightleftharpoons Co(L)(HL)E_2}$

Table 5. Analysis of steels for cobalt

B.C.S. No.	Description	No. of detns.	Mean, %	Cobalt content,* %
149/3	High-purity iron granules	3	0·0062	0·007
221/1	Carbon steel	3	0·042	0·018*
239/2	Carbon steel	3	0·024	0·02*
235/2	Ti-stabilized stainless steel	3	0·055	0·056*

* Result not given British Chemical Standard certification, owing to insufficient independent analyses.

where E^- represents the eosinate anion. An alternative formulation would involve the double deprotonation of Co–PAPHY before the reaction with eosinate:

$$(4)' \quad Co(L)(HL)^{2+} \rightleftharpoons CoL_2^+ + H^+$$
$$(5) \quad CoL_2^+ + E^- \rightleftharpoons CoL_2E$$

Attempts to elucidate the nature of the extracted ternary complex by Job's method and the mole-ratio method proved to be unsuccessful owing to the large excesses of eosin and PAPHY required for complete reaction and extraction of the complex. However, at the acidity used throughout this study (pH 5·6), it is likely that Co–PAPHY would exist as the singly deprotonated form, suggesting that the correct formula for the complex is $Co(L)(HL)E_2$ where HL represents the protonated form of the ligand.

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DETERMINATION OF URANIUM IN MINERALS AND ROCKS

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Summary—A method is described for the determination of uranium in minerals and rocks by spectrophotometry and fluorimetry. After treatment of the sample with hydrochloric acid, uranium is separated from matrix elements by adsorption on a column of the strongly basic anion-exchange resin Dowex 1 X8 from an organic solvent system consisting of IBMK, tetrahydrofuran and 12*M* hydrochloric acid (1:8:1 v/v). Following removal of iron, molybdenum and co-adsorbed elements by washing first with the organic solvent system and then with 6*M* hydrochloric acid, the uranium is eluted with 1*M* hydrochloric acid. In the eluate, uranium is determined by means of the spectrophotometric arsenazo III method or fluorimetrically. The suitability of the method for the determination of both trace and larger amounts of uranium was tested by analysing numerous geochemical reference samples with uranium contents in the range 10^{-1}–10^4 ppm. In practically all cases very good agreement of results was obtained.

Spectrophotometric and fluorimetric methods are employed extensively for the determination of uranium in a variety of geological samples, including materials of very low uranium contents such as basaltic rocks, and of uranium-rich minerals, as for instance torbernite, carnotite, uraninite and pitchblende.[1] For the successful analysis of both types of uranium-bearing materials the very sensitive spectrophotometric method of uranium determination can be used, which is based on measurement of the absorbance of the green uranium(IV)–arsenazo III complex in moderately concentrated hydrochloric acid medium.[1] Interferences are caused by thorium, zirconium, titanium, rare earth elements, molybdenum, and iron, so it is necessary to separate uranium from these elements and also from other components such as the main constituents of minerals and rocks. For this purpose, methods based on liquid–liquid extraction and ion-exchange have found widespread application.[1]

In the present paper an application is described of a single separation step which is based on anion-exchange in an organic solvent system. Following this quantitative separation, uranium can be determined, free from interferences, by either the arsenazo III method or fluorimetrically.

EXPERIMENTAL

Reagents

Ion-exchanger. The strongly basic anion-exchanger Dowex 1 X8 (100–200 mesh; chloride form) was used. To purify the exchanger (which contained, *e.g.*, iron and zinc) 200 g of the resin were treated in succession with 2 litres of 1*M* nitric acid, 2 litres of 6*M* hydrochloric acid, 2 litres of 1*M* hydrochloric acid, 3 litres of distilled water and 1 litre of reagent grade methanol. This batch of resin was air-dried and 3 g of it were slurried in a few ml of the IBMK–THF–HCl mixture (see below) and transferred to an ion-exchange column, with the same mixture used as a rinse.

Standard uranium solutions. Aliquots of a stock solution containing 10 mg of uranium (as uranyl chloride) per ml of 12*M* hydrochloric acid were diluted with water to obtain standard solutions in 9*M*, 6*M* and 1*M* hydrochloric acid containing 0·1–10^4 ppm of uranium.

IBMK–THF–HCl mixture. A mixture of IBMK (isobutyl methyl ketone), THF (tetrahydrofuran) and 12*M* hydrochloric acid (1:8:1 v/v) was prepared several hours before use (in order to prevent the formation of air-bubbles in the resin bed). This solution can be stored for at least a week without loss of effectiveness.

Arsenazo III solution. Freshly prepared and filtered 0·1% aqueous solution.

Other reagents. "Fluorbase" (200 mg) pellets consisting of 95% sodium fluoride and 5% lithium fluoride (Nordrhein-Chemie, 41 Duisburg 12, West Germany), zinc metal (dust or finely granulated zinc), oxalic acid, 1·0, 6, 9 and 12*M* hydrochloric acid, 1*M* nitric acid, and reagent-grade methanol.

Apparatus

The ion-exchange separations of uranium were performed in columns of the type and dimensions described earlier.[2]

Determination of distribution coefficients

The distribution coefficients (K_d-values) of uranium and some of the more strongly adsorbed metal ions were determined by using the batch-equilibrium method, and the column technique was employed to measure the K_d-values of iron, molybdenum and other elements which are weakly retained by the resin.[3] The usually high distribution coefficients of uranium were determined after equilibration (for 4 hr) of 1 g of the resin with 20 ml of the organic solvent–hydrochloric acid mixture tested (see Table 1) containing 20 mg of uranium, followed by filtration, etc.[3] In the determinations of the batch and column distribution coefficients of the other elements only 1 mg each of the metal ions was used (see Table 2).

Procedures

Dissolution of samples. To 1·0 g of the thoroughly homogenized sample, in a 250-ml beaker, 100 ml of concentrated hydrochloric acid are added, the beaker is covered with a watch-glass, and the mixture is heated on a sand-bath until its volume has been reduced to about 30 ml. Subsequently the solution is evaporated to dryness under an infrared lamp, another 100 ml of concentrated hydrochloric acid are added and the solution is evaporated to dryness again under the heat-lamp. To the residue 30 ml of 6*M* hydrochloric acid are added, the mixture is heated under the lamp for several minutes and then let stand (preferably overnight). Afterwards, insoluble material (mainly silica) is removed by filtering off on a dense filter, 6*M* hydrochloric acid being used for washing the filter paper and residue free from iron. The filtrate is evaporated to dryness on a steam-bath and the residue is taken up in about 30 ml of the IBMK–THF–HCl mixture. If two phases are formed, more solvent mixture is added until a homogeneous solution is obtained* in which however, a portion of the solute (mainly silica) usually reappears as a suspension, owing to the decrease of solubility on addition of the IBMK–THF–HCl mixture. This insoluble material is filtered off on a dense filter, and washed with IBMK–THF–HCl solution. The filtrate (usually 50–100 ml) is the sorption solution for the ion-exchange separation.

Ion-exchange separation. The sorption solution is passed through the ion-exchange column containing 3 g of the resin (pretreated with 10 ml of the IBMK–THF–HCl mixture), at a flow-rate of about 0·8 ml/min. Iron and molybdenum are removed by washing the column with 50 ml of the IBMK–THF–HCl mixture, and copper, cobalt, *etc.* as well as organic solvents left in the resin bed are eluted with 100 ml of 6*M* hydrochloric acid. The adsorbed uranium is then eluted with 100 ml of 1*M* hydrochloric acid.

The resin column may be used for the isolation of uranium from further samples provided that 30 ml of the IBMK–THF–HCl mixture are used to pretreat it following the elution of uranium.

Quantitative determination of uranium. The uranium eluate is evaporated to dryness on a steam-bath or under an infrared lamp and the residue is dissolved in 9*M* hydrochloric acid and transferred to a 25-ml standard flask and diluted to volume with the acid. If this solution contains >1 ppm of uranium (*i.e.*, >25 μg of uranium) it is necessary to dilute it (or an aliquot) with the same acid to a suitable volume in which this concentration is not exceeded.

A. Spectrophotometric method. Ten ml of the 9*M* hydrochloric acid solution of the uranium are transferred to a 100-ml wide-neck Erlenmeyer flask, 0·3 g of oxalic acid and 1·10 g of zinc are added and the flask is covered loosely with a stopper. During the reduction the flask is shaken carefully until all the zinc has dissolved. Immediately afterwards 1·0 ml of the arsenazo III solution is added and the absorbance is measured at 665 nm against a reagent blank prepared in the same way. A calibration curve for the range 1–10 μg of uranium is constructed according to the reduction procedure described above. Beer's law is strictly obeyed up to 10 μg of uranium (absorbance 0·400). Higher amounts give strong positive deviations from linearity. The absorbance remains constant for at least 100 min. If less than 0·2 μg of uranium is present in the 10 ml of test solution ($<0·5$ ppm in the original sample) this method is less reliable (because of the low absorbance) than the fluorimetric procedure described below.

B. Fluorimetric method. A suitable volume (*e.g.*, 0·1 ml) of the uranium eluate or of the 25 ml of the 9*M* hydrochloric acid solution containing the uranium is evaporated in a small platinum dish[4] and after addition of a "Fluorbase" pellet, a melt is prepared under strictly controlled conditions.[1] The fluorescence intensity of the cold flux is measured and compared with the intensity of fluxes of known uranium concentrations.

RESULTS AND DISCUSSION

The dissolution procedure described, in which only hydrochloric acid is used, proved to be highly satisfactory for all of the samples analysed although it is in principle based on leaching only. Investigation of the completeness of dissolution showed that the portions insoluble in hydrochloric acid never retained more than about 0·1% of the total uranium content.

During filtration of the IBMK–THF–HCl mixture to remove the insolubles, some of the silica passes into the filtrate but this was found not to interfere with the subsequent anion-exchange separation of uranium. The silica passes right through the resin bed and hence does not block the column.

Investigations of the effect of varying the concentrations of IBMK, hydrochloric acid and of water-miscible organic solvents on the adsorption of uranium and iron on Dowex 1 gave the results presented in Table 1.

At high acid concentrations in the presence of IBMK, acetone or tetrahydrofuran, the K_d-values and elution volumes for iron are considerably lower than those for the other systems shown in Table 1. That is not surprising, because these media contain three CIESE-active components,[4–6] namely hydrochloric acid and IBMK mixed with either acetone or tetrahydrofuran so that iron(III) chloride shows practically no tendency to be adsorbed on the anion-exchanger. This is also true for molybdenum although to a lesser extent in most of the media; like iron, molybdenum is also readily extracted by IBMK or other ketones or ethers from hydrochloric acid solutions.[3] Investigations using molybdenum dissolved in the systems in which elution volumes for iron of 2 or 3 ml were measured (Table 1) have shown that for molybdenum similarly small elution volumes, which are necessary to effect complete removal of molybdenum, were obtained with only three media *i.e.*, in the 1:8:1, 4:5:1 and 8:1:1 v/v IBMK–THF–HCl mixtures. In all other mixtures the elution volumes for molybdenum were found to exceed 50 ml. As will later be shown in Table 3, the virtually complete removal (separation) of molybdenum and iron is essential for the accurate spectrophotometric determination of uranium.

From Table 1 it is also seen that uranium (as the anionic chloride complex) is strongly adsorbed from virtually all of the systems investigated—the smallest but still sufficiently high distribution coefficients being found in the media containing acetone or tetrahydro-

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* If after addition of the organic solvent mixture a total volume of 100 ml should be reached without obtaining homogeneity, 1 ml of concentrated hydrochloric acid is added—this causes immediate disappearance of the two phases.

Table 1. Distribution coefficients of uranium and iron on Dowex 1, X8 in IMBK–HCl mixtures containing varying concentrations of organic solvents

Composition of the IMBK–HCl systems			Distribution coefficients	
IMBK, % *v/v*	Organic solvent, % *v/v*	HCl, % *v/v*	Uranium(VI)	Iron(III)*
80	10 (Methanol)	10 (12*M*)	$1{\cdot}25 \times 10^3$	1 (3)
50	40 (Methanol)	10 (12*M*)	$1{\cdot}74 \times 10^3$	3 (>50)
10	80 (Methanol)	10 (12M)	$20{\cdot}3 \times 10^3$	>50
80	10 (Methanol)	10 (6*M*)	two-phase mixture	
50	40 (Methanol)	10 (6*M*)	$6{\cdot}65 \times 10^3$	7 ($\gg 50$)
10	80 (Methanol)	10 (6*M*)	$4{\cdot}80 \times 10^3$	>50
80	10 (Methanol)	10 (1*M*)	two-phase mixture	
50	40 (Methanol)	10 (1*M*)	650	>50
10	80 (Methanol)	10 (1*M*)	460	>50
80	10 (Ethanol)	10 (12*M*)	625	1 (3)
50	40 (Ethanol)	10 (12*M*)	$3{\cdot}50 \times 10^3$	1 (>50)
10	80 (Ethanol)	10 (12*M*)	$14{\cdot}3 \times 10^3$	>50
80	10 (Ethanol)	10 (6*M*)	two-phase mixture	
50	40 (Ethanol)	10 (6*M*)	$2{\cdot}20 \times 10^3$	1 (>50)
10	80 (Ethanol)	10 (6*M*)	$3{\cdot}00 \times 10^3$	>50
80	10 (Ethanol)	10 (1*M*)	two-phase mixture	
50	40 (Ethanol)	10 (1M)	two-phase mixture	
10	80 (Ethanol)	10 (1*M*)	330	>50
80	10 (Propan-l-ol)	10 (12*M*)	610	1 (3)
50	40 (Propan-l-ol)	10 (12*M*)	$3{\cdot}60 \times 10^3$	1 (3)
10	80 (Propan-l-ol)	10 (12*M*)	$57{\cdot}0 \times 10^3$	50
80	10 (Propan-l-ol)	10 (6*M*)	two-phase mixture	
50	40 (Propan-l-ol)	10 (6*M*)	$4{\cdot}80 \times 10^3$	1 (>50)
10	80 (Propan-l-ol)	10 (6*M*)	$16{\cdot}0 \times 10^3$	>50
80	10 (Propan-l-ol)	10 (1*M*)	two-phase mixture	
50	40 (Propan-l-ol)	10 (1*M*)	two-phase mixture	
10	80 (Propan-l-ol)	10 (1*M*)	$1{\cdot}23 \times 10^3$	>50
80	10 (Acetic acid)	10 (12*M*)	830	1 (3)
50	40 (Acetic acid)	10 (12M)	$9{\cdot}80 \times 10^3$	2 (>50)
10	80 (Acetic acid)	10 (12*M*)	$\gg 10^5$	$\gg 50$
80	10 (Acetic acid)	10 (6*M*)	two-phase mixture	
50	40 (Acetic acid)	10 (6*M*)	$20{\cdot}0 \times 10^3$	2 (>50)
10	80 (Acetic acid)	10 (6*M*)	$>10^5$	$\gg 50$
80	10 (Acetic acid)	10 (1*M*)	two-phase mixture	
50	40 (Acetic acid)	10 (1*M*)	two-phase mixture	
10	80 (Acetic acid)	10 (1*M*)	$>10^5$	$\gg 50$
80	10 (Propan-2-ol)	10 (12*M*)	580	1 (2)
50	40 (Propan-2-ol)	10 (12*M*)	$3{\cdot}40 \times 10^3$	1 (5)
10	80 (Propan-2-ol)	10 (12*M*)	$85{\cdot}0 \times 10^3$	1 (>50)
80	10 (Propan-2-ol)	10 (6*M*)	two-phase mixture	
50	40 (Propan-2-ol)	10 (6*M*)	$3{\cdot}70 \times 10^3$	1 (50)
10	80 (Propan-2-ol)	10 (6*M*)	$60{\cdot}0 \times 10^3$	30 ($\gg 50$)
80	10 (Propan-2-ol)	10 (1*M*)	two-phase mixture	
50	40 (Propan-2-ol)	10 (1*M*)	two-phase mixture	
10	80 (Propan-2-ol)	10 (1*M*)	$6{\cdot}80 \times 10^3$	$\gg 50$
80	10 (Methyl glycol)	10 (12*M*)	two-phase mixture	
50	40 (Methyl glycol)	10 (12*M*)	$3{\cdot}50 \times 10^3$	1 (>50)
10	80 (Methyl glycol)	10 (12*M*)	$14{\cdot}0 \times 10^3$	3 (>50)
80	10 (Methyl glycol)	10 (6*M*)	two-phase mixture	
50	40 (Methyl glycol)	10 (6*M*)	$4{\cdot}80 \times 10^3$	2 (>50)
10	80 (Methyl glycol)	10 (6*M*)	$22{\cdot}0 \times 10^3$	10 ($\gg 50$)
80	10 (Methyl glycol)	10 (1*M*)	two-phase mixture	
50	40 (Methyl glycol)	10 (1*M*)	$1{\cdot}60 \times 10^3$	2 ($\gg 50$)
10	80 (Methyl glycol)	10 (1*M*)	$10{\cdot}3 \times 10^3$	30 ($\gg 50$)
80	10 (Acetone)	10 (12*M*)	500	1 (2)
50	40 (Acetone)	10 (12*M*)	600	1 (2)
10	80 (Acetone)	10 (12*M*)	610	1 (3)
80	10 (Acetone)	10 (6*M*)	two-phase mixture	
50	40 (Acetone)	10 (6*M*)	two-phase mixture	
10	80 (Acetone)	10 (6*M*)	480	1 (>50)
80	10 (Acetone)	10 (1*M*)	two-phase mixture	
50	40 (Acetone)	10 (1*M*)	two-phase mixture	
10	80 (Acetone)	10 (1*M*)	$1{\cdot}05 \times 10^3$	1 (>50)
80	10 (Tetrahydrofuran)	10 (12*M*)	380	1 (2)
50	40 (Tetrahydrofuran)	10 (12*M*)	550	1 (2)
10	80 (Tetrahydrofuran)	10 (12*M*)	550	1 (3)
80	10 (Tetrahydrofuran)	10 (6*M*)	two-phase mixture	
50	40 (Tetrahydrofuran)	10 (6*M*)	two-phase mixture	
10	80 (Tetrahydrofuran)	10 (6*M*)	310	1 (5)
80	10 (Tetrahydrofuran)	10 (1*M*)	two-phase mixture	
50	40 (Tetrahydrofuran)	10 (1*M*)	two-phase mixture	
10	80 (Tetrahydrofuran)	10 (1*M*)	100	1 (20)

* The elution volume (ml) of iron (1-g column of Dowex 1) is shown in brackets.

Table 2. Distribution coefficients of metal ions in IBMK–THF–HCl (1:8:1) (1 g of Dowex 1 X8; 1-mg load)

Metal ion	Distribution coefficient	Metal ion	Distribution coefficient
UO_2(II)	550	Be(II)	2
Fe(III)	1*	Mg(II)	2
Mo(VI)	2*	Ca(II)	2
Cu(II)	125	Na(I)	1
Co(II)	50	K(I)	1
Pb(II)	75	Al(III)	1
Mn(II)	110	Ce(III)	3
Cd(II)	170	V(V)	<1
Zn(II)	200	Ti(IV)	2
Ni(II)	50	Zr(IV)	1
Cr(III)	1	Th(IV)	2

* The elution volume on a 1-g column of the resin is equivalent to 3 ml.

furan. From the latter media the 1:8:1 v/v mixture was selected as the most suitable for the separation of uranium from geological samples. In this system the distribution coefficient of uranium (550) is high enough to guarantee the complete adsorption of even mg-amounts of uranium and the K_d-values and elution volumes of iron and molybdenum are very low (see also Table 2), so they can be separated from uranium most effectively. An additional advantage of this medium stems from the fact that the tendency for formation of two phases on dissolution of the chloride residue in IBMK–THF–HCl mixtures decreases with increasing concentration of tetrahydrofuran in the mixtures.

Investigations of the adsorption behaviour of numerous elements on Dowex 1 from the selected IBMK–THF–HCl mixture gave the results presented in Table 2. Atomic-absorption spectrophotometry was used for the necessary analyses. From these distribution coefficients it is evident that during the sorption process not only uranium but also copper, cobalt, lead, manganese, cadmium and zinc will be adsorbed on the resin. Previous experience has shown however, that under the conditions of analysis, *i.e.*, in the presence of large amounts of chlorides as is the case after treatment of the geological samples with hydrochloric acid, some of these elements (and also those, *e.g.*, lead, for which the adsorption decreases with increase in the chloride concentration) are much less strongly adsorbed than their K_d-values would indicate (salt-effect).

The washing with IBMK–THF–HCl mixture immediately after passage of the sorption solution through the resin bed removes residual iron and molybdenum* so that these will not interfere with either the spectrophotometric or the fluorimetric procedure for uranium assay. Other elements which, if not separated from uranium, may cause interferences in either or both of these methods, are eluted subsequently with 6*M* hydrochloric acid. Thus, this eluent quantitatively eliminates from the resin all of the adsorbed elements listed in Table 2 except uranium, cadmium and zinc (The distribution coefficients in 6*M* hydrochloric acid are 283, >100 and >100 for uranium, cadmium and zinc respectively.) At the same time the residual organic solvents are also removed from the resin bed. On subsequent elution of uranium with 1*M* hydrochloric acid ($K_d \sim 1$), cadmium and zinc ($K_{d_{Cd}} \sim 10^3$; $K_{d_{Zn}} > 100$) are not co-eluted with it.

The ion-exchange separation method described was applied to the analysis of numerous geological speci-

Table 3. Effect of iron and molybdenum on the spectrophotometric determination of uranium with arsenazo III (5·0 μg of uranium taken)

Fe present, μg	U found, μg	Mo present, μg	U found, μg
0	5·00	0	5·10
50	5·00	5	5·40
100	5·00	50	5·80
150	5·00	75	4·90
200	4·94	100	4·50
300	4·80	200	0·00
500	4·54	300	0·00
1000	4·00	400	0·00
5000	1·53	500	0·00

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* Complete removal of iron (and also molybdenum) is impossible if it has been adsorbed from 6*M* hydrochloric acid or when an IBMK–THF–HCl sorption solution containing more than 100 mg of iron/30 ml is passed through the resin column.

Table 4. Results of uranium determinations in reference samples from the International Atomic Energy Agency, Vienna, Austria[7]

	U_3O_8 %					
	Spectrophotometry		Fluorimetry		Other laboratories	
Sample	A	B	A	B	I	II
S-1 (Torbernite; Australia)	0·456	0·457 (3000)	0·456	0·455 (3000)	0·483	0·471
S-2 (Torbernite; Spain)	0·298	0·300 (3000)	0·300	0·300 (3000)	0·313	0·313
S-3 (Carnotite; U.S.A.)	0·401	0·402 (3000)	0·401	0·402 (3000)	0·415	0·418
S-4 (Uraninite; Australia)	0·378	0·377 (3000)	0·379	0·378 (3000)	0·377	0·375
S-12 (Pitchblende; Spain)	0·016	0·016 (100)	0·016	0·016 (100)	0·014	0·014
S-13 (Pitchblende; Spain)	0·035	0·035 (100)	0·035	0·035 (100)	0·037	0·039

A = Results obtained for an unspiked sample.

B = Results obtained after deduction of a spike (shown in parentheses as μg of uranium added per g of sample) added before the dissolution of the sample.

I = Arsenazo III method.[7]

II = Mean of all methods used for uranium determination.[7]

mens (see later) and to test-solutions containing known amounts of uranium (1, 10 and 100 μg), molybdenum (5 mg), iron (100 mg) and cobalt (1 mg). Analyses of these mixtures showed that in the entire uranium eluate not more than 25 μg of iron were present (determined by atomic-absorption spectrophotometry) even if as much as 100 mg of this element were present in the sorption solution. Molybdenum and cobalt were completely separated, no detectable amounts being found in the uranium eluate.

The effect of iron and molybdenum on the spectrophotometric determination of uranium with arsenazo III was tested with various concentrations of these elements. From Table 3 it is seen that the tolerance limit for iron is relatively high, up to 150 μg of iron not interfering with the uranium determination. Thus, the method is much less sensitive to iron than the fluorimetric procedure in which much smaller quantities of iron cause an appreciable quenching of the uranium fluorescence.[1] On the other hand molybdenum has practically no influence on the fluorimetric method but interferes seriously when arsenazo III is used, giving a positive error when <75 μg are present and a large negative error when >100 μg are present in the solution measured (Table 3). In the presence of 200–500 μg of molybdenum no uranium was found. Interferences by iron and molybdenum are not to be expected to occur, however, after the ion-exchange

Table 5. Results of uranium determinations in reference rock samples

		Uranium, *ppm*†					
		Spectrophotometry		Fluorimetry			
Source*	Sample	A	B	A	B	Other laboratories§	Ref.
1	Sediment-1 (Shale; Germany)	93·6	94·8 (100)	91·2	93·1 (100)	104·2 (mean)	8
	Sediment-2 (Shale; Sweden)	2·76	2·85 (5)	2·73	2·63 (5)	3·67 (mean)	8
	Sediment-3 (Limestone; Iran)	3·24	3·23 (5)	3·25	3·36 (5)	3·34 (mean)	8
2	MRG-1 (Gabbro)	0·30	0·25 (1·0)	0·21	0·19 (1·0)	—	
	SY-2 (Syenite rock)	246	250 (200)	250	255 (200)	50–500	9
	SY-3 (Syenite rock)	634	630 (500)	600	623 (500)	100–1000	9
3	NIM-G (Granite)	15·80	16·00 (10·0)	16·37	16·17 (10·0)	10–63 (14)	10
	NIM-L (Lujavrite)	15·00	15·80 (10·0)	16·37	16·05 (10·0)	8–38 (13)	10
	NIM-N (Norite)	0·38	0·37 (1·0)	0·35	0·35 (1·0)	0·21–0·7 (0·5)	10
	NIM-P (Pyroxenite)	0·30	0·30 (1·0)	0·26	0·26 (1·0)	0·21–0·7 (0·5)	10
	NIM-S (Syenite)	0·60	0·55 (1·0)	0·56	0·50 (1·0)	0·06–0·9 (0·6)	10
	NIM-D (Dunite)	0·18	0·18 (1·0)	0·16	0·13 (1·0)	0·14–2 (0·5)	10
4	Granite GA	4·75	4·80 (5·0)	4·78	4·70 (5·0)	1·7; 2; 4·26; 4·86	11
	Granite GH	15·81	15·84 (15)	15·7	15·7 (15)	10; 12; 14·2; 19·71	11
	Basalte BR	1·66	1·69 (1·0)	1·46	1·40 (1·0)	0·9; 1·9; 2·1; 2·65	11
	Biotite Mica-Fe	66·10	66·00 (50)	60·31	60·81 (50)	35;40; 57; 94	11
	Phlogopite Mica-Mg	0·16	0·10 (1·0)	0·10	0·10 (1·0)	1·2	11
	Diorite DR-N	1·50	1·47 (1·0)	1·38	1·45 (1·0)	1; 2	11
	Serpentine UB-N	0·090	0·095 (1·0)	0·08	0·075 (1·0)	—	
	Bauxite BX-N	4·92	4·98 (5·0)	4·16	4·30 (5·0)	—	
	Disthène DT-N	1·43	1·40 (1·0)	1·37	1·39 (1·0)	—	
5	USGS-G-2 (Granite)	2·26		2·22		(2·0)	
	USGS-GSP-1 (Granodiorite)	2·42		2·45		(1·96)	
	USGS-AGV-1 (Andesite)	1·31		1·35		1·56‡ (1·88)	

* 1, IAEA, Vienna; 2, Canadian Standard Reference Materials Project; 3, National Institute for Metallurgy, Johannesburg; 4, Centre de Recherches Pétrographiques et Géochimiques, Vandoeuvre-lès-Nancy; 5, U.S. Geological Survey.

† A, B — See footnotes to Table 4.

§ Figures in parentheses are quoted from Flanagan[12]

‡ Determined fluorimetrically after separation by the THF–methyl glycol–HCl method.[4]

Table 6. Results of uranium determinations in Canadian radioactive ore standards[13]

	Uranium, %				
	Spectrophotometry		Fluorimetry		Other laboratories
Sample	A	B	A	B	(mean of all results)[13]
DH	0·194	0·176 (1500)	0·190	0·181 (1500)	0·177
DL	0·0042	0·0042 (50)	0·0042	0·0040 (50)	0·0039
BL-1	0·0230	0·0227 (250)	0·0227	0·0210 (250)	0·0219
BL-2	0·431	0·439 (5000)	0·431	0·433 (5000)	0·450
BL-3	0·923	0·925 (10^4)	0·922	0·930 (10^4)	1·016
BL-4	0·171	0·170 (1500)	0·171	0·174 (1500)	0·173

A,B—See footnotes to Table 4.

separation, because the amount of iron accompanying uranium in the eluate is always much lower than 150 μg and molybdenum is separated quantitatively. Furthermore, thorium, zirconium, titanium, rare-earth elements and phosphate, which also strongly interfere with the arsenazo III method,[1] will have no effect on the determination of uranium because they are completely separated by the anion-exchange. Thus, 100 mg of sodium phosphate gave no interference, and up to 100 mg of sulphate did not interfere with the ion-exchange separation of uranium.

The results of uranium determinations in numerous reference samples are shown in Tables 4–6. The spectrophotometric method gives somewhat higher results than fluorimetry when very iron-rich samples, *e.g.*, Biotite Mica-Fe (total Fe as Fe_2O_3 = 25·75%) and Bauxite BX-N (total Fe as Fe_2O_3 = 23·21%) (see Table 5) are analysed, because the amount of iron accompanying uranium into the eluate causes quenching of the uranium fluorescence. Apart from these few instances in which the fluorimetric procedure gives lower results, the uranium results are generally in reasonably good agreement with the results obtained in other laboratories, exceptions being Sediment-2 and Phlogopite Mica-Mg (see Table 5).

Because the method is based on separations on anion-exchange columns, which can be performed more or less automatically, it is possible to analyse numerous samples simultaneously, *i.e.*, the procedure is very well suited for the routine determination of uranium over a concentration range of about five orders of magnitude.

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ATOMIC-ABSORPTION DETERMINATION OF BERYLLIUM IN LIQUID ENVIRONMENTAL SAMPLES

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Summary—A method is described for the atomic-absorption determination of beryllium in liquid environmental samples after separation by solvent extraction and cation-exchange. The beryllium is first isolated from natural waters and beverages by chloroform extraction of its acetylacetonate from a solution at pH 7 and containing EDTA. The chloroform extract is then mixed in the ratio of 3:6:1 with tetrahydrofuran and methanol containing nitric acid, and passed through a column of Dowex 50 X8 (H^+-form). After removal of acetylacetone, chloroform and tetrahydrofuran by washing the resin bed with methanol-HNO_3, beryllium is eluted with 6*M* hydrochloric acid and determined by atomic-absorption spectroscopy. The method was successfully applied to determine beryllium in tap-, river- and sea-water samples, mineral waters and wines. Beryllium contents in the range from <0·01 to 2·3 μg/l. were found in these materials.

Determinations of trace quantities of beryllium in liquid environmental samples, *e.g.*, natural waters and beverages, are gaining increased importance with the growing interest in pollution of the environment with this toxic element. Analytical techniques based on atomic-absorption spectrophotometry,[1,2] emission spectroscopy,[3–10] fluorimetry[11–13] and spectrophotometry[14–20] can be employed. To avoid interference by matrix elements and to increase the sensitivity, suitable preconcentration techniques are often used to separate beryllium before its quantitative determination. Especially suitable for quantitative isolation of trace amounts of beryllium from natural waters are separation methods based on the chloroform (or carbon tetrachloride) extraction of beryllium acetylacetonate[3,13,18,19] or co-precipitation with suitable collectors such as the hydrous oxides of iron(III),[6,11,14–16,20] aluminium[15,16] and manganese,[20] or titanium phosphate.[17] Other techniques are based on the adsorption of beryllium on various sorbents such as a 1:1 mixture of activated charcoal and chlorinated lignin,[7] silica gel[12] and the strong-acid cation-exchanger Dowex 50 X8 (in the Fe^{3+} or Mn^{2+} form and treated with excess of ammonia solution).[20] Combinations of these methods may also be employed, *e.g.*, co-precipitation of beryllium with ferric hydroxide and subsequent separation by anion-exchange.[15]

In the present paper, a combination of separation techniques is described, which utilizes chloroform extraction of beryllium acetylacetonate[21,22] as the first preconcentration step, followed by cation-exchange enrichment of beryllium directly from the organic extract.

EXPERIMENTAL

Solutions and reagents

Ion-exchange resin. Dowex 50 X8 (100–200 mesh; H^+-form) was used. For purification, 500 g of the resin were treated successively with 2 litres of 6*M* nitric acid, 500 ml of 0·1*M* nitric acid, 2 litres of distilled water and 500 ml of reagent-grade methanol. The purified resin was air-dried. Before use 4 g of the cation-exchanger were slurried with a few ml of $CHCl_3$–THF–MeOH solution and transferred to the ion-exchange column as completely as possible with the same solution.

Standard beryllium solutions. An exactly weighed amount of beryllium nitrate tetrahydrate was dissolved in 1*M* nitric acid to obtain a stock solution containing 630 ppm of beryllium. From this solution, standard solutions 0·1*M* in nitric acid and 0·6*M* in hydrochloric acid were prepared, which contained from 0·006 to 630 ppm and from 0·003 to 630 ppm of beryllium respectively.

$CHCl_3$-THF-MeOH solution. This solution, of 0·1*M* overall acidity, is prepared by mixing 30 ml of chloroform with 60 ml of tetrahydrofuran (THF) and 10 ml of MeOH–HNO_3 mixture (of 1*M* overall acidity).

MeOH–HNO_3 mixture. A mixture with 1*M* overall acidity is prepared by dilution of 69 ml of concentrated nitric acid to 1 litre with methanol. To obtain the MeOH–HNO_3 mixture of 0·1*M* overall acidity which is used for the ion-exchange separation of beryllium, 10 ml of this solution are diluted to 100 ml with methanol.

THF–MeOH solution. This consists of a 9:1 v/v mixture of tetrahydrofuran and MeOH–HNO_3 mixture (of 1*M* overall acidity). The overall acidity of this THF–MeOH solution is 0·1*M*.

Other reagents. Acetylacetone, 5% aqueous acetylacetone solution, chloroform, solid EDTA (disodium salt), 10% and 0·1*M* aqueous EDTA solutions, 5% and 20% solutions of sodium hydroxide, 0·1*M*, 0·6*M*, 6*M* and concentrated hydrochloric acid, 1% methanolic solution of arsenazo I, 2*M* sodium acetate, tetrahydrofuran, methanol and concentrated nitric, sulphuric, perchloric, and hydrobromic acids. The reagents used were all stable for at least 6 months

Apparatus and operating conditions

A Perkin–Elmer 303 atomic-absorption spectrophotometer (equipped with a Hitachi–Perkin–Elmer Recorder 56 connected to a read-out accessory) was used with the following instrumental settings.

Grating:	ultraviolet
Wavelength:	234·9 nm
Scale expansion:	up to 30X
Slit:	5 (3 mm; 2 nm bandpass)
Source:	beryllium hollow-cathode lamp
Lamp current:	30 mA
Burner:	one-slit burner for the acetylene–nitrous oxide flame
Acetylene pressure:	8 psig; 14 on flowmeter (arbitrary scale)
Nitrous oxide-pressure:	30 psig; 6 on flowmeter (arbitrary scale)
Noise suppression:	up to 5

Under these conditions the sensitivity for 1% absorption was found to be 0·015 ppm of beryllium in 0·6*M* hydrochloric acid. The detection limit for beryllium was 0·001 ppm. The calibration curve was linear up to 0.5 μg of beryllium per ml.

The spectrophotometric calibration curve (Beckman DB-GT instrument, 1 cm cells) was linear up to a beryllium concentration of 1·0 μg/ml.

The separations of beryllium were performed in ion-exchange columns of the type and dimensions described earlier.[23]

Determination of distribution coefficients

The weight distribution coefficients (K_d-values on Dowex 50) of beryllium were determined by using the batch equilibrium method.[22]

Pretreatment of samples and solvent extraction of beryllium

Natural waters and mineral waters. To 1 litre of the water sample (saline or non-saline), in the polyethylene bottle in which it was collected, 10 ml of concentrated hydrochloric acid are added and after filtration the sample is let stand for about 24 hr (degassing of the sample; mainly for removal of CO_2). Then 3 g of EDTA are added and dissolved, the pH is adjusted to about 7 with 20% sodium hydroxide solution (about 20–25 ml are required) and after addition of 2 ml of acetylacetone the mixture is shaken thoroughly until complete homogeneity is attained. Finally the pH of the solution is adjusted to 7 by careful addition of 20% and 5% sodium hydroxide solutions and let stand for at least 2 hr (preferably overnight) so that beryllium can react quantitatively with the acetylacetone. Then the sample solution is transferred to a 2-litre separatory funnel, 20 ml of chloroform are added and beryllium acetylacetonate is extracted by vigorous shaking for 1 min. After phase separation the organic extract is passed through a dry filter paper to remove aqueous droplets adhering to the organic layer. The extraction of the sample solution is repeated twice with 10 ml of chloroform each time and a shaking period of 30 sec. After filtration through dry filter paper these last two extracts are combined with the first and thus about 30 ml of chloroform–acetylacetone solution are obtained ("beryllium extract"). From this organic mixture beryllium is isolated by the cation-exchange procedure described below.

Wines. To the wine sample (1 litre) concentrated hydrochloric acid is added to make it 0·6*M* in this acid and after about 24 hr the acidified wine is filtered and 250 ml of it, in a 600-ml beaker, are evaporated to about one-third of the original volume. Subsequently 50 ml of concentrated nitric acid are added (preferably after the concentrated wine sample has been allowed to cool to room temperature) and the mixture is evaporated to dryness on a steam-bath. The residue is taken up in 100 ml of a 3:1:1 mixture of concentrated nitric, sulphuric and perchloric acids and the solution is first heated on a steam-bath (until its volume is reduced to about 50 ml) and then evaporated to dryness on a sand-bath. To destroy perchlorate, 25 ml of concentrated hydrobromic acid are added and after evaporation of the solution to dryness on the steam-bath the residue is dissolved in about 20 ml of 0·1*M* hydrochloric acid or water. Then 20 ml of 10% EDTA solution are added, the pH is adjusted to about 7 with sodium hydroxide, 2 ml of 5% aqueous acetylacetone solution are added, and then the same extraction procedure is followed as described above for the analysis of waters except that only half the volume of chloroform is used, *i.e.*, 10 ml for the first and 5 ml each for the two subsequent extractions.

Ion-exchange separation

The beryllium extract (about 30 ml)* is mixed with 60 ml of tetrahydrofuran and 10 ml of MeOH–HNO_3 mixture (overall acidity 1*M*) and the resulting solution (the sorption solution, overall acidity 0·1*M*) is passed through a 4-g column of the cation-exchanger (pretreated with 10 ml of $CHCl_3$–THF–MeOH solution) at a flowrate of about 60 ml/hr. The resin bed is then washed with about 5 ml of THF–MeOH solution, followed by about 10 ml of MeOH–HNO_3 mixture (overall acidity 0·1*M*) and finally beryllium is eluted with 50 ml of 6*M* hydrochloric acid (beryllium eluate).

Quantitative determination of beryllium

Atomic-absorption spectroscopy. The beryllium eluate is evaporated under an infrared lamp, the residue is dissolved in 1 ml of 6*M* hydrochloric acid, and after dilution with water to 10 ml the solution is aspirated into the acetylene–nitrous oxide flame. A calibration curve is constructed by aspirating suitable beryllium standard solutions before and after each batch of samples.

A reagent blank is run through the whole procedure (starting with addition of the first reagent) and finally deducted from the beryllium found in the sample.

Spectrophotometry. The beryllium eluate is evaporated and the residue is taken up in 1 ml of 6*M* hydrochloric acid; then 1 ml of arsenazo I solution and 1 ml of 0·1*M* EDTA solution are added, and the solution is diluted to 10 ml with 2*M* sodium acetate. The absorbance is measured at 580 nm against a reagent blank. The absorbance is 0·350 for 1 ppm of beryllium in the solution measured.

RESULTS AND DISCUSSION

Acidification of the samples with concentrated hydrochloric acid prevents the adsorption of beryllium on the walls of the sample container and co-precipitation of beryllium with hydroxides and phosphates of iron *etc.* which may occasionally be present in relatively large amounts, e.g., in some mineral waters and especially in wine samples.

The chloroform extraction of beryllium acetylacetonate is carried out in the presence of EDTA to prevent the co-extraction of most of the main and trace constituents of liquid environmental samples. Thus, a beryllium extract is obtained which is virtually free from elements interfering with the assay of beryllium.

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* To prepare the sorption solution from the beryllium extract (about 20 ml) obtained from a wine sample, mix the extract with about 40 ml of tetrahydrofuran and 7 ml of MeOH–HNO_3 mixture (overall acidity 1*M*).

Unfortunately the assay cannot be done directly on the chloroform extract by atomic-absorption spectroscopy. Therefore, an attempt was made to determine beryllium in aqueous medium after removal of chloroform by evaporation. However, the volatility of beryllium acetylacetonate caused considerable losses of the element (especially when only submicrogram amounts were present) even when the evaporation was carried out at very low heat and with 4–5 ml of concentrated hydrochloric acid and 25 ml of methanol added to the chloroform extract. The hydrochloric acid was added to liberate beryllium from its acetylacetone chelate and methanol was added to obtain a homogeneous mixture with the chloroform.

Therefore a means was sought for separating beryllium from both the chelating agent and the chloroform without the application of heat. As a result, the cation-exchange method utilizing adsorption of beryllium on Dowex 50 from the mixed $CHCl_3$–THF–MeOH medium containing nitric acid was developed. In this mixture the presence of tetrahydrofuran is necessary to obtain a homogeneous solution, and the methanol is the component regulating the flow-rate through the ion-exchange column. In the absence of methanol the viscosity of the sorption solution is extremely low, so that a flow-rate is attained at which complete adsorption of beryllium is not guaranteed. Nitric acid has to be present in the mixture so that beryllium is in the ionic form which is adsorbed on the cation-exchanger during the sorption process, after which residual chloroform and acetylacetone are removed by washing the resin bed with THF–MeOH solution and MeOH–HNO_3 mixture. Thus, after the elution of beryllium with 6*M* hydrochloric acid an eluate is obtained which does not contain organic substances which could give rise to the formation of beryllium compounds that are volatile during evaporation of the eluate.

Through the combination of this ion-exchange separation step with the extraction of beryllium acetylacetonate from the water sample it is possible to isolate submicrogram and microgram amounts of this element from both saline and non-saline waters. Table 1 shows that beryllium recoveries are in the range 93–103%.

That the separation of beryllium is not affected by large quantities of foreign ions (which are usually only trace constituents of natural waters) is demonstrated by the results presented in Table 2.

The only two elements which are co-extracted with beryllium to a considerable extent are iron and copper, and then only from sea-water (see footnote to Table 2) because the dissolved salts act as salting-out agents during the extraction. In the cation-exchange separation of beryllium these co-extracted elements are co-adsorbed with the beryllium irrespective of the acidity used (the beryllium adsorption was found to decrease only slightly with increasing nitric acid concentration in the $CHCl_3$–THF–MeOH–HNO_3 mixture (Table 3).

In the absence of the organic solvents, distribution coefficients for beryllium of 255 and 900 were measured in 0·1*M* hydrochloric and 0·1*M* nitric acid media respectively. Under the conditions of elution, *i.e.*, in 6*M* hydrochloric acid, the distribution coefficient for beryllium was <1. Iron and copper are co-eluted with the beryllium but do not interfere with the atomic-absorption determination nor with the spectrophotometric method (because of the masking action of the EDTA added). However, the spectrophotometric results often showed a positive bias of about 3–5%; this is most probably due to the effect of small amounts of coloured organic matter in the residue obtained after evaporation of the beryllium eluate. Another disadvantage of the spectrophotometric method is its low sensitivity: beryllium concentrations below 0·06 μg/ml in the final solution measured cannot be determined with sufficient accuracy. Since this concentration is rarely reached in beryllium eluates obtained from 1-litre samples, the arsenazo I method was not used for most of the liquid environmental samples. The much more sensitive atomic-absorption spectroscopy technique (in which, contrary to recent information,[1] sodium was not

Table 1. Effect of concentration on beryllium recovery from tap- and sea-water

Amount of Be added to 1 litre of the water sample, *μg*	Tap-water* Beryllium found *μg/l.*	%	Sea-water† Beryllium found *μg/l.*	%
0·63	0·62	98	0·65	103
1·26	1·19	94	1·25	99·5
6·30	5·90	93	5·95	94·5
12·6	11·9	94·5	11·8	94·0
63·0	60·5	96	60·8	96·5
126	120	95·5	123	97·8
630	611	97	621	98·5

* Vienna tap-water was taken and found to contain $0{\cdot}02_7$ *μg* of beryllium per litre. This concentration was subtracted from those found.

† Artificial sea-water was prepared by dissolving the following chemicals in one litre of tap-water: NaCl (28 g), KCl (0·8 g), $MgCl_2.6H_2O$ (1 g), $MgSO_4.7H_2O$ (6·96 g) and $CaCl_2.2H_2O$ (1·325 g). Its beryllium concentration was $0{\cdot}02_6$ *μg*/l, which was subtracted from the values found.

Table 2. Effect of foreign ions on beryllium recovery from artificial sea-water (1·26 μg of beryllium were added to each litre sample)

Foreign ion added to 1-litre sample of artificial sea-water, *mg*	Beryllium recovered, *μg*	%	Foreign ion present in beryllium eluate, *μg*	%
—	1·23	98	—	—
Cr(III) 0·8	1·23	98	3·5	0·4
Fe(III) 2·0*	1·25	99	1×10^3	50
Co(II) 1·05	1·23	98	1·0	0·1
Ni(II) 0·95	1·23	98	1·5	0·2
Cu(II) 1·13*	1·25	99	150	13
Mn(II) 0·7	1·24	98·5	1·8	0·25
UO_2(II) 0·01	1·24	98·5	0·04	0·4
All metal ions listed above (~7 mg)	1·24	98·5	not determined	

* When the same amounts of these elements were added to corresponding samples of tap-water the concentrations of iron and copper in the beryllium eluates were found to be considerably lower, 40 and 3 μg respectively.

Table 3. Distribution coefficients of beryllium at varying overall acidities of the $CHCl_3$–THF–MeOH mixture (sorption solution)

Overall acidity	K_d
0·1*M* HNO_3*	580
0·5*M* HNO_3	560
1·0*M* HNO_3	540

* This is the acidity at which beryllium is adsorbed on Dowex 50 when applying the separation procedure described.

found to interfere) being preferred. Sometimes even the atomic-absorption method is not sensitive enough to determine beryllium accurately. Thus, in certain samples it was possible to detect beryllium (detection limit = 0.001 ppm) but the signals were not sufficiently strong to give reliable results.

Numerous samples of Austrian waters were analysed by the methods described above. Good agreement was obtained between results for spiked and unspiked samples. For sea-water (Adriatic Sea and Pacific Ocean) results ranging from <0·01 to 0·02 μg/l. were obtained, in agreement with the range of 0·001–0·03 μg/l. quoted in the literature.[24]

In most of the natural non-saline surface waters investigated, only very low beryllium contents were found (0·01–0·03 μg/l.); this is due to the relative insolubility of the oxide and hydroxide of beryllium at the normal pH range for these waters. Also, in the weathering process beryllium is concentrated in hydrolysates, and like aluminium does not go into solution to any appreciable degree.

On the other hand, some mineralwaters were found to have beryllium concentrations higher by several orders of magnitude than those found for most saline and non-saline waters (Table 4). Measurements of the pH-values and calcium contents (as a

Table 4. Results of determinations of beryllium in samples of bottled mineral waters

Trade name and geographical origin of sample	Beryllium contents, *μg/l.* A	B
Vöslauer, Bad Vöslau, Lower Austria	<0·01	~0·00$_5$ (0·063)
Römerquelle, Bad Vöslau, Lower Austria	<0·01	~0·00$_7$ (0·063)
Hunyadi Janos, Saxlehner's Bitterquelle, Budapest, Hungary	<0·01	<0·01 (0·063)
Radenska, Radenska Slatina, Yugoslavia	0·02$_5$	0·03 (0·063)
Güssinger, Burg Güssing, Burgenland	0·05$_5$	0·06 (0·063)
Gasteiner, Bad Gastein, Salzburg	0·06	0·05$_5$ (0·063)
Gleichenberger Johannisbrunnen, Bad Gleichenberg, Styria	0·11	0·10 (0·126)
Donat, Rogaska Slatina, Yugoslavia	0·75	0·85 (0·630)
Thalheimer, Thalheim/Judenburg, Styria	1·02	1·07 (1·260)
Preblauer, Preblau, Carinthia	2·30	2·25 (3·150)

A = Beryllium contents determined by atomic-absorption spectrophotometry following solvent extraction and cation-exchange of beryllium.

B = Same as for A but after deduction of a spike (the figure in parentheses).

Table 5. Beryllium in wine samples (vintage 1974).

Trade name and geographical origin	Beryllium contents, μg/l.
Red wines	
St. Laurent, Loiben/Wachau, Lower Austria	0·07
Poisdorfer, Poisdorf, Lower Austria	0·07
Burgunder, Kirchberg a. Wagram, Lower Austria	0·08
Rotwein, Sonnenberg/Baden, Lower Austria	0·09
Rotspecht, Rusterberg, Burgenland	0·11
White wines	
Räuschl, Loiben/Wachau, Lower Austria	<0·01
Neuburger, Baden, Lower Austria	0·05
Neuburger, Kirchberg am Wagram, Lower Austria	0·08
Weinzierlberg (Grüner-Veltliner), Drasenhofen, Lower Austria	0·09
Neusiedler Seekönig, Rusterberg, Burgenland	0·15

measure of the carbonate concentrations) showed that the mineral waters with extremely high beryllium contents are considerably more alkaline than the others in which the beryllium levels are comparable to those of the non-saline waters. For instance, the calcium concentration in the Thalheimer and Preblauer samples was 450 and 340 mg/l. respectively, while in the samples of Vöslauer and Römerquelle it was 100 and 140 mg/l. The pH-values for the last two mineral waters were found to be lower by about 2 and 3·5 pH units than those of Thalheimer and Preblauer respectively.

In an oil-field water from a deep oil-well, (Litzelsdorf 1) containing appreciable amounts of dissolved carbonates, a beryllium content of about 0·10 μg/l. was found. Because of the presence of large quantities of organic substances the isolation of beryllium from this oil-field water was most probably not quite quantitative (it was very difficult to obtain two distinct phases during the extraction of beryllium acetylacetonate with chloroform) so the beryllium concentration may actually be higher.

According to previous experience[25] beryllium is regarded as one of the trace elements which is either not contained in wines under normal conditions or cannot be detected with certainty. That this is not the case, however, is illustrated by the results shown in Table 5 from which it is seen that in only one out of ten different wine samples (collected at random) was the beryllium content below the limit for accurate determination. It is also evident that wines originating from the same locality contain very similar beryllium concentrations. Before separation of beryllium the wine samples have to be wet-ashed by the method described. Direct extraction of beryllium from wine is not possible because of the presence of the alcohol.

In conclusion it should be mentioned that in place of the solvent extraction procedure beryllium can also be concentrated quantitatively on a 4-g column of the cation-exchanger Dowex 50 from one litre of non-saline water which is 0·1*M* in nitric acid. However, this cation-exchange method was abandoned in favour of the extraction method because the latter can be performed much more rapidly and is also applicable to natural waters of high salinity such as sea-water and mineral-waters.

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APPLICATION OF ION-EXCHANGE SEPARATIONS TO DETERMINATION OF TRACE ELEMENTS IN NATURAL WATERS—IX

SIMULTANEOUS ISOLATION AND DETERMINATION OF URANIUM AND THORIUM

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Summary—A method is described for the determination of uranium and thorium in samples of natural waters. After acidification with citric acid the water sample is filtered and sodium citrate and ascorbic acid are added. The resulting solution of pH 3 is passed through a 4-g column of Dowex 1 X8 (citrate form) on which both uranium and thorium are adsorbed as anionic citrate complexes. Thorium is eluted with 8*M* hydrochloric acid and separated from co-eluted substances by anion-exchange in 8*M* nitric acid medium on a separate 2-g column of the same resin in the nitrate form. After complete removal of iron by washing with a mixture consisting of IBMK, acetone and 1*M* hydrochloric acid (1:8:1 v/v) and treatment of the resin with 6*M* hydrochloric acid, the uranium is eluted from the 4-g column with 1*M* hydrochloric acid. In the eluate thorium is determined spectrophotometrically (arsenazo III method) while fluorimetry is employed for the assay of uranium. The procedure was used for the determination of uranium and thorium in numerous water samples collected in Austria, including samples of mineral-waters. The results indicate that a simple relationship exists between the uranium and thorium contents of waters which makes it possible to calculate the approximate thorium content of a sample on the basis of its uranium concentration and *vice versa*.

Investigations of the isolation of trace quantities of uranium and thorium from natural waters have shown that, except for a method described by Korkisch *et al.*,[1] anion-exchange procedures are not available by means of which both elements can be separated simultaneously from a single water sample without its preliminary evaporation. In that method, the anionic ascorbate complexes of uranium, thorium and some other elements such as molybdenum, vanadium and titanium are first adsorbed on Amberlite IRA-400 or Dowex 1 (in the ascorbate form) from the water sample containing ascorbic acid and adjusted to a pH of 4–4·5. Thorium and uranium are eluted with 0·1*M* hydrochloric acid directly into a small column of Dowex 50, on which both elements are adsorbed. From this resin uranium is eluted with 1*M* hydrochloric acid and determined polarographically by means of the catalytic nitrate wave. Subsequently thorium is eluted with 3*M* sulphuric acid and determined spectrophotometrically by the Thoronol method. Disadvantages of the technique are that molybdenum, vanadium and titanium are co-adsorbed and co-eluted with uranium and thorium and interfere seriously with their determination. Furthermore, the volume of water sample from which uranium and thorium can be adsorbed on the anion-exchanger is rather critical; the effect of the principal anions in waters, especially sulphate, on the adsorbability of ascorbate complexes is most pronounced.

Although the effect of anions on the adsorption of thorium from samples of high salinity cannot be completely eliminated, the present method has the additional advantage of speed over a previous method of thorium isolation, based on evaporation of the water sample and anion-exchange in 7*M* nitric acid.[2] For uranium isolation the present method is of about the same efficiency but greater versatility than the thiocyanate method described in a previous paper,[3] because thorium is isolated quantitatively at the same time.

EXPERIMENTAL

Reagents

Ion-exchange resin. Dowex 1 (Bio-Rad AGl, X8; 100–200 mesh; chloride form) was used. To prepare the citrate form, 4 g of the resin were slurried with a few ml of 6*M* hydrochloric acid and after about 30 min transferred to the ion-exchange column as completely as possible with the same acid. Subsequently the resin bed was washed successively with 20 ml of water, 50 ml of 10% aqueous sodium citrate solution and 30 ml of wash-solution. The nitrate form of the resin was prepared as described earlier.[2]

Standard solutions. Aliquots of stock solutions of thorium (5 mg/ml) and uranium (1 mg/ml) (both as chlorides) in 6*M* hydrochloric acid were diluted with 1*M* hydrochloric acid to obtain standard solutions containing from 1 to 10 ppm of thorium and uranium.

Wash-solution. Ten g of citric acid, 3 g of sodium citrate and 2 g of ascorbic acid were dissolved in distilled water and the solution was diluted with water to 1 litre (this solution has a pH of 3).

IBMK–acetone–1M HCl solution. A mixture of isobutyl methyl ketone (IBMK), acetone and 1*M* hydrochloric acid (1:8:1 v/v). It is not recommended to use the freshly prepared mixture, because bubbles may form in the resin bed. Solutions more than about one week old should also not be used (polymerization of acetone by the action of hydrochloric acid). Ideally the mixture should be prepared 12–24 hr before use.

Other reagents. Citric acid, trisodium citrate dihydrate (solid and as 10% aqueous solution), ascorbic acid, 0·2% arsenazo III solution (freshly prepared and filtered), 2% potassium permanganate solution, concentrated formic acid, 1*M*, 6*M*, 8*M*, and concentrated hydrochloric acid, 8*M* nitric acid.

Apparatus

The separations of uranium and thorium were performed in ion-exchange columns of the type and dimensions described earlier.[4]

Determination of distribution coefficients

The weight distribution coefficients (K_d-values) of uranium, thorium and other elements were determined by the batch equilibrium method.[5]

Pretreatment of samples

As soon as possible after the water sample is taken (in a plastic bottle), 1 litre of it is acidified with 10 g of citric acid. After complete dissolution of this acid the sample is filtered through a dense filter and to the filtrate 3 g of sodium citrate and 2 g of ascorbic acid are added and the solution* (sorption solution) is shaken until these reagents are dissolved completely. It a larger or smaller volume of sample is required for analysis the amounts of all reagents added are varied accordingly.

Ion-exchange separation

Adsorption of uranium and thorium. About 12 hr after preparation the sorption solution is passed through a 4-g column of the anion-exchanger (citrate form, pretreated with 30 ml of the wash-solution) at a flow-rate of about 50 ml/hr, then the resin is washed with 100 ml of the wash-solution.

Separation of thorium. The adsorbed thorium is eluted with 50 ml of 8*M* hydrochloric acid and the eluate is evaporated under an infrared lamp until the co-eluted organic acids (mainly citric acid) start to decompose. At this point 10 ml of 8*M* nitric acid are added, the solution is evaporated once more and the residue of decomposed citric acid containing the thorium is dissolved in 50 ml of 8*M* nitric acid. The resulting solution (usually brown) is passed through a column containing 2 g of the anion-exchanger (nitrate form, pretreated with 50 ml of 8*M* nitric acid) at a flow-rate of about 50 ml/hr, the resin is washed with 50 ml of 8*M* nitric acid and thorium is eluted with 50 ml of 6*M* hydrochloric acid (thorium eluate).

Separation of uranium. After the elution of thorium from the 4-g column, the resin is washed with 100 ml of IBMK–acetone–1*M* HCl solution to remove all of the iron, then with 100 ml of 6*M* hydrochloric acid, and finally uranium is eluted† with 100 ml of 1*M* hydrochloric acid (uranium eluate).

Quantitative determinations

Thorium. The thorium eluate is evaporated to dryness on a steam-bath and the residue is taken up in 10 ml of 1*M* hydrochloric acid. Then 5 ml of 2% potassium permanganate solution are added and the solution is again evaporated to dryness (oxidation of organic matter from the resin). The residue is dissolved in 10 ml of 6*M* hydrochloric acid and after addition of 2 ml of concentrated formic acid the solution is evaporated to dryness on a steam-bath (destruction of residual nitrate). The residue is dissolved in 5 ml of concentrated hydrochloric acid and transferred to a 10-ml standard flask to which 1 ml of arsenazo III solution (filtered immediately before use) is added, followed by water to dilute the solution to 10 ml. The absorbance of the resulting solution is measured at 660 nm against a reagent blank and its thorium content determined from a calibration curve constructed in the same way. Beer's law is obeyed in the thorium range 0–1·5 μg/ml. An absorbance of 0·560 corresponds to 1·0 μg/ml.

Uranium, fluorimetric method. The uranium eluate is evaporated to dryness on a steam-bath or under an infrared lamp and the residue is dissolved in 2 ml of 6*M* hydrochloric acid. A suitable volume of this solution (*e.g.*, 0·1 ml) is evaporated in a small platinum dish[6,7] and after the addition of a "Fluorbase" pellet,[8] a melt is prepared under strictly controlled conditions.[6,7] The fluorescence intensity of the cold flux is measured and compared with the intensity of fluxes of known uranium concentrations.

Uranium, spectrophotometric method. If the 2 ml of 6*M* hydrochloric acid (see fluorimetric method above) contain more than about 0·5 μg of uranium the spectrophotometric arsenazo III method[8] can be used.

RESULTS AND DISCUSSION

Previous investigations by Korkisch and Hazan[9] have shown that the anionic citrate complexes of uranium and thorium are adsorbable on strongly basic resins from both aqueous and organic solvent systems. This fact has been utilized for the simultaneous enrichment of these two elements directly from samples of natural waters, as described above.

Studies on the effect of concentration of citric acid on the recovery of uranium and thorium gave the results presented in Table 1.

At citric acid concentrations below 1% the two elements are not completely retained by the anion-exchanger. On the other hand recovery of uranium and

Table 1. Effect of concentration of citric acid on the recovery of uranium and thorium

Citric acid present in the sorption solution (≡ 1 litre of tap water), %	Contents found, μg/l.			
	Uranium		Thorium	
	A	B	A	B
0·1	0·0	4·2	0·0	5·0
0·5	0·0	4·3	0·3	5·3
1·0	0·20	5·2	1·7	6·7
2·0	0·19	5·2	1·8	6·7
3·0	0·20	5·2	1·7	6·7

A = Results obtained without a spike.

B = Results when a spike of 5-μg each of uranium and thorium was added to the water samples (Vienna tap water taken 20 min after opening the tap, 9 January, 1975) before passing them through the 4-g anion-exchange columns.

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* If its pH is not in the range 3–4, more citric acid and/or sodium citrate should be added.

† Before the elution it is advisable to remove bubbles from the resin bed by gentle stirring with a glass rod.

Table 2. Effect of the pH of the sorption solution on the recovery of uranium and thorium

pH of sorption solution (≡ 1 litre of tap water)	Contents found, $\mu g/l.$			
	Uranium		Thorium	
	A	B	A	B
3	0·20	0·19	1·6	1·6
4	0·18	0·18	1·6	1·7
5	0·0	0·0	1·5	1·5
6	0·0	0·0	1·3	1·2
7	0·0	0·0	0·5	0·6

A = Results without a spike.

B = Results after deduction of 5-μg spikes of uranium and thorium added to the water samples before passing them through the 4-g anion-exchange columns.

Table 4. Effect of some co-adsorbed metal ions on the separation and determination of uranium and thorium

Amount of metal ion added to 1 litre of tap water, mg	Contents found*, $\mu g/l.$	
	Uranium	Thorium
Fe(III) 10	0·19	1·7
V(V) 1	0·18	1·4
Cr(III) 1	0·19	1·4
Mn(II) 1	0·20	1·7
Co(II) 1	0·18	1·5
Ni(II) 1	0·17	1·6
Cu(II) 1	0·18	1·7
Zn(II) 1	0·15	1·6
Cd(II) 1	0·18	1·6
— —	0·20	1·6

* These results were obtained after deduction of known amounts of uranium (1·0 μg) and thorium (5·0 μg) added to the water samples before passing them through the 4-g anion-exchange columns.

thorium is quantitative at 1–3% citric acid concentration, and at the 1% citric acid level is not affected by the simultaneous presence of 3 g of sodium citrate and 2 g of ascorbic acid per litre. Under these conditions the pH of the sorption solution is very nearly 3, which according to Table 2 guarantees complete adsorption of uranium and thorium. These two elements are also quantitatively retained at pH 4 but not at lower acidities (see Table 2).

The ascorbic acid in the sorption solution reduces iron(III) to iron(II), which according to Table 3 is much less strongly retained than iron(III) by the anion-exchanger. Thus, if the concentration of iron(II) is about 1000 μg/l., less than about 5% of it is adsorbed on the resin under the conditions used, and about 50% of this is removed by passing the wash-solution through the resin bed. Another 25% of the adsorbed iron(II) is eluted together with thorium by the 8*M* hydrochloric acid while the residual 25% of iron is removed by elution with the IBMK–acetone–1*M* HCl solution (in this medium the K_d-values of iron and uranium are 1 and 1050 respectively).[8] Thus, it is possible to separate uranium completely from iron, which interferes with the fluorimetric assay of uranium by quenching its fluorescence.

In the elution of thorium with 8*M* hydrochloric acid ($K_d < 1$), which separates it from uranium, not only citric acid is co-eluted (displaced from the resin by the hydrochloric acid) but also several of the metal ions such as aluminium, titanium, zirconium, chromium, nickel and vanadium which are co-adsorbed with uranium and thorium during the sorption process. Not contained in this thorium eluate are uranium [both uranium(VI), $K_d \simeq 10^3$ and also uranium(IV) $K_d \simeq 50$ are retained by the resin at this acidity],[5] cobalt, copper, molybdenum and zinc (as well as traces of cadmium and manganese). Many of these elements are relatively strongly retained by the resin from the sorption solution (see distribution coefficients listed in Table 3). The effect of these elements as well as that of vanadium was therefore studied with respect to the separation and determination of uranium and thorium. From Table 4 it is seen that they did not affect the recoveries of uranium and thorium.* Vanadium, aluminium, titanium *etc.* (see above) are co-eluted with thorium and thus separated

Table 3. Distribution coefficients of metal ions in the sorption solution (in each case 1 mg of the metal ion was dissolved in 20 ml of the solution and equilibrated with 1 g of Dowex 1 X8, citrate form).

Metal ion	Distribution coefficient	Metal ion	Distribution coefficient
UO_2(II)	$4·0 \times 10^4$	Fe(II)*	100
Th(IV)	$1·6 \times 10^4$	Ni(II)	80
Ti(IV)	5×10^4	Co(II)	70
Zr(IV)	4×10^4	Cr(III)	40
Al(III)	$3·3 \times 10^3$	Zn(II)	25
V(V)	$\gg 10^4$	Pb(II)	10
Mo(VI)	$\gg 10^4$	Cd(II)	2
W(VI)	$3·3 \times 10^3$	Mn(II)	1
Cu(II)	195	Tl(I)	1

* For iron(III) a distribution coefficient of $1·2 \times 10^3$ was measured in the absence of ascorbic acid.

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* Since the main cationic constituents of natural waters, *i.e.*, calcium, magnesium and the alkali metals, are not retained under the conditions of uranium and thorium adsorption their effect on the recovery of these two elements was not investigated.

Table 5. Effect of citric acid concentration on the spectrophotometric determination of thorium by the arsenazo III method

Citric acid concentration in measured solution, *mg/ml*	Absorbance* of 10-*ml* measured solution containing 0 *μg* of thorium	2	4	10
0	0·0	0·110	0·225	0·560
5	0·02	0·07	0·130	0·390
10	0·03	0·06	0·120	0·350
20	0·04	0·05	0·110	0·340
40	0·04	0·04	0·100	0·330

* At 660 nm, 1-cm cells.

from uranium by the 8*M* hydrochloric acid. Cobalt, copper *etc.* are separated from uranium by elution with 6*M* hydrochloric acid; at this acid concentration the K_d-value of uranium is 283.[7] On subsequent elution of uranium with 1*M* hydrochloric acid an eluate is obtained which contains only uranium and molybdenum because co-adsorbed zinc and cadmium are not eluted under these conditions.

For the separation of thorium from citric acid, which strongly interferes with the spectrophotometric thorium determination (see Table 5), a second anion-exchange procedure is employed, utilizing adsorption of the anionic nitrate complex of thorium[2] on Dowex 1 from 8*M* nitric acid. This separation is less time-consuming than wet-ashing procedures for removal of citric acid. An additional advantage is that all elements co-eluted with thorium by 8*M* hydrochloric acid (including titanium and zirconium, which strongly interfere with the arsenazo III method) are separated quantitatively from the thorium, so the thorium can be determined spectrophotometrically free from interferences.

On acidification of a natural non-saline water with citric acid the bicarbonates and carbonates of calcium, magnesium, *etc.* are transformed into citrates so that only sulphate will be present as a major foreign anion during the adsorption of uranium and thorium on the anion-exchanger (citrate form). That this anion has a decided influence on the recovery of thorium from water samples is evident from the results presented in Table 6 from which it is seen that quantitative isolation of thorium is possible from up to 2 litres of sample but not from 5 litres, although the distribution coefficient of $1{\cdot}6 \times 10^4$ indicates that thorium is adsorbable to practically the same extent as uranium ($K_d = 4 \times 10^4$, Table 3). The reason for this anomalous behaviour is that in contrast to thorium, uranium forms a very stable anionic sulphate complex at low acidities[5] so that the continuous displacement of citrate by sulphate during the sorption process does not affect the uranium adsorption. Consequently uranium is adsorbed quantitatively (as anionic citrate and sulphate complexes) from 5 litres of tap water while less than 10% of the thorium is retained by the resin, which after passage of 5 litres of sorption solution has been transformed into a resin which is no longer exclusively (or even principally) in the citrate form, but rather in the sulphate form owing to the adsorption of sulphate in course of the sorption process, this causing continuous displacement of thorium from the resin bed. This effect of sulphate becomes most pronounced when analysing mineral-waters. Thus, from the results shown in Table 7 it is seen that considerable losses of thorium but not of uranium are observed in the presence of large amounts of sulphate. For instance, the most significant loss of thorium was observed with Thalheimer, which contains 590 mg of sulphate per litre, whereas there was no loss of thorium from Preblauer, which contains only 30 mg of sulphate per litre. This strong influence of sulphate and also of chloride (which has a similar but smaller effect) on thorium adsorption makes it impossible to apply the present method to the analysis of natural waters of high salinity, including sea-water and oil-field waters. However, for the analysis of non-saline waters of normal hardness the method can be used most successfully, as can be seen from the results of water analyses presented in Tables 6 and 8.

In a series of analyses of Austrian water samples from the Salzburg area, the results for uranium and thorium were in excellent agreement for spiked and unspiked samples, showing quantitative recovery for both elements. The range of concentrations was 0·1–3 *μg/l.* for uranium and 0·8–4 *μg/l.* for thorium.

Table 6. Effect of the volume of water sample on determinations of uranium and thorium in Vienna tap-water

Volume of water,* *l.*	Contents found, *μg/l.* Uranium A	B	Thorium A	B
0·5	0·20	0·17	2·0	1·9
1·0	0·19	0·18	1·9	2·0
2·0	0·18	0·17	1·9	1·8
5·0	0·19	0·20	<0·2	<0·2

A = Results without a spike.

B = After deduction of 1 *μg* of uranium and 10 *μg* of thorium added to the water samples before passing them through the 4-g anion-exchange columns.

* On 8 February 1975 the water sample was taken in the Institute for Analytical Chemistry, 20 min after opening the tap.

Table 7. Results of determinations of uranium and thorium in samples of bottled mineral waters

	Contents found, *μg/l.*				
	Uranium		Thorium		
Trade name and geographical origin of sample	A	B	A	C	D
Gleichenberger Johannisbrunnen, Bad Gleichenberg, Styria	<0·01	<0·01	0·80	1·36 (1·0)	−24%
Güssinger, Burg Güssing, Burgenland	0·073	0·077	0·70	1·30 (1·0)	−24%
Radenska, Radenska Slatina, Yugoslavia	0·170	0·200	0·50	1·05 (1·0)	−30%
Donat, Rogaska Slatina, Yugoslavia	0·223	0·167	1·30	1·65 (1·0)	−28%
Gasteiner, Bad Gastein, Salzburg	0·30	0·24	1·10	1·70 (1·0)	−19%
Römerquelle, Bad Vöslau, Lower Austria	1·88	2·21	0·65	0·98 (1·0)	−41%
Preblauer, Preblau, Carinthia	1·60	2·00	2·10	4·25 (2·0)	+4%
Vöslauer, Bad Vöslau, Lower Austria	2·47	2·65	1·30	2·15 (1·0)	−7%
Thalheimer, Thalheim/Judenburg, Styria	4·31	4·40	0·85	0·70 (1·0)	−62%

A = Results without a spike (uranium determined fluorimetrically and thorium spectrophotometrically).

B = After deduction of comparable known amounts of uranium added to the samples before passing them through the 4-g anion-exchange columns.

C = After addition of the spike shown in parentheses.

D = Thorium lost during passage of the sorption solution (1 litre of mineral water) through the 4-g anion-exchange column.

An interesting correlation was found between the weight ratio of uranium to thorium and the uranium concentration (Fig. 1). It appears that high uranium contents are always accompanied by large U:Th ratios (*i.e.*, relatively low thorium contents) while the opposite is true for samples with small uranium concentrations. Since the results of 19 out of 20 samples analysed followed this pattern rather closely, this curve may be used to determine the approximate thorium contents of samples of which the uranium concentrations are known, and *vice versa*. Thus, taking the uranium content of Vienna tap-water (0·18 μg/l.) as an example, this corresponds to a U:Th ratio of about 1:10 which is equivalent to a thorium content of 0·18 × 10 = 1·80 μg. This value comes very close to the actual thorium contents measured in tap-water (Tables 1, 2, 4, 6).

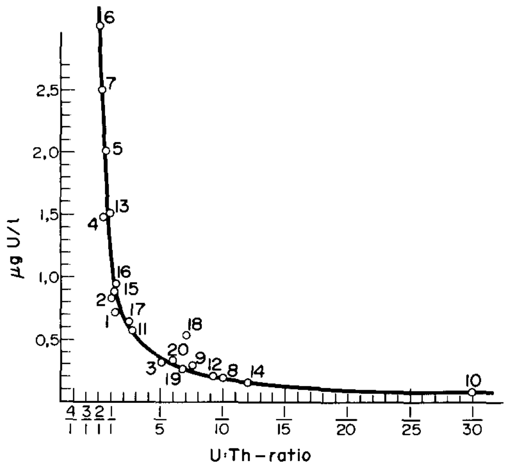

Fig. 1. Plot of uranium concentration *vs.* U:Th w/w ratio for 20 natural waters. (Salzburg area).

Table 8. Comparison of results of uranium determinations obtained by two different methods

	Uranium contents, *μg/l.*		
	This method		Thiocyanate method[3]
Water sample no. (see Fig. 1)	A	B	C
6	3·05	2·93	2·70
7	2·52	2·46	2·54
10	—	0·10	0·10*
13	1·60	1·46	1·40
18	0·50	0·50	0·50

A = Arsenazo III method.

B = Fluorimetric method.

C = Arsenazo III determination.

* Fluorimetric determination.

It remains to be seen, whether this is a universal principle that can be applied to all non-saline waters.* It does not apply to sea-water, for which it predicts a thorium content of 1·7 μg/l., whereas the actual content is less than 5 × 10^{-4} μg/l.[10]

The relatively large deviation from the curve shown by the results for sample 18 is most probably due to the presence of large quantities of finely dispersed brown particulate matter in this sample, which dissolved to some extent on acidification. This sample also had exceptionally high beryllium contents.

Since the ion-exchange separations described in the present paper can be performed more or less automatically, numerous samples can be analysed simultaneously and thus the method is suitable for the routine determination of uranium and thorium in natural water.

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CHARAKTERISIERUNG VON IONENAUSTAUSCHERN AUF KUNSTHARZBASIS DURCH PYROLYSE–MASSENSPEKTROMETRIE

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Zusammenfassung—Bei der Pyrolyse–Massenspektrometrie von Ionenaustauschern auf Kunstharzbasis erhält man in 5 s Fingerprint-Spektren, deren Aussagen mit denen der Pyrolyse–Gaschromatogramme vergleichbar sind. Diese schnelle Aufnahmezeit wird durch den Verzicht auf die gaschromatographische Auftrennung der Pyrolyseprodukte, die *ca.* 60 min beträgt, ermöglicht. Aufgrund der geringen Elektronenenergie von 16 eV werden im Massenspektrum weitgehend nur die Molekülbanden der einzelnen Verbindungen des Pyrolysats wiedergegeben. Diese mit Hilfe der Pyrolyse–Gaschromatographie zugeordneten Verbindungen lassen Rückschlüsse auf den Aufbau des Austauschers zu: Bau der Matrix, Vernetzer, funktionelle Gruppe und deren Verknüpfungsstelle mit der Matrix sowie Beladungszustand.

Zur Identifizierung und Strukturaufklärung von Aüstauschern auf Kunstharzbasis durch die Pyrolyse–Gaschromatographie werden diese bei 800° thermisch fragmentiert, die entstehenden Pyrolyseprodukte gaschromatographisch getrennt und die Pyrolyse–Gaschromatogramme ausgewertet.[1–4]

In der vorliegenden Arbeit wird die Pyrolyse–Massenspektrometrie als neue Untersuchungsmethode für Austauscher auf Kunstharzbasis eingeführt. Hierbei werden die Pyrolyseprodukte nicht mehr gaschromatographisch getrennt, sondern gelangen direkt in die Ionenquelle eines Massenspektrometers. Die Identifizierung der Molekülbanden erfolgt nach qualitativer Analyse mittels Pyrolyse–Gaschromatographie. Durch die Kürze der Analysenzeit und die Aussagekraft der Pyrolyse–Massenspektren stellt somit die Pyrolyse–Massenspektrometrie eine wertvolle Ergänzung der oben zitierten Untersuchungen zur Charakterisierung der Ionenaustauscher auf Kunstharzbasis durch die Pyrolyse–Gaschromatographie dar.

Mit Hilfe der Pyrolyse-Massenspektrometrie werden Biopolymere und Bakterien[5,6] unter Verwendung von Quadrupol-Massenspektrometern und Kunststoffe mit Sektorfeld-Geräten[7] untersucht. Eine bessere Identifizierung der Pyrolysate gelingt mit dem Feldionisations-Massenspektrometer.[8] Zur Untersuchung gelangen die in den Veröffentlichungen[1–4] beschriebenen Ionenaustauscher auf Kunstharzbasis und Dowex A 1 Chelating Resin.

EXPERIMENTELLER TEIL

Geräte und Chemikalien

Massenspektrometer, Pyrolysegerät;[1] Schreiber Oscilloport, Siemens/Erlangen; Pyren *p.a.*, Merck/Darmstadt; Dowex A 1 Chelating Resin, Serva/Heidelberg; weiteres Ionenaustauschermaterial und Probenvorbereitung.[1–4]

Arbeitsbedingungen

Um eine zweite Fragmentierung in der Ionenquelle zu vermeiden, muß deren Elektronenenergie von 80 auf 16 eV gesenkt werden. Somit erhält man weitgehend nur die Molekülbanden der eingeschleusten Verbindung. Die gewählte Elektronenenergie wird von dem höchsten Energiepotential der Pyrolyseprodukte bestimmt. Dieses beträgt für CO_2 13,9 eV. Aus apparativen Gründen ist es günstiger, mit 16 eV und daher mit 150 μA Elektronenstrom zu arbeiten, wodurch eine größere Empfindlichkeit erzielt wird.

Die genaue Einstellung des Massenspektrometers, die mehrmals täglich überprüft wird, erfolgt bei einer Elektronenenergie von 80 eV mit Pyren, das mit Hilfe des Festkörpereinlasses in die Ionenquelle eingebracht wird. Die Elektronenenergie wird dann schrittweise unter ständigem Nachfokussieren auf 16 eV gesenkt.

Um gute Reproduzierbarkeit der Ergebnisse zu erhalten, wird ein elektronischer Schalter verwendet, der die manuelle Auslösung der Spektrenaufnahme automatisiert. Das Pyrolysat gelangt durch ein Kupferrohr im Ofen des Gaschromatographen und die Einlaßleitung direkt in die Ionenquelle des Massenspektrometers. In dieser registriert der EID (Electron Impact Detector) die Ankunft der Pyrolyseprodukte und leitet das Signal zum GC-Schreiber weiter. Hat die Schreibfeder eine bestimmte Höhe erreicht, wird durch den Schalter die Aufnahme des Massenspektrums ausgelöst. Der Einschaltpunkt läßt sich am GC-Schreiber kontinuierlich einstellen. Abbildung 1 zeigt schematisch die Wirkungsweise des Schalters. Die automatische Einschaltung des Massenspektrometers erlaubt es, bei der Aufnahme der Massenspektren die Spitze des Totalionenstromes zu erfassen.

Das parallel zum Massendurchlauf aufgenommene EID-Gaschromatogramm, das auch als Registrierung des Totalionenstromes angesehen werden kann, gibt den Zeitverlauf der Pyrolyse und die Einschleusung der Pyrolyseprodukte in die Ionenquelle wieder. Abbildung 2 zeigt die Registrierung des Totalionenstromes.

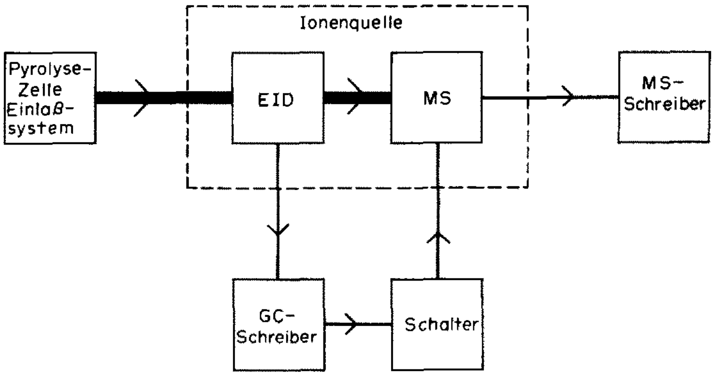


Abb. 1. Wirkungsweise des automatischen Schalters.

Da die Pyrolyse 2 s dauert, nach 1 s der maximale Totalionenstrom erreicht ist und der Massendurchlauf in 2 s erfolgt, erhält man nach 5 s das Fingerprint-Pyrolyse-Massenspektrum. Alle Arbeitsbedingungen zur Aufnahme der Pyrolyse-Massenspektren sind in Tab. 1 zusammengefaßt.

PYROLYSE-MASSENSPEKTREN

Abbildung 3 gibt das Pyrolyse-Massenspektrum von Dowex 50 W X10, H^+-Form in Abhängigkeit von der Elektronenenergie wieder.

Das obere Spektrum ist wesentlich bandenreicher und somit schwieriger zu deuten, wohingegen bei dem unteren fast nur die reinen Molekülpeaks auftreten.

Zur Messung der Reproduzierbarkeit werden an verschiedenen Tagen zehnmal die Pyrolyse-Massenspektren von Dowex 1 X4, Cl^--Form aufgenommen. Das Massenspektrometer wird vor jeder Aufnahme vollständig neu eingestellt. Tabelle 2 enthält die Intensitäten der zwölf stärksten Banden des Dowex 1 X4. Es sind die Mittelwerte und Standardabweichungen von zehn Messungen aufgeführt.[4] Die stärkste Bande ist auf 100% Intensität gesetzt, die anderen prozentual umgerechnet.

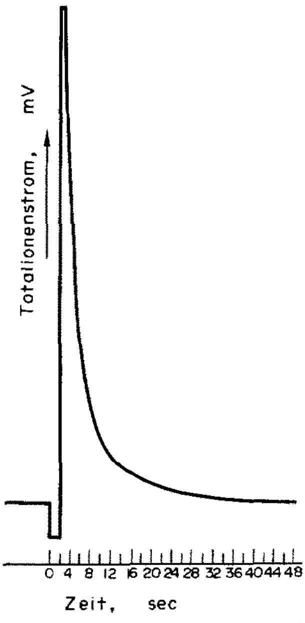


Abb. 2. Totalionenstrom bei der Pyrolyse-Massenspektrometrie.

Die Abb. 4–7 zeigen die Pyrolyse-Massenspektren von Dowex 1 X4, Dowex 2 X8, Amberlite IR-4B jeweils in der Cl^--Form und Amberlite IRC-50, H^+-Form.

Tabelle 3 gibt die charakteristischen Banden und deren Herkunft wieder. Außerdem ist die relative Intensität (% *B*) der Banden zu entnehmen.

In Tab. 4 und 5 sind die Ergebnisse, die bei verschiedenen Beladungszuständen von zwei Anionenaustauschern erhalten werden, zusammengestellt. Die Pyrolysetemperatur beträgt hier 400°.

DISKUSSION

Die an verschiedenen Tagen mit jeweils neuer Einstellung des Massenspektrometers aufgenommenen Spektren zeigen gute Reproduzierbarkeit. Die Zahl der Banden bleibt konstant. Geringe Intensitätsänderungen lassen sich dadurch erklären, daß die Menge des auf die Pyrolyse-Wendel aufgetragenen Austauschermaterials in geringen Grenzen schwankt. Außer-

Tabelle 1. Zusammenfassung der Versuchsdaten

Pyrolyse-Temperatur	800° bzw. 400°
Pyrolysezeit	2 s
Trägergasstrom	He 10 cm^3/min
Temperatur des Einspritzblockes, der Säule, des Trenners, der Einlaßleitung	250°
Säule	Kupferrohr (50 cm lang; 1,5 mm Innendurchmesser)
Temperatur der Ionenquelle	270°
Elektronenenergie	(*a*) 80 eV, 300 μA (*b*) 16 eV, 150 μA
Massendurchlauf	100 Massen/s
Massenintervall	0–200
Empfindlichkeit	0,1–1 V
Massenskala	linear
Papiervorschub	20 cm/s
Probemenge	*ca.* 350 μg Austauscher

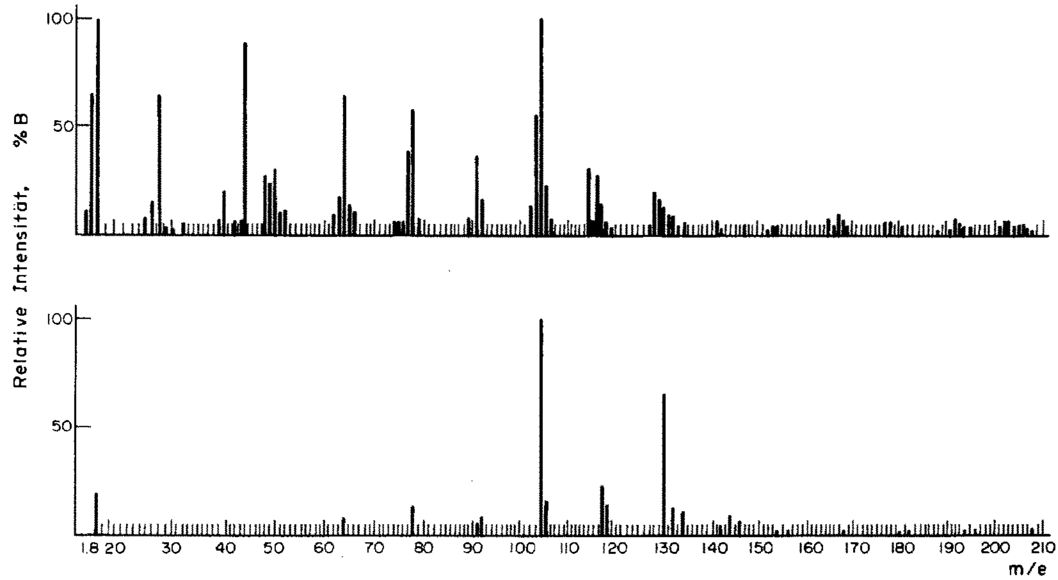


Abb. 3. Einfluß der Elektronenenergie auf die Pyrolyse-Massenspektren von Dowex 50 W X10, H^+-Form. Oben: 80 eV, 300 μA. Unten: 16 eV, 150 μA.

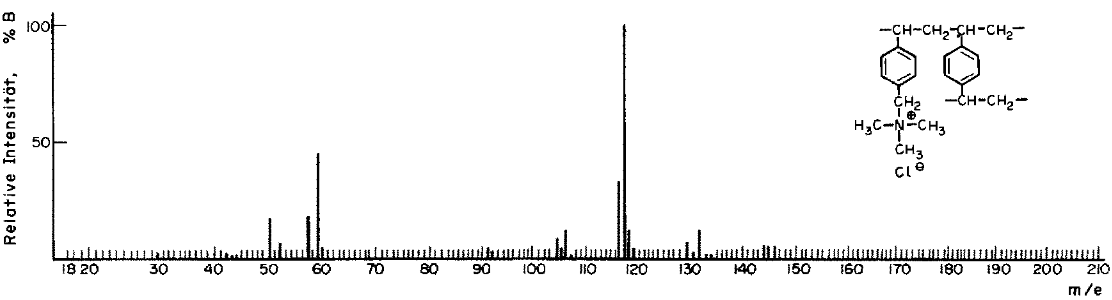
Tabelle 2. Mittelwerte (*B*) und Standardabweichungen (s_p) der Pyrolyse-Massenspektren von Dowex 1 X4, Cl^--Form

m/e	% *B*	s_p
118	100	—
59	43,3	4,7
117	32,3	3,5
58	17,8	2,8
50	15,6	3,2
106	10,8	3,4
132	11,4	2,2
52	5,6	1,3
104	6,8	1,5
145	4,8	1,3
91	3,8	1,1
30	1,0	0,1

dem kommt es bei einer dickeren Austauscherschicht infolge der schlechten Wärmeleitfähigkeit des Austauschers in der oberen Schicht zu einer etwas anderen Fragmentierung. Die Intensitätsschwankungen lassen sich durch gleichmäßiges Auftragen des Austauschers auf die Pyrolyse-Wendel in engen Grenzen halten. Die Einführung eines Schalters zur automatischen Auslösung des Massenspektrums erhöht die Reproduzierbarkeit sehr. Zudem erleichtert er die Aufnahme der Spektren.

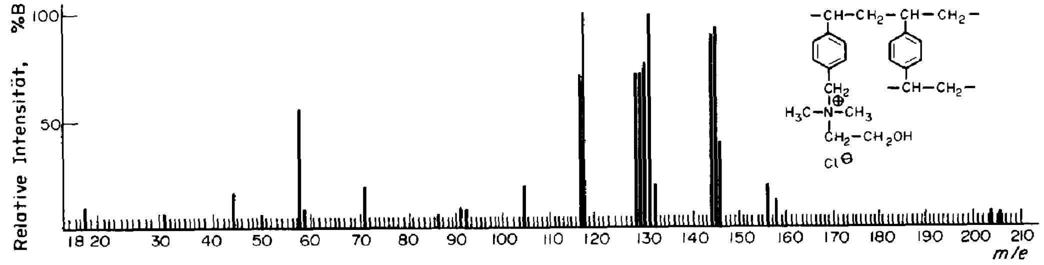
Mit Hilfe der Pyrolyse-Massenspektren kann man auch Anionenaustauscher identifizieren, die sich nur durch den Ersatz einer CH_3-Gruppe durch eine C_2H_4OH-Gruppe in der Ankergruppe unterscheiden.

Bei den Anionenaustauschern auf Styrol-DVB-Basis und Dowex A 1 Chelating Resin ist die Basisbande *m/e* = 118 (*m*- und *p*-Methylstyrol), da die Ankergruppen über Methylenbrücken an die Benzolkerne gebunden sind. Dagegen wird bei dem kernsubstituierten Kationenaustauscher Dowex 50 W *m/e* = 104 (Styrol) zur Basisbande. Bei Amberlite IR-4B ist das Auftreten der Banden *m/e* = 94 und 108 (Phenol bzw. *o*/*p*-Kresol) charakteristisch. Aliphatische Kohlenwasserstoffe und DVB treten vorwiegend bei Amberlite IRC-50 und IRA-68 auf, da hier eine Acryl-DVB-Matrix vorliegt. Bei Dowex 44 lassen sich Grundkörper und Vernetzer nicht unterscheiden.



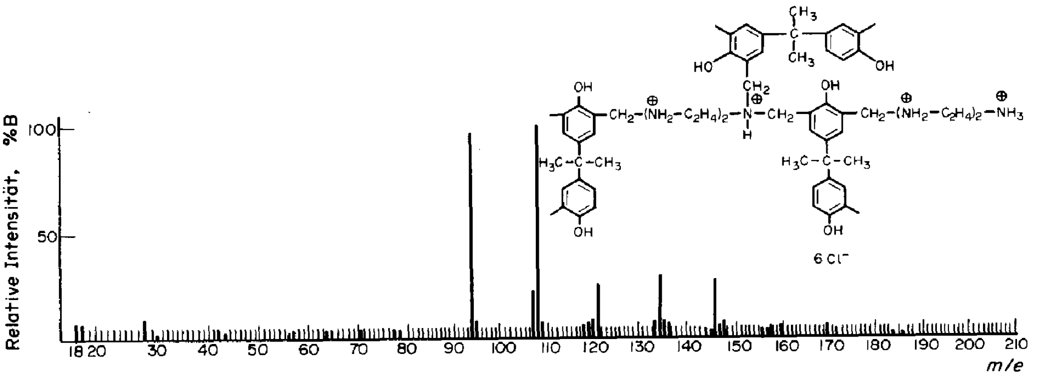
50 = Methylchlorid, 59 = Trimethylamin, 118 = m,p-MSt, 130 = DVB, 132 = ÄVB, 145 = Dimethylindol

Abb. 4. Pyrolyse-Massenspektren (16 eV, 150 μA). Dowex 1 X4, Cl^--Form.



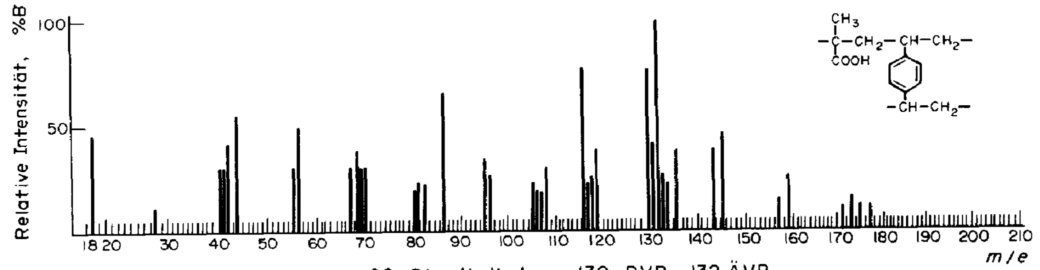
31 = Methylamin, 44 = CO_2, 59 = Trimethylamin, 71 = unbekannt, 118 = m,p-Methylstyrol, 130 = DVB
131 = Methylindol, 132 = ÄVB, 145 = Dimethylindol

Abb. 5. Pyrolyse-Massenspektren (16 eV, 150 μA). Dowex 2 X8, Cl^--Form.



17 = NH_3, 94 = Phenol, 108 = Kresol

Abb. 6. Pyrolyse-Massenspektren (16 eV, 150 μA). Amberlite IR-4B, Cl^--Form.



44 = CO_2, 56 = Buten, 86 = Dimethylbutan, 130 = DVB, 132 ÄVB

Abb. 7. Pyrolyse-Massenspektren (16 eV, 150 μA). Amberlite IRC-50, H^+-Form.

Tabelle 3. Charakteristische Banden, deren Herkunft und relative Intensität

Austauscher	m/e	Verbindung	Herkunft	% B
Dowex 50 W X10, H^+-Form	66	SO_2	Ankergruppe	7,2
	104	Styrol	Matrix	100,0
	130	DVB	Vernetzer	66,6
Dowex 1 X4, Cl^--Form	50	Methylchlorid	Gegenion	18,1
	59	Trimethylamin	Ankergruppe	36,2
	118	*m/p*-MSt	Matrix	100,0
	130	DVB	Vernetzer	44,7
Dowex 2 X8, Cl^--Form	50	Methylchlorid	Gegenion	10,1
	31	Methylamin	Ankergruppe	9,8
	44	CO_2		16,7
	59	Trimethylamin		16,7
	118	*m/p*-MSt	Matrix	100,0
	130	DVB	Vernetzer	76,7
Amberlite IR-4B, Cl^--Form	17	NH_3	Ankergruppe	7,8
	30	Formaldehyd	Vernetzer	3,5
	94	Phenol	Matrix	36,1
	108	*o/p*-Kresol		100,0
	122	2,4-Dimethylphenol		25,5
Amberlite IRC-50, H^+-Form	44	CO_2	Ankergruppe	56,0
	42	Propen	Matrix	42,3
	56	Buten		50,0
	86	Dimethylbutan		65,4
	130	DVB	Vernetzer	76,9
Dowex Chelating Resin A 1, H^+-Form	44	CO_2	Ankergruppe	4,5
	59	Trimethylamin		5,0
	104	Styrol	Matrix	46,1
	118	*m/p*-MSt		100,0
	130	DVB	Vernetzer	13,7
Amberlite XE-243, Cl^--Form	44	Acetaldehyd	Ankergruppe	6,3
	50	Methylchlorid	Gegenion	6,1
	58	Trimethylamin	Ankergruppe	7,5
	118	*m/p*-MSt	Matrix	100,0
	104	Styrol		43,8
	130	DVB	Vernetzer	25,6
Amberlite IRA-93, Cl^--Form	50	Methylchlorid	Gegenion	3,7
	59	Trimethylamin	Ankergruppe	9,0
	104	Styrol	Matrix	9,8
	118	*m/p*-MSt		100,0
	130	DVB	Vernetzer	18,4
Amberlite IR-45, Cl^--Form	45	Dimethylamin	Ankergruppe	2,3
	104	Styrol	Matrix	98,0
	118	*m/p*-MSt		100,0
	130	DVB	Vernetzer	13,5
Amberlite IRA-68, Cl^--Form	50	Methylchlorid	Gegenion	67,7
	59	Trimethylamin	Ankergruppe	100,0
	42	Propen	Matrix	24,2
	56	Buten		16,1
	130	DVB	Vernetzer	11,3
Dowex 44, Cl^--Form	50	Methylchlorid	Gegenion	80,9
	94	Dimethylpyrrol	Matrix	80,9
	42	Propen		51,1
	28	Stickstoff	Vernetzer	44,5

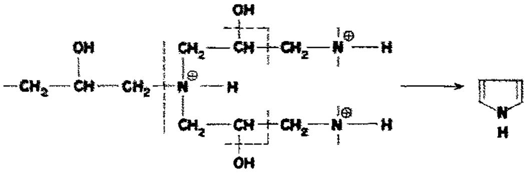
Tabelle 4. Pyrolyse-Massenspektren von Dowex 1 X4

	m/e	Verbindung	% *B*
F^--Form	59	Trimethylamin	100,0
	50	Methylchlorid	2,0
	34	Methylfluorid	1,2
Cl^--Form	59	Trimethylamin	100,0
	50	Methylchlorid	57,1
Br^--Form	59	Trimethylamin	100,0
	96	Methylbromid	64,7
	94		60,0
J^--Form	142	Methyljodid	100,0
	59	Trimethylamin	26,9
OH^--Form	59	Trimethylamin	100,0
	32	Sauerstoff	18,9
	44	CO_2	3,7
CH_3COO^--Form	59	Trimethylamin	100,0
	44	Acetaldehyd	18,9
	74	Methylacetat	9,6
NO_2^--Form	59	Trimethylamin	100,0
	30	Stickoxid	13,5
	45	Dimethylamin	6,0
	44	Distickstoffmonoxid	5,8
NO_3^--Form	59	Trimethylamin	100,0
	30	Stickoxid	15,0
	45	Dimethylamin	8,0
	44	Distickstoffmonoxid	5,2

Tabelle 5. Pyrolyse-Massenspektren von Dowex 2 X8

	m/e	Verbindung	% *B*
Cl^--Form	58	Trimethylamin	100,0
	59		9,7
	50	Methylchlorid	60,0
	42	Propen	9,7
	44	CO_2	9,7
Br^--Form	58	Trimethylamin	100,0
	59		17,7
	94	Methylbromid	43,6
	96		41,0
	42	Propen	6,4
	44	CO_2	7,7
J^--Form	142	Methyljodid	100,0
	58	Trimethylamin	58,5
	59		8,3
	44	CO_2	5,0
	42	Propen	5,4
OH^--Form	44	CO_2	100,0
	58	Trimethylamin	35,5
	59		22,6
	29	Formaldehyd (M-1)	24,2
	42	Propen	10,6
CH_3COO^--Form	58	Trimethylamin	100,0
	59		11,3
	44	Acetaldehyd, CO_2	17,2
	42	Propen	10,9

Durch Zerschlagung des Austauschergerüstes und Bindungsneubildungen entstehen verschiedene stickstoffhaltige Verbindungen, wie z.B. Pyrrole. Die Entstehungsmöglichkeit dieser Verbindungen ergibt sich aus dem folgenden Schema:



Man findet sehr viel Methylchlorid, bedingt durch die Cl^--Form des Austauschers.

Zur Ermittlung der Beladungszustände führt man die Pyrolyse bei 400° durch, da bei dieser Temperatur vorwiegend die Ankergruppen zersetzt werden. Als charakteristische Pyrolyseprodukte sind die entsprechenden Methylester bzw. deren Zersetzungsprodukte nachzuweisen.

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DIRECT DETERMINATION OF CADMIUM IN BLOOD WITH A TEMPERATURE-CONTROLLED HEATED GRAPHITE-TUBE ATOMIZER

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Summary—By temperature-controlled heating during the atomization step a selective vaporization between Cd and the matrix is achieved. A final temperature of 830° gives an optimized signal for Cd without too high a background absorption. The sensitivity is 0·1 μg/l. (0·01 μg of Cd/100 ml of blood) with a detection limit of 0·6 μg/l. (0·06 μg/100 ml of blood).

Atomic-absorption spectroscopy has become the most commonly used technique for the determination of cadmium in biological materials. Other techniques for cadmium determination are neutron-activation analysis and emission spectrography. The biological effects of cadmium have been reviewed by Friberg *et al.*[1] For determination in whole blood an extraction procedure is necessary to increase the sensitivity of the method. For a direct determination of cadmium in blood, flameless atomizers must be used. A problem will immediately arise when carrying out a direct determination on a biological fluid. The bulk of the sample will, in most cases, vaporize in the same temperature region as the metal. Several commercial instruments have background correctors for automatic subtraction of the non-specific absorption. In general, these correctors cannot subtract more than 0·4–0·8 absorbance units. To fulfil this requirement the two beams in the spectrophotometer, *i.e.*, from the hollow-cathode lamp and the deuterium or hydrogen lamp, have to be aligned exactly in the graphite tube. If not, a false correction may be achieved. This might become a serious source of error because the non-specific absorption is in most cases not reproducible. To improve the accuracy of the cadmium absorbance signal the cadmium peak and the non-specific peak should be separated in time when registered on a chart-recorder, and the non-specific absorbance should not exceed the stipulated maximum correction of the instrument. This will imply that a slow heating rate must be used to obtain a time-resolution. As the sensitivity for a metal is directly correlated to the heating rate of the atomizer, the improvements in time-resolution between metal and matrix absorbance caused by lowering the heating rate will be offset by the decreased sensitivity.

Attempts to attain selective vaporization of cadmium from the bulk of a biological matrix have been made by Ross and Gonzalez.[2] They used a Perkin–Elmer HGA-2000 with a background corrector. For resolution of the cadmium and the non-specific absorption when analysing urine samples, the final temperature had to be 1300°. In this way they were able to determine cadmium in 20-μl samples of urine and 20% solutions of serum with reproducibilities of the order of 5%. The sensitivity was 0·25 ppM† (1% absorption) in a 20-μl sample or 5 pg absolute.

Cruz and van Loon[3] have made a critical study of the possibilities of using graphite furnaces for trace element determinations in complex heavy-matrix solutions. They used a Perkin-Elmer HGA-70 as well as the newer model HGA-2000. They tested only for lead in blood but found that cadmium, among other elements, was almost impossible to vaporize without causing co-volatilization of the matrix when inorganic materials containing large amounts of sodium and potassium salts were analysed. Some separation was achieved when the final temperature was lowered, but at the expense of a lowered analytical response for cadmium. Similarly Segar and Gonzalez[4] were unsuccessful in determining cadmium in sea-water.

Just recently a procedure for the determination of cadmium in biological materials by using the I.L. tantalum-strip atomizer has been presented by Ulluci and Hwang.[5] For blood, instead of a direct determination they used a micro-extraction procedure with the APDC–MIBK system. The advantage lies in the fact that very small samples, *e.g.*, from finger punctures, can be used. If sample size is not a limiting factor, little advantage is achieved compared to a flame determination on the organic phase.

In this paper a simple technique using a temperature-controlled graphite-tube atomizer is described. The temperature control permits a selective vaporization of metal and matrix at a high heating rate, thus yielding very good sensitivity.

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† Parts per milliard

EXPERIMENTAL

Apparatus

A graphite furnace with a 10-cm graphite tube (Ringsdorff RWO spectrographic graphite) was used. The furnace is gas-tight and has a large dead volume. The gas is not flushed through the tube, but fills the whole volume. The construction has been presented in detail elsewhere.[6] The spectrophotometer is mounted on an optical rail with quartz lenses and with a Heath Scanning Monochromator 700 E with a spectral dispersion of 20 Å/mm at the exit slit. A Hamamatsu photomultiplier was used. The spectrometer is supplied with a hydrogen background-corrector. The amplifier is a sample-and-hold amplifier with absorbance outputs for metal lamp, hydrogen lamp or the corrected absorbance outputs for metal lamp, hydrogen lamp or the corrected absorbance. The three different signals can be monitored simultaneously if required. The metal lamp and the hydrogen lamp are electrically modulated at 100 Hz. Subtraction of the background is made in a circuit with time constants of 20, 50, 100, 200, or 500 msec.

The graphite furnace is supplied with a temperature-controlled heating (TCH) unit which has been described in detail.[7] The temperature of the centre of the graphite tube is measured with a photo-diode. The output from the diode is compared with a preset value on the TCH-unit. Heating of the tube proceeds with maximum power supplied to the furnace up to the desired temperature. Thereafter the power is decreased, keeping the temperature constant at the required temperature. This construction enables the atomizer to be heated at a maximum rate, independent of the final temperature setting. The instrumental parameters are given in Table 1.

Sample preparation

The blood samples were diluted with water: 0·1 ml of whole blood (heparinized) was diluted with 0·9 ml of distilled water with a pneumatic diluter (AutoChem Instrument AB, Sweden). To the samples were added 20 μl of heparin and 20 μl of 2% Triton X-100. The sample was mixed thoroughly in a mechanical shaker (Shiltern). Standards were made from a 1000-ppm solution of $CdCl_2$ and a calibration curve was obtained by standard addition to the blood sample.

RESULTS AND DISCUSSION

Matrix effects

If a temperature-controlled atomizer is used, the problems with time-resolution of the metal and non-specific absorption are almost negligible, as will be seen in Fig. 1. When a blood sample containing cadmium is atomized, with different final temperatures, the signal increases with temperature up to that at which the vapour pressure of the element is sufficiently high to give a rapid atomization. For cadmium an optimized signal is achieved at 830°. A further temperature rise will not increase the absorbance peak. If, on the other hand, the non-specific absorption is registered by means of a hydrogen lamp, the background absorption will increase with the final temperature. At 950° the amount of non-specific absorption is large enough to create problems in automatic background correction. The useful temperature region is very small as the temperature must reach 750° but not exceed 950°. If an automatic background corrector is used, the final temperature can be chosen between 830° and 900°, where an optimized analytical response is obtained. If an instrument without background corrector is used, an even lower final temperature must be set, to make the non-specific absorption as small as possible. From this figure it can be seen why difficulties have arisen when using a commercial furnace for this determination. In that case, a final temperature of at least 1300° must be chosen to obtain a sufficiently good response, as a higher final temperature implies a better sensitivity. The atomic vapour is formed between 700° and 900° but the non-specific absorption starts to form at 850°. The possibilities of time-separating these two absorption sources is a function of the rate at which this temperature region is traversed. The advantage of TCH over commercial atomizers is obvious, as the final temperature can be set independently of the heating rate. A fast heating rate can be chosen to obtain an optimized sensitivity even if the final temperature is set as low as 830°. One does not have to compromise between sensitivity and time-separation of metal and background absorption.

Table 1. Instrumental parameters

Graphite atomizer	
Inert gas	Nitrogen
Dry sequence	100°, 60 sec
Ash sequence	600°,60 sec
Atomize sequence	830°
Spectrophotometer	
Operating mode	Background correction
Metal lamp (Varian) current	3 mA
Hydrogen lamp (Varian) current	20 mA
Photomultiplier voltage	800 V
Slit-width	200 μm (S.B.W. = 0·4 nm)
Wavelength	228·8 nm

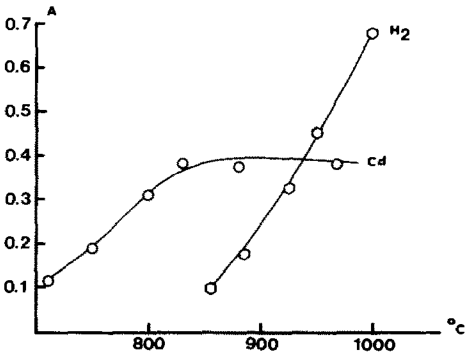

Fig. 1. Determination of optimized absorbance for Cd in blood and of non-specific absorption as a function of final temperature in the atomization step (3 μl of diluted blood with 6·5 ppM of added Cd).

The non-specific absorption would be expected to be irreproducible. This would make it very difficult to obtain reproducible results if an instrument without automatic background correction were used. In Fig. 2 is shown an example of the variations in non-specific absorption for different sample volumes.

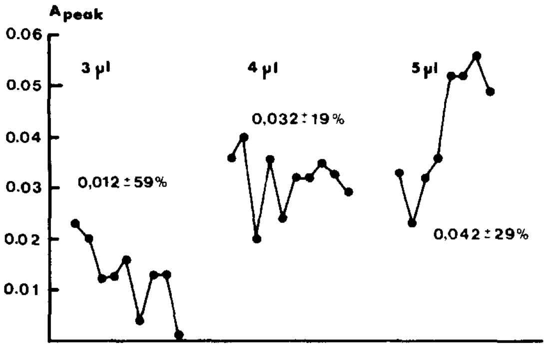

Fig. 2. Variation of non-specific absorption for different sample volumes (average and range are shown).

Table 2. Comparison between direct determination of Cd and an extraction procedure

Sample no.	No. of detns.	Mean value ± 1 std. devn., *μg/100 ml*	Lab A (APDC–MIBK), *μg/100 ml*
1688	5	3·4 ± 0·60	3·9
500	8	1·1 ± 0·35	1·0
503	7	1·5 ± 0·04	1·4
557	2	1·5 ± 0·15	1·3
640	11	2·4 ± 0·30	2·6
605	1	2·5	2·9
536	3	1·6 ± 0·18	1·2
558	3	3·0 ± 0·26	3·0
518	7	1·3 ± 0·20	0·9
604	4	2·3 ± 0·17	2·5

Diluted blood samples were atomized with a final temperature of 830° (TCH). The amount of non-specific absorption, measured with the aid of a hydrogen lamp, was registered on a chart-recorder. The samples were ashed at 600° before atomization. It is seen that the amount of background increases with sample volume.

The major analytical problem is that this variation is very high. If an instrument without background corrector is used, the normal method is first to run a sample with the metal lamp and then to change to a hydrogen lamp and run a sample to get the amount of non-specific absorption. Even if a large number of background determinations are performed, a rather uncertain correction is achieved and the procedure is very time-consuming. For a 4-μl sample the amount of non-specific absorption corresponds to a Cd-value of 0·3 μg/100 ml of blood.

Gas parameters

The graphite furnace that was used has quite large dimensions, so the tube is surrounded by a dead volume several times larger than the volume occupied by the graphite tube itself. When gas is flushed through the system it is not directed through the tube as in the new Perkin–Elmer HGA-74. This large dead volume will absorb the expansion of the gas inside the tube when it is heated. The effect of different gas parameters was tested on an aqueous cadmium solution: 8 pg of cadmium were atomized under argon or nitrogen atmospheres. No significant difference was observed whether the gas flowed during the atomization cycle or not. This is because the gas is not directed through the tube. Furthermore, no effect on the analytical response was observed if argon was replaced by nitrogen.

In the ashing cycle the choice of gas is very important for effectiveness of ashing. In Fig. 1 it was seen that with a nitrogen atmosphere the ashing was effective enough to keep the amount of background absorption sufficiently low to be properly corrected for. If argon was used, the matrix produced a much higher background adsorption. Mixing the argon with oxygen or hydrogen during the drying and ashing cycle did not improve the ashing effectiveness. Nitrogen seemed to be the most effective gas for a complete ashing of the blood matrix. The reasons for the differences between argon and nitrogen have not been examined yet.

Calibration and results

No interferences were observed when blood was compared with a pure water solution. Tests on known additions of a water standard to a blood sample gave 100% recovery within experimental error, hence normally the calibration is best carried out by making standard additions to one blood sample and using the slope of the curve as the calibration factor for the rest of the blood samples.

A series of blood samples was analysed by the procedure described and compared with results from another laboratory, Table 2. Laboratory A used the conventional extraction procedure as for lead[8] but with a final determination of cadmium in the MIBK-phase by using a Perkin-Elmer HGA-72. The agreement between direct determination and the extraction procedure is quite good. The reproducibility is about 10%. In the determinations, differently diluted samples were analyzed.

Different sample volumes were used in the range 1–5 μl. No difference was observed in the cadmium values when the volume was changed. It is, however, better to use a large sample volume to obtain a bigger signal height; 3 or 4 μl were used in the experiments. Larger volumes gave residues in the graphite tube after the atomization.

Direct determination of Cd in undiluted blood was also tried. The blood sample was haemolysed by addition of 0·1 ml of Triton X-100 to 5 ml of whole blood. The blood sample was then shaken vigorously, and 1 μl was inserted into the graphite tube. In Table 3 are shown results for determinations in triplicate. The columns at the right show the peak absorbance values. The reproducibilities are about the same as for diluted blood samples. A disadvantage is, however, that residues are formed in the graphite tube after a few determinations.

Table 3. Determination of Cd in undiluted blood (1 μl).

Sample	$\mu g/100\ ml$			Peak absorbance
A	0·66	0·72	0·71	0·28
B	1·41	1·62	1·50	0·55
C	1·47	2·04	1·68	0·60
D	1·98	1·78	2·15	0·66

Sensitivity

The sensitivity for diluted blood is 0·01 μg/100 ml (1% absorption) or $2{\cdot}5 \times 10^{-13}$ g for a 4-μl sample. The detection limit, defined as a signal that is twice the standard deviation in blank runs (10 determinations on blood with very low cadmium content), is 0·06 μg/100 ml.

The cadmium values in blood, for normally exposed persons, are a few tenths of a microgram per 100 ml (a few ppM). The sensitivity for a direct determination is sufficient to detect normal values. Reproducibility can vary a lot depending on the homogeneity of the blood sample. In order to get a representative sample the blood must be totally haemolysed. If so, the direct determination procedure gives a rapid determination of cadmium in blood, with a typical error of 10%.

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DETERMINATION OF SHORT-LIVED RADIONUCLIDES IN FRESH FALL-OUT DEBRIS FOR IDENTIFICATION OF NUCLEAR WEAPON TESTS

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Summary—Radiochemical procedures for the assay of short-lived fission and activation products are described. They are rapid and quantitative and the radionuclides separated are radiochemically pure. Ratios of some of the short-lived radionuclides obtained by these measurements for selected Chinese and French nuclear tests are given and provide information about the fissile material used in the tests.

The programmes of nuclear weapon testing by China and France contribute considerable quantities of short-lived radionuclides to the atmosphere. The measurement of this short-lived activity by γ-ray spectrometry alone is not sufficient for the identification of a weapon test, so a chemical separation of the fission and induced products is necessary. The chemical methods selected must take into account the complicated composition of the sample, be rapid and quantitative and have high chemical yield. The methods presented in this paper meet these criteria and also permit joint assay of various radionuclides from a single sample.

The sample material is a swab collected by rubbing the surface of commercial aircraft with cotton soaked in organic solvent. These samples are routinely collected on arrival of the aircraft at Bombay to estimate the background levels of the atmosphere before and after nuclear tests. The results are used to get information about detonation, *e.g.*, fissile material used, mode of detonation *etc.*, by comparison of the activity ratios of selected fission products such as ^{89}Sr, ^{111}Ag, ^{132}Te and ^{99}Mo. These fission products, being short-lived, do not suffer interference by products from earlier tests.

There are two important activation products which help in deciding whether the test was with a conventional H-bomb using a three-stage device with ^{238}U in the third stage. These are neptunium-239 and uranium-237 which are produced from ^{238}U by (n, γ) and (n, 2n) reactions respectively. ^{237}U, in a nuclear weapon, is also produced from ^{235}U by double neutron capture but its production by this reaction is very small compared with that from the (n, 2n) reaction in a conventional H-bomb test. Other activation products also help in determining parameters of the weapon test. However, the samples collected for our studies gave hardly any measurable quantities of these activation products and therefore only ^{237}U and ^{239}Np are discussed in this paper.

EXPERIMENTAL

Sample preparation

The sampling method collects considerable quantities of insoluble silica, iron, sulphate and phosphate compounds. Because of the difficulty with which these compounds dissolve, a leaching procedure for the dissolution of the sample is used.[1] The cotton swab is digested with a mixture of 3*M* hydrochloric acid and 0·1*M* hydrofluoric acid in the presence of known amounts of carriers. The heating time is reduced to a minimum to reduce the attack on the glassware. The solution is filtered through a Whatman No. 54 paper on a Büchner funnel. This process is repeated 3 or 4 times and finally the residue is leached with 6*M* nitric acid and filtered off. It is found that more than 95% of the total activity is leached out by this process. All parts of the filtrate are then pooled and a suitable aliquot is taken for the determination of each individual nuclide.

Chemical procedures

The chemical procedures developed in our laboratory are described below. Barium-140 is usually determined directly from the gamma-ray spectrum through its daughter ^{140}La. For this a known fraction of the leach solution (usually a tenth of the total volume) is evaporated in a beaker to minimum volume and transferred to a 5·0-cm diameter "Perspex" planchette which, after drying, is sealed and counted by a 256-channel pulse-height analyser, using a Ge(Li) detector. In general, the final isolation of the precipitate is carried out by filtration with a special filter funnel using a 1-in. Whatman No. 542 paper and the chemical yield is obtained by weighing the precipitate. The sample is then mounted on a planchette and counted conventionally. The filter funnel is made of "Perspex", and has a threaded base, a 2·5-cm diameter circular perforated disc and a vertical reservoir 2·4 cm i.d. and 12 cm in height.

Separation of strontium and barium.[2] A known volume of the leach solution with known quantities of carriers (150 mg of Sr + 100 mg of Ba) is placed in a beaker. The solution is warmed and anhydrous sodium carbonate added. The insoluble carbonates are filtered off (Whatman No. 540 paper) and redissolved in 6*M* nitric acid.

The volume of the solution is reduced to 40 ml by evaporation and 65 ml of fuming nitric acid (s.g. 1·52) are added slowly to the ice-cooled solution. The crystals of barium and strontium nitrates are allowed to settle. The supernatant liquid is decanted and the crystals are dissolved in distilled water. The volume of the solution is again brought to 40 ml and the nitrate precipitation repeated twice with 60 ml of fuming nitric acid. The nitrate crystals are then dissolved in water and strontium and barium precipitated by addition of ammonium carbonate. The solution is warmed for about 10 min to coagulate the carbonates and finally filtered.

The precipitate is dissolved in $6M$ hydrochloric acid and barium is precipitated as chromate by addition of 10 ml of $1{\cdot}5M$ sodium chromate and adjustment of the pH to 3·5–4. The chemical yield and activity are then measured.

The filtrate from the chromate separation is warmed and ammonium carbonate added to precipitate strontium. The precipitate is filtered off (Whatman No. 540 paper) and dissolved in $6M$ hydrochloric acid. The solution is warmed with absolute alcohol (2 or 3 drops) to reduce any chromate. Twenty mg of yttrium carrier are added and the yttrium is precipitated by slow addition of freshly prepared ammonia solution to remove yttrium-90 and other rare-earth activity. The solution is warmed, cooled and filtered and the time noted. Ammonium carbonate (2–3 g) is added to the filtrate, the solution is warmed and the strontium carbonate allowed to settle. The activity is then determined after filtration.

After the counting of ^{89}Sr and ^{90}Sr activity, the precipitate is ignited to constant weight in a platinum crucible to obtain the chemical yield. The residue is dissolved in $3M$ hydrochloric acid and stored with 20 mg of yttrium carrier for equilibration and subsequent milkings.

Separation of silver and molybdenum.[3] A known volume of the leach solution, with known amounts of carriers, is placed in a beaker and evaporated almost to dryness. To the residue are added 2 ml of conc. nitric acid and 2 ml of bromine water, and the resultant solution is slowly heated to oxidize tin and molybdenum. The solution is cooled and diluted and a few drops of $6M$ hydrochloric acid are added, with constant stirring, to precipitate insoluble chlorides. The precipitate is centrifuged, washed with distilled water and dissolved in ammonia solution. Ten mg of iron carrier are added to the solution and iron hydroxide scavenging is carried out to remove impurities such as Sr and Ce. To the filtrate are added 10 ml of saturated thioacetamide solution and silver sulphide is precipitated on gentle heating. The precipitate is centrifuged, dissolved in 5 ml of conc. nitric acid and boiled to remove sulphur completely. The solution is then cooled. The scavenging cycle with iron hydroxide and precipitation as silver sulphide is repeated. The filtrate is finally adjusted to pH 3·5 with $6M$ hydrochloric acid. The precipitate is digested by gentle heating and allowed to settle. It is then filtered off and the chemical yield and activity are measured.

The filtrate from the precipitation of silver chloride is adjusted to pH 8·5 with ammonia solution. To the solution are added 10 mg of iron carrier and hydroxide scavenging is carried out to remove Cr and Nb impurities. The filtrate is adjusted to pH 3·5 with $6M$ nitric acid and 10 ml of 4% α-benzoinoxime solution in ethanol are added. The precipitate is centrifuged and dissolved in a mixture of 10 ml of fuming nitric and 3 ml of perchloric acid and the solution evaporated slowly to dryness. Iron hydroxide scavenging is once again carried out to remove Zr, Nb, I_2 *etc.* The filtrate is finally adjusted to pH 3 with $6M$ nitric acid. Three ml of saturated lead nitrate solution are added to the solution, which is then gently heated to precipitate lead molybdate, which is collected, weighed and counted.

Separation of tellurium. A known fraction of the leach solution with 40 mg of tellurium carrier is evaporated to dryness. The residue is taken up in a small quantity of hydrochloric acid and evaporated again to dryness. This is repeated 2 or 3 times to bring the residue into the chloride form. The residue is then taken up in $3M$ hydrochloric acid and freshly prepared sulphur dioxide is passed through it. Elemental tellurium is precipitated. It is then dissolved in *aqua regia*, reprecipitated and redissolved in *aqua regia*. Ten mg of iron carrier are added to the solution and pure tellurium is precipitated, dried, weighed and counted.

Separation of neptunium and uranium.[4] A measured fraction of the leach solution with known amounts of ^{233}U, ^{237}Np and ^{236}Pu tracers is taken in a beaker along with 1 mg of iron carrier, 1 g of hydroxylamine hydrochloride and 10 ml, for every 100 ml of leach solution, of a 4:1 v/v mixture of saturated boric acid solution and conc. nitric acid. The solution is warmed and ammonia solution added slowly to precipitate hydroxides. The precipitate is filtered off, washed and dissolved in $6M$ nitric acid and the solution evaporated almost to dryness. The residue is taken up in 15 ml of $1M$ nitric acid and neptunium is converted into oxidation state IV by addition of 1 ml of 15% hydroxylamine hydrochloride solution and 0·3 ml of $3M$ ferrous sulphamate. Neptunium is twice extracted with $0{\cdot}5M$ thenoyotrifluoroacetone in xylene by shaking for about 10 min in a 100-ml separating funnel. The organic phase is washed with an equal volume of $1M$ nitric acid and the washings are added to the aqueous phase. Neptunium is stripped from the organic phase with an equal volume of $8M$ nitric acid, which is then evaporated to dryness with $1M$ hydrochloric acid and the residue taken up with two 3-ml portions of electrolyte solution ($1M$ ammonium chloride, $0{\cdot}01M$ oxalic acid) and placed in an electrolysis cell. Neptunium is deposited on a 2·5-cm diameter stainless-steel disc for 20 min at a current density of 1–1·2 A.

The aqueous phase left after the neptunium extraction is three times evaporated to dryness with a little nitric acid and the residue is finally taken up in 10 ml of $1M$ nitric acid. Ten g of aluminium nitrate, 3 or 4 drops of cerium carrier (10 mg of Ce^{4+}/ml) and 10–15 drops of hydrogen peroxide are added to the solution and uranium is extracted by shaking with an equal volume of ethyl acetate for 1 min. The organic phase is slowly evaporated on a hot-plate. The residue is taken up in 10 ml of $1M$ nitric acid and the uranium extraction with ethyl acetate is repeated twice more. Finally the uranium is electroplated on a stainless-steel disc similarly to neptunium.

RESULTS AND DISCUSSION

The chemical procedures described above are rapid and quantitative and the radionuclides separated are free from contamination by other fission products. The β-emitting isotopes are counted in a low-background assembly using an end-window GM counter with a lower thickness of the sample. The necessary corrections for the loss due to self-absorption *etc.* are made and the final count-rate is used to estimate the concentration of each nuclide. The purity of each separated nuclide is checked by following the radioactive decay and in the case of β-emitting nuclides by using appropriate aluminium absorbers.

The chemical yields of uranium and neptunium are determined radiometrically by adding ^{233}U and ^{237}Np tracers and in the case of fission products the yields are determined gravimetrically by adding an appropriate inactive carrier. The chemical yields of separated radionuclides are 65–80% for strontium and barium, 85–90% for silver, 50–55% for molybdenum, 70–80% for tellurium, 82–85% for neptunium and 55–60% for uranium. The overall errors in the estimation of these nuclides are within 10%. The time taken for the entire analysis is 5–10 hr.

Table 1. Expected activity ratios of selected fission products at the time of fission[5]

Isotope ratio	Fission-spectrum neutron fission of			14-MeV neutron fission of		
	^{235}U	^{238}U	^{239}Pu	^{235}U	^{238}U	^{239}Pu
^{111}Ag/^{89}Sr	0·05	0·23	1·46	1·97	2·5	5·2
^{111}Ag/^{140}Ba	0·01	0·03	0·12	0·42	0·40	0·90
^{99}Mo/^{111}Ag	465	168	41·0	12·2	14·8	8·0

Table 2. Observed activity ratios in fall-out samples from selected Chinese tests

Isotope ratio	Observed ratio	Test number and date of test		Type of bomb deduced
^{111}Ag/^{89}Sr	0·116	First	(16.10.64)	A-bomb using ^{235}U
	0·068	Second	(14.5.65)	A-bomb using ^{235}U
	0·273	Third	(9.5.66)	A-bomb using ^{235}U
	0·84	Sixth	(17.6.67)	H-bomb
	0·98	Eighth	(27.12.68)	H-bomb
^{111}Ag/^{140}Ba	0·023	First	(16.10.64)	A-bomb using ^{235}U
	0·010	Second	(14.5.65)	A-bomb using ^{235}U
	0·045	Third	(9.5.66)	A-bomb using ^{235}U
	0·023	Fourth	(27.10.66)	A-bomb using ^{235}U
	0·028	Fifth	(28.12.66)	A-bomb using ^{235}U
	0·23	Sixth	(17.6.67)	H-bomb
	0·16	Eighth	(27.12.68)	H-bomb
^{99}Mo/^{111}Ag	111·0	Fifth	(28.12.66)	A-bomb using ^{235}U
	153·0	Seventh	(24.12.67)	A-bomb using ^{235}U
	31·8	Eighth	(27.12.68)	H-bomb
	38·8	Tenth	(29.9.69)	H-bomb
^{237}U/^{140}Ba	0·16	Second	(14.5.65)	A-bomb using ^{235}U
	0·15	Fourth	(27.10.66)	A-bomb using ^{235}U
	2·82	Sixth	(17.6.67)	H-bomb
	1·57	Tenth	(29.9.69)	H-bomb
^{239}Np/^{140}Ba	0·30	Second	(14.5.65)	A-bomb using ^{235}U
	0·10	Fourth	(27.10.66)	A-bomb using ^{235}U
	42·5	Sixth	(17.6.67)	H-bomb
	19·2	Eighth	(27.12.68)	H-bomb

Table 3. Observed activity ratios in fall-out samples from selected French tests

Isotope ratio	Observed ratio	Test date	Type of bomb concluded
^{111}Ag/^{89}Sr	1·40	18.7.66	A-bomb using ^{239}Pu
	1·06	11.9.66	A-bomb using ^{239}Pu
	0·95	5.6.67	A-bomb using ^{239}Pu
	0·78	2.7.67	A-bomb using ^{239}Pu
^{111}Ag/^{140}Ba	0·14	18.7.66	A-bomb using ^{239}Pu
	0·10	11.9.66	A-bomb using ^{239}Pu
	0·10	5.6.67	A-bomb using ^{239}Pu
	0·013	24.8.68	H-bomb
^{99}Mo/^{111}Ag	24·8	5.6.67	A-bomb using ^{239}Pu
	30·8	2.7.67	A-bomb using ^{239}Pu
	257·0	7.7.68	H-bomb
	48·2	24.8.68	H-bomb
^{237}U/^{140}Ba	0·02	18.7.66	A-bomb using ^{239}Pu
	0·02	11.9.66	A-bomb using ^{239}Pu
^{239}Np/^{140}Ba	4·3	18.7.66	A-bomb using ^{239}Pu
	4·1	11.9.66	A-bomb using ^{239}Pu

The expected activity ratios of selected nuclides at the time of fission are given in Table 1. Tables 2 and 3 give the observed ratios from some Chinese and French tests. The fission product ratios measured correspond with those expected. Furthermore, the mode of detonation and the fissile material used in the weapon are also determined by comparing these measured ratios with the expected activity ratios given in Table 1. The most sensitive ratio for the determination of fissile material is $^{111}Ag/^{89}Sr$, as ^{235}U and ^{239}Pu fission in A-bomb tests give ratios which differ by a factor of 29. A thermonuclear reaction is identified by comparing the observed ratios with corresponding ^{238}U 14-MeV fission ratios, though more significant are the ratios of ^{237}U and ^{239}Np to ^{140}Ba. This is because the $^{237}U/^{140}Ba$ value varies between 0·02 and 0·2 for purely fission devices, depending on whether ^{239}Pu or ^{235}U is used as fissile material, and for thermonuclear devices it is usually higher than 2·0. Similarly the $^{239}Np/^{140}Ba$ value is higher for H-bombs as the amount of ^{238}U is much larger and the number of neutrons liberated in the reaction is also about 10 times that for an A-bomb of the same energy.[4]

Some variations in the ratios are observed. For example, the expected ratio for $^{111}Ag/^{140}Ba$ for the fission-spectrum neutron fission of ^{235}U is 0·018,[5] while for the second and third Chinese A-bomb tests these values are 0·01 and 0·045 respectively. Similarly the $^{111}Ag/^{140}Ba$ values for the sixth and eighth Chinese tests are 0·23 and 0·16 respectively, compared with the value of 0·40 for 14-MeV fission of ^{238}U.[5] These variations could be due to a difference in neutron energies at the time of detonation.

If the tests are held close together, the activity collected will contain short-lived isotopes from earlier tests, thus making it difficult to make detailed measurements of the sample. In such cases the fission products ^{99}Mo and ^{132}Te ($t_{1/2} = 67$ and 77 hr respectively) are used to express activity ratios relative to other fission products.

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SHORT COMMUNICATIONS

MICROWAVE-INDUCED PLASMA COUPLED TO A TANTALUM-STRIP VAPORIZATION ASSEMBLY FOR TRACE ELEMENT ANALYSIS

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Thermal vaporization devices have proved to be useful for introduction of the analyte into microwave-induced plasmas and several applications have recently been reported.[1–5] Nixon *et al.* utilized a tantalum-strip vaporization assembly for analyte introduction into an inductively-coupled plasma.[6] This report describes a similar tantalum-strip assembly coupled to a microwave-induced argon plasma and an application of this system in the analysis of samples with complex matrices.

The bomb technique[7] was used to destroy the organic matrix and a modification of the extraction procedure developed by Kinrade and Van Loon[8] using ammonium pyrrolidinedithiocarbamate (APDC) and sodium diethyldithiocarbamate (DDC) was used to separate the trace elements from the alkali and alkaline-earth metal salts. The quantitative recovery of both volatile and non-volatile trace elements was investigated through standard-addition studies on Se, Cd, Pb and Cu in various matrices. In addition, Cu was determined in various biological samples, in order to compare the results with those of a flameless atomic-absorption study carried out in these laboratories, for which the same samples were used.

EXPERIMENTAL

Apparatus

The instrumentation utilized in this study is listed in Table 1. Figure 1 is a block diagram of the experimental arrangement. The tantalum vaporization assembly and its operation are similar to that described by Nixon *et al.*[6]

Decomposition bombs. A drawing of the cross-section of the decomposition bomb is shown in Fig. 2.* This bomb is a modification of the design suggested by Krogh.[10] The modifications are as follows: the Teflon cup has been redesigned so that the inner pressure causes formation of a tight seal between the Teflon cap and body, a spring has been installed to keep the bomb tightly sealed during the cooling process and the Teflon sleeve has been omitted.

Table 1. Experimental instrumentation

2450 MHz Microwave generator	Opthos Instrument Co.
Microwave coupling cavity No. 5	NBS Report[9] Opthos Instrument Co.
Quartz tube	1·3 mm i.d.
Tantalum strip assembly	Barnes Engineering Co.
Power supply	Laboratory constructed
Monochromator	Jarrell-Ash, 0·5 m Ebert with 1180 grooves/mm grating blazed for 3000 Å. Reciprocal linear dispersion 16 Å/mm in the first order
Entrance slit	Fixed slit, 100 μm, straight edge
Detector	1P28 Photomultiplier tube mounted at 150-μm exit slit
Electronics	Jarrell-Ash MVAA 82500 Atomic Absorption Spectrometer used in emission mode
Read-out	Hewlett Packard model 7101B recorder

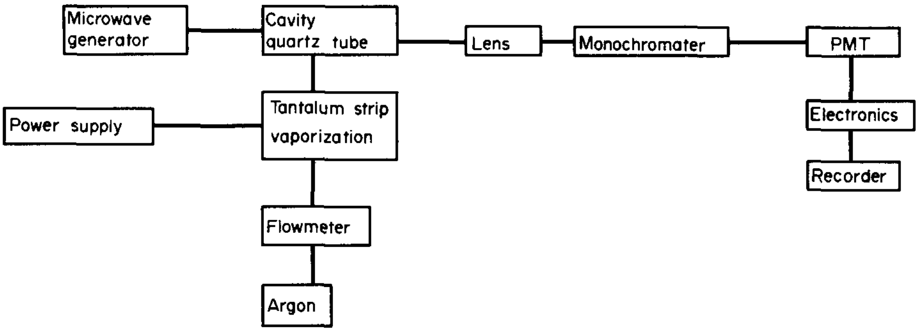

Fig. 1. Block diagram of apparatus.

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* A more detailed drawing of the decomposition bomb is available upon request.

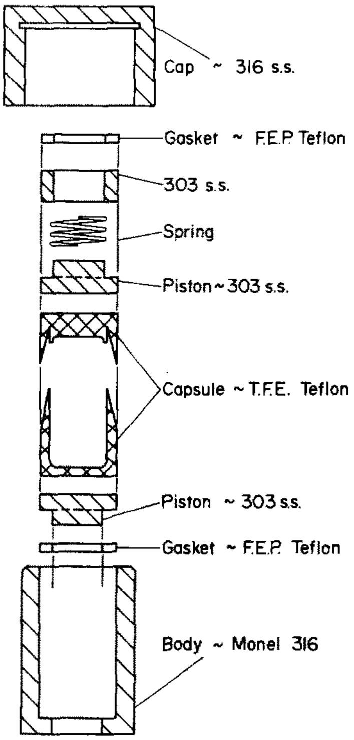

Fig. 2. Drawing of decomposition bomb.

Two different types of steel were required in the construction of the cap and body to prevent stripping of the threads.

Reagents

Stock solutions were prepared from Fisher atomic-absorption standards or alternatively by dissolving pure metals or reagent grade salts in acid diluted with demineralized water.

Nitric acid. Redistilled.

Chloroform. Reagent grade washed with demineralized water.

APDC–DDC. The reagents, 500 mg of each, were placed in a 50-ml flask, treated with demineralized water, and the solution was filtered through glass wool and extracted with three 10-ml portions of chloroform and then centrifuged.

Potassium hydrogen phthalate buffer pH 5·5. Sodium hydroxide solution (36·6 ml, 0·1*M*) was added to potassium hydrogen phthalate solution (50·0 ml, 0·1*M*).

Argon. Commercial grade, purified by passage through a train of concentrated sulphuric acid, Anhydrone, Ascarite and glass wool.

Procedure

Sample preparation. To illustrate the applicability to tissue, a fish sample (Northern Pike) was filleted and all bones removed. It was then blended (Osterizer Model 403) to produce a homogeneous composite. Lettuce was also blended to produce a homogeneous composite. The baby-food pears were taken directly out of the jar. Samples (3–5 g) were then weighed into the Teflon cup of the bomb.

From 0·28 to 0·35 g of bovine liver samples were obtained by carefully removing a section of the hepatic membrane and taking 1 cm^2 of undisturbed tissue. The samples were then ground in an agate mortar and weighed into the bombs. Only a small fraction of the total liver was sampled.

Human serum was prepared by taking fresh blood from a donor and allowing it to clot. It was then centrifuged for 10 min at 2500 rpm, and 1·0 ml of serum was taken for analysis.

Human ceruloplasmin, type III, was obtained from Sigma Chemical as a 5% solution in 0·25 *M* sodium chloride–0·05 *M* sodium acetate at pH 7. It was desalted by passage through a Sephadex G-25 desalting column equilibrated with 0·2 *M* ammonium acetate/acetic acid solution. The middle fraction was collected.

Sample digestion. After insertion of the sample into the bomb 3·0 ml of nitric acid was added and the bomb sealed and placed in an oven at 140° for 2 hr. The bomb was cooled with a stream of air for about 30 min.

Extraction. The Teflon cup was removed from the bomb and placed in a small ice-bath. The pH of the solution in the cup was adjusted (Fisher micro combination electrode) to pH 5·5, by adding dropwise 50% sodium hydroxide solution to reach pH 2 and then 1 *M* sodium hydroxide to reach the final pH. This solution was then transferred quantitatively to a 60-ml separatory funnel; 5·0 ml of the potassium hydrogen phthalate pH 5·5 buffer were added and mixed, followed by 10·0 ml of chloroform and 5·0 ml of the APDC–DDC solution. The mixture was shaken for 2 min and then shaken by mechanical shaker for 13 min. The separatory funnel was centrifuged and the chloroform drained into a glass-stoppered flask.

Specroscopic analysis. After the argon flow-rate was set at 900 ml/min, the plasma was initiated with a Tesla coil and the microwave power was adjusted to 45 W. The alignment of the argon plasma with the monochromator was optimized by maximizing the intensity of the 3093·41-Å argon line. Radiation from the appropriate hollow-cathode lamp was reflected into the monochromator with a removable mirror for optimization of the analytical response for a given element. A 5·0 μl portion of the chloroform solution was pipetted (Drummond Wiretrol 5-μl pipette) onto the tantalum strip. The solvent was evaporated by drying without heat for 40 sec with the injection port open. The port was closed and the tantalum strip heated (approximately 150–200°) for 80 sec. at a low current setting. After this drying sequence, the strip was fired for 1 sec at a high current setting (i.e., at approximately 1800°) and the peak height of the resulting emission signal was recorded on a strip-chart recorder. Standards bracketing the sample were run through the procedure. The sample and standard peak heights, corrected for reagent blank, were compared to determine the element concentration.

Standard recoveries. A 5·0-ml portion of demineralized water was pipetted into the Teflon cup. The desired amount of the element was added from a microlitre pipette (MLA precision pipette), then 3·0 ml of nitric acid were added and the procedure above, starting with the sample digestion, was used to determine the recoveries.

Spiked samples After the sample had been weighed into the Teflon cup, the desired amount of an element was added with a microlitre pipette (MLA precision pipette) followed by 3·0 ml of nitric acid and the procedure was used to determine the recovery.

RESULTS AND DISCUSSION

The decomposition bomb shown in Fig. 2 provided a seal that did not show visible signs of leaking when 0·5–0·9 g (dry weight) of sample was decomposed, even after 30 such decompositions. Attempts to analyse the nitric acid digest of most samples directly for trace elements did not succeed because there were severe matrix effects and spectral interferences from the large amount of alkali and alkaline earth metal salts present, several elements formed volatile nitrosyl compounds and consequently were lost during the drying stage, and nitric acid attacked the tantalum strip, causing it to oxidize rapidly. Therefore, the chelate

Table 2. Absolute detection limits

Element	Wavelength, Å	Detection limit, *ng**
As	1936·96	0·6
Se	1960·26	0·6
Cd	2288·02	0·02
Zn	2138·56	0·02
Pb	4057·83	0·3
Cu	3247·54	0·05
Sb	2311·47	0·5
Sn	2863·33	1·1
Bi	2230·61	0·2

* Sample volume 5 μl.

extraction procedure was developed, with chloroform chosen as the solvent since it evaporated very rapidly from the tantalum surface, extracted the chelate quantitatively, formed only a slight emulsion and could be drained directly from the separatory funnel after centrifugation.

A disadvantage of this procedure is that it does not extract As and Be, two toxic elements which would have been of interest in this study.

The characteristics of the microwave-induced plasma have already been discussed.[1] The position of the plasma tended to wander within the tube. In order to stabilize it, a small metal bar was placed against the quartz tube near the lower portion of the plasma. Since the plasma was attracted to the metal bar, it remained fixed at the front wall of the tube. The emission from the elements was viewed just below the centre of the plasma, as this position appeared to give the best response for most of the elements.

The injection port was left open during the evaporation of the chloroform so that a large amount of chloroform would not enter the quartz tube, possibly extinguishing the plasma or causing the plasma to be concentrated and to etch the tube.

The detection limits for the system are shown in Table 2. These values were determined by measuring the signal-to-noise ratio at a sample level approximately ten times the detection limit and calculating the sample level which would have generated a signal-to-noise ratio of 2. Co and Ni were not determined owing to reaction of these elements with the tantalum strip.[11]

As an example of the precision of the system, relative standard deviations for 5 replicate determinations of 1·25, 1·67 and 2·50 ng of Cu (aqueous standards) were 1·4, 1·1 and 0·87%, respectively.

Standards alone and standards added to the samples (spiked samples) were taken through the entire procedure and the results are shown in Tables 3 and 4. Each recovery shown is an average of 4 separate determinations with 5 emission signals recorded for each determination. The spike levels were chosen to indicate that recovery of both volatile and non-volatile elements by the bomb digestion–solvent extraction procedure was quantitative. They do not indicate the lower or upper limits of the method.

A background correction was made for selenium, by using the 1965·0 Å line. This background is due to traces of organic compounds left in the nitric acid digest, causing an emission continuum.

Table 3. Standard recoveries

Element	Amount added, *μg*	Amount recovered, *μg**	Recovered, %	Average deviation, %	Range, %
Se	5·00	5·05	101	1·6	97·8–103
Cd	2·00	1·98	99·1	0·7	98·2–100
Pb	5·00	5·10	102	3·6	96·6–106
Cu	2·00	2·02	101	1·4	97·4–103

* Average of 4 determinations.

Table 4. Spiked recoveries

Element	Original content, *μg/g*	Amount added, *μg*	Amount of spike recovered, *μg**	Recovery, %	Average deviation, %	Range, %
		Pears**				
Se	0·00	5·00	4·92	98·3	4·1	94·5–105
Cd	0·00	2·00	2·08	104	2·0	101–108
Pb	0·00	5·00	4·78	95·5	4·8	91·2–105
Cu	0·61	2·00	1·93	96·7	5·4	89·9–103
		Fish†				
Se	0·00	5·00	4·75	95·0	0·6	93·7–97·0
Cd	0·00	2·00	1·90	94·9	1·8	91·2–98·0
Pb	0·00	5·00	5·10	102	1·0	100–106
Cu	0·59	2·00	1·97	98·5	2·5	94·5–102
		Lettuce‡				
Se	0·00	5·00	4·98	99·6	3·7	95·4–109
Cd	0·09	2·00	1·96	97·8	2·4	92·5–102
Pb	0·00	5·00	4·81	96·2	3·1	89·7–102
Cu	0·50	2·00	1·97	98·4	2·6	95·6–106

* Average of 4 determinations.
** 4 g sample taken.
† 3 g sample taken (Northern Pike).
‡ 5 g sample taken.

The results for the portion of bovine liver sampled yielded for Cu an average of 23 $\mu g/g$ with an average deviation of ± 3 μg. These results compare favourably with those of the flameless atomic-absorption (FAA study[12] which gave an average of 28·9 $\mu g/g$. The human serum study gave an average Cu value of 102 $\mu g/100$ ml with an average deviation of ± 5 μg. (FAA[12] gave 98 $\mu g/100$ ml). The generally accepted value for copper in human serum is 100 $\mu g/100$ ml. The sensitivity is high enough for the sample sizes to be reduced at least tenfold, an important factor in pediatric screening or when working with small animals.

The desalted human ceruloplasmin yielded a copper content of 5·5 ppm, *ca.* 20% higher than that obtained by FAA,[12] but no ashing or extraction was required. The copper content of the ceruloplasmin (0·32%) is high enough to allow the sample to be highly diluted so that the organic matrix is destroyed in the plasma without interference. The desalting eliminates any alkali or alkaline earth metal interference and hence extraction is unnecessary. Ceruloplasmin was the only sample in this study for which ashing and extraction were unnecessary.

In view of these results, it can be concluded that the tantalum-strip vaporization assembly/microwave-induced plasma system (if necessary, combined with bomb decomposition and chelate extraction) offers a sensitive technique for the determination of some trace elements in samples with complex matrices.

The major advantage of this system over non-flame atomic absorption is the potential capability for multielement trace analysis. A study[13] in which a similar system was coupled to a vidicon detector has been completed which demonstrates this advantage.

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Summary—This report describes a tantalum-strip assembly coupled to a microwave-induced plasma. Detection limits obtained for several elements by using the apparatus are given. A procedure using bomb decomposition and chelate extraction in conjunction with the tantalum-strip assembly/microwave-induced plasma system for the determination of trace elements in samples with complex matrices is also described. Recoveries from spiked standards are given.

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LINEAR TITRATION PLOTS FOR POLYFUNCTIONAL WEAK ACIDS AND BASES

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(*Received* 8 *July* 1975. *Accepted* 5 *October* 1975)

Requests for a Fortran version of an Algol program for calculating linear plots for the potentiometric titration of a number of weak acid systems[1] have led us to develop the program in additional directions. The plot for the titration of a dibasic weak acid with a strong base has been extended to cover polybasic weak acids with up to six functional groups and a corresponding plot has been devised for the titration of a polyacidic weak base with a strong acid. The plots can be used to give a graphical solution, or the equivalence volumes can be obtained from a least-squares fit of the function. Activity coefficient corrections can be made through an iterative process. Copies of the program are available on request.

THEORY

For convenience, charges have been omitted from ionic symbols; f_i is the activity coefficient of the ith protonated

The results for the portion of bovine liver sampled yielded for Cu an average of 23 $\mu g/g$ with an average deviation of ± 3 μg. These results compare favourably with those of the flameless atomic-absorption (FAA study[12] which gave an average of 28·9 $\mu g/g$. The human serum study gave an average Cu value of 102 $\mu g/100$ ml with an average deviation of ± 5 μg. (FAA[12] gave 98 $\mu g/100$ ml). The generally accepted value for copper in human serum is 100 $\mu g/100$ ml. The sensitivity is high enough for the sample sizes to be reduced at least tenfold, an important factor in pediatric screening or when working with small animals.

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THEORY

For convenience, charges have been omitted from ionic symbols; f_i is the activity coefficient of the ith protonated species, f_A the activity coefficient of the unprotonated form of the acid or base, V_e the equivalence volume of titrant and V the volume of titrant added. K_w is the thermodynamic autoprotolysis constant of water and, assuming $f_H = f_{OH} = f_\pm$, [OH] is given by $K_w/\{H\}f_\pm$, $\{H\}$ being the hydrogen-ion activity.

Weak acid titrations

V_0 ml of a solution of a weak acid, H_hAP_q, with k acidic functional groups, are titrated with a strong base, BOH, of molar concentration m. P is a univalent ion with the charge-sign necessary to maintain electrical neutrality, h is the number of protons per molecule removable by titration, a is the negative charge on A and $q = |h - a|$. If charge p is assigned to P and $K_i = [H_iA]f_i/(\{H\}^i[A]f_A)$ is the ith association constant of the weak acid, the mass-balance equations are:

$$\begin{aligned} T_A &= [A] + [HA] + \cdots + [H_iA] + \cdots + [H_kA] \\ &= [A]\left(1 + \sum_{i=1}^{k} K_i\{H\}^i f_A/f_i\right) \\ &= \frac{mV_e}{h(V_0 + V)} \end{aligned} \tag{1}$$

$$p[P] = -(h - a)T_A \tag{2}$$

$$[B] = T_B = mV/(V_0 + V). \tag{3}$$

The charge-balance equation is

$$\begin{aligned} [B] + [H] + p[P] = [OH] + a[A] + (a-1)[HA] + \cdots \\ + (a-i)[H_iA] + \cdots \\ + (a-k)[H_kA] \end{aligned} \tag{4}$$

Substituting from equations (1), (2) and (3) in equation (4), we obtain

$$\begin{aligned} T_B + [H] - (h - a)T_A \\ = [OH] + a.T_A - [A]\sum_{i=1}^{k} iK_i\{H\}^i f_A/f_i. \end{aligned}$$

On rearrangement and further substitution in terms of the measured quantities $\{H\}$, V and V_0, we obtain:

$$\frac{mV}{V_0 + V} + \frac{\{H\}}{f_\pm} - \frac{K_w}{\{H\}f_\pm} = \frac{mV_e}{h(V_0 + V)}\left\{h - \frac{\alpha}{1 + \beta}\right\}.$$

Hence

$$\begin{aligned} \{h(V_0 + V)(\{H\} - K_w/\{H\})/f_\pm \\ + mV\alpha/(1 + \beta)\}/\{h - \alpha/(1 + \beta)\} = m(V_e - V) = F_{PA} \end{aligned} \tag{5}$$

In equation (5)

$$\alpha = \sum_{i=1}^{k} iK_i\{H\}^i f_A/f_i \quad \text{and} \quad \beta = \sum_{i=1}^{k} K_i\{H\}^i f_A/f_i.$$

A plot of F_{PA} against V is linear and intercepts the V-axis at $V = V_e$.

Weak base titrations

V_0 ml of a weak base, H_hAP_q, with k basic functional groups are titrated with a strong acid, HX, of molar concentration m; $k - h$ protons can be added to each molecule. P, p, q, a, K_i, α and β are defined as above. The mass- and charge-balance equations may be written:

$$T_A = [A](1 + \beta) = \frac{mV_e}{(k - h)(V_0 + V)} \tag{6}$$

$$p[P] = -(h - a)T_A \tag{7}$$

$$[X] = mV/(V_0 + V) \tag{8}$$

$$\begin{aligned} [H] + p[P] = [OH] + [X] + a[A] + \cdots \\ + (a - i)[H_iA] + \cdots + (a - k)[H_kA] \end{aligned} \tag{9}$$

Substituting and rearranging as before, we obtain

$$\begin{aligned} \{(k - h)(V_0 + V)(\{H\} - K_w/\{H\})/f_\pm \\ + mV(\alpha/(1 + \beta) - k)\}/\{h - \alpha/(1 + \beta)\} = m(V_e - V) = F_{PB} \end{aligned}$$

A plot of F_{PB} against V is linear and intercepts the V-axis at $V = V_e$.

Effect of an error in the association constant

The extent of the deviation from the true function produced by an inaccurate value of the association constant has already been discussed,[1] but the apparent equivalence volume indicated by the intercept of the inaccurate function on the V-axis was not considered. For a monobasic weak acid of concentration c, the function F_{PA} reduces to

$$F_{PA} = (1 + K_1\{H\}f_A/f_i)(V_0 + V)\theta + mVK_1\{H\}f_A/f_i,$$

where $\theta = (\{H\} - K_w/\{H\})/f_\pm$. If the function calculated with an inaccurate constant $K_1' = rK_1$ is designated Φ_{PA}, we have:

$$\Phi_{PA} = (1 + K_1'\{H\}f_A/f_i)(V_0 + V)\theta + mVK_1'\{H\}f_A/f_i.$$

Therefore,

$$F_{PA} - \Phi_{PA}/r = (1 - r^{-1})(V_0 + V)\theta \tag{10}$$

Φ_{PA} intercepts the V-axis at $V = V_e'$, the apparent equivalence volume and the value of θ at this point is θ_e'. By definition the error in V_e is $\Delta V_e = V_e' - V_e$.

Since at $V = V_e'$, $\Phi_{PA} = 0$, we have from equation (10)

$$F_{PA} = (1 - r^{-1})(V_0 + V_e')\theta_e'$$

and from equation (5)

$$F_{PA} = m(V_e - V_e') = m\Delta V_e$$

Hence

$$\Delta V_e = \frac{(r^{-1} - 1)(V_0 + V_e)\theta_e'}{m - (r^{-1} - 1)\theta_e'}$$

and the relative error is

$$\frac{\Delta V_e}{V_e} = \frac{(1 + m/c)(r^{-1} - 1)}{1 - r^{-1} + m/\theta_e'} \tag{11}$$

For a monoacidic weak base, we obtain by a similar process

$$F_{PB} = \frac{(1 + K_1\{H\}f_A/f_i)(V_0 + V)\theta - mV}{-K_1\{H\}f_A/f_i}$$

$$\Phi_{PB} = \frac{(1 + K_1'\{H\}f_A/f_i)(V_0 + V)\theta - mV}{-K_1'\{H\}f_A/f_i}$$

$$F_{PB} - r\Phi_{PB} = (r - 1)(V_0 + V)\theta$$

When

$$\Phi_{PB} = 0,\ V = V_e' = V_e + \Delta V_e \quad \text{and} \quad \theta = \theta_e',$$

hence

$$F_{PB} = (r - 1)(V_0 + V_e + \Delta V_e)\theta_e' = -m\,\Delta V_e,$$

$$\Delta V_e = \frac{(1 - r)(V_0 + V_e)\theta_e'}{m + (r - 1)\theta_e'}$$

$$\frac{\Delta V_e}{V_e} = \frac{(1 - r)(1 + m/c)}{r - 1 + m/\theta_e'}$$

If $r > 1$, Φ_{PA} results in an overestimate of V_e, and Φ_{PB} in an underestimate, and conversely for $r < 1$. The magnitude of the error produced by a given value of r depends principally on θ_e'. The stronger the acid or base, and

Table 1. Results of titrations, with literature data

Titrand and data source	Source of association constants	Theoretical		Observed	
		V_e, *ml*	Titrant concn., *M*	V_e, *ml*	BCALC, *M*
*Citric acid[4]	5	7·33	0·1244†	7·35	0·130
*Succinic acid[4]	6	7·94	0·1244†	8·00	0·124
*Malic acid[4]	7	8·01	0·1244†	7·95	0·128
Lysine hydrochloride[8]	8	10·00	0·100†	10·00	0·099
Glycine[8]	9	5·00	0·100†	5·07	0·098
Glycine[10]	9	25·00	0·100‡	24·2	0·103

* pH values were recalculated with use of modern values[11] for the standard potentials of the quinhydrone and saturated calomel electrodes.

† Sodium hydroxide.

‡ Hydrochloric acid.

the lower its concentration, the smaller θ'_e, and hence the error, becomes.

CALCULATION

A Fortran program has been written to carry out the calculations. The value of the function F_{PA} or F_{PB} for each addition, V, of titrant is calculated by a subroutine ALLONE and the best straight line through the points (V, F_{PA}) or (V, F_{PB}) is determined by an unweighted least-squares fit using a subroutine LEAST. If the ionic strength changes in the course of the titration, activity coefficients can be calculated iteratively by a subroutine ACTCO, which uses the equation

$$-\log f_z = A.z^2\{I^{1/2}/(1 + BaI^{1/2}) - bI\}$$

where A and B are the Debye–Hückel parameters, a and b are adjustable parameters supplied to the program and z is the charge on the ion. The ionic strength, I, is calculated by a function subroutine MU. Iteration in the cycle ALLONE–V_e–MU–ACTCO–ALLONE proceeds until successive values of V_e agree within 0·01%. The subroutines LEAST and ACTCO can be used with another program dealing with mixtures of acids.[2] The use of ACTCO is not contingent on the particular equation used and it should be possible to accommodate any other method of calculating activity coefficients.

The equivalence volume, V_e, and the slope of the plot, BCALC, are printed with their respective standard deviations. Systematic errors can cause curved plots (evident from the large standard deviations), but usually a good graphical solution can be obtained and the co-ordinates of the plot are therefore also printed. BCALC provides a check on the calculations, since errors, whether resulting in curvature or not, cause BCALC to differ from its theoretical value, m, the concentration of the titrant.

Scope of the method

The program allows for up to six acidic or basic functional groups per molecule, but it has not been tested with more than three. All forms of acids or bases are covered, *e.g.*, citric acid, $k = h = a = 3$; trisodium citrate, $k = a = 3$, $h = 0$; glycine, $k = 2$, $h = a = 1$; glycine hydrochloride, $k = h = 2$, $a = 1$; ammonia, $k = 1$, $h = a = 0$. The acids or bases may be very weak and may have overlapping dissociation steps. The limitations due to the neglect of activity coefficients and, in part, to errors in the association constants have been discussed before,[1] together with a comparison with Gran's method.[3]

The greatest accuracy would be achieved if the association constants of an acid or base were determined with the same apparatus before any analytical titrations were carried out, but a practicable method should be capable of producing accurate results with literature values for the constants and independently obtained pH readings. The results of some calculations with published titration data are given in Table 1.

The agreement between theoretical and observed results is reasonable, given the unfavourable conditions. In the case of the glycine–hydrochloric acid titration the plot was scattered more than usual and the few titration points were badly distributed for our purposes. Other results have been reported earlier.[1]

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Summary—Procedures are derived for obtaining the equivalence volumes in the potentiometric titrations of polyfunctional weak acids and weak bases by a linear titration plot method. The effect of errors in the equilibrium constants on the accuracy is considered. A Fortran program is available to do the calculations.

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ION-EXCHANGE BEHAVIOUR OF PYRIDINIUM TUNGSTOARSENATE

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The cation-exchange behaviour of salts of heteropoly acids is well established. Smit *et al.*,[1] while investigating the properties of the ammonium salts of heteropoly acids observed that ammonium tungstoarsenate and tungstophosphate become colloidally dispersed and cannot be used as cation-exchangers. We have replaced the ammonium ion in the tungstoarsenate salt with organic bases and have found that pyridinium tungstoarsenate is chemically and thermally stable and possesses promising exchange properties, comparable to those of the ammonium salt.

The work described in this paper is concerned with the sorption of some univalent and bivalent cations on the exchanger, evaluation of the constants and an interpretation of the mechanism.

EXPERIMENTAL

Sodium tungstate and arsenic pentoxide, used in these studies, were reagent grade chemicals. The salts of sodium, potassium and lithium were of analytical reagent quality. Their solutions were prepared in doubly distilled water.

Pyridinium nitrate was obtained as a white crystalline compound, by mixing nitric acid and distilled pyridine in equimolar quantities. It was crystallized from water and alcohol and dried in a vacuum desiccator, Pyridinium tungstoarsenate was obtained as follows.

Arsenic pentoxide (4·6 g), dissolved in concentrated sodium hydroxide solution and diluted to 140 ml, was added slowly with constant stirring to a solution of sodium tungstate (105·6 g dissolved in 180 ml of water). The mixture was then acidified with concentrated hydrochloric acid and 40 g of pyridinium nitrate were added in small amounts with constant stirring. The mixture was heated over a water-bath for 30 min, then left for 24 hr and filtered. The product was washed with dilute acid and distilled water and dried at 90°.

The pyridinium tungstoarsenate was then analysed. Tungsten was determined as the thiocyanate complex. Pyridine was determined spectrophotometrically at 256 nm. Arsenic was determined by dissolving a known amount of the product in 0·1*N* sodium hydroxide and back-titrating the excess of alkali.

The exchange isotherms with various cations were obtained by estimating spectrophotometrically the amount of pyridinium ion liberated by different concentrations of a particular cation in presence of 0·001*M* pyridinium nitrate. The amount of exchanger (0·1 g), the total volume of the solution (20 ml) and the acidity of the medium (0·01*M* nitric acid) were the same in all cases.

In order to ascertain the stoichiometry of the exchange reactions both the solid and liquid phases were analysed after exchange. The experiments were carried out at 32°.

RESULTS AND DISCUSSION

The values obtained for pyridine, tungsten and arsenic in the compound pyridinium tungstoarsenate are given below and compared with the theoretical values calculated on the bases of the formula $(C_5H_5NH)_3W_{12}AsO_{40}$. [Found: C_5H_5N, 7·6%; As, 2·0%; W, 69·9%; $(C_5H_5NH)_3W_{12}AsO_{40}$ requires C_5H_5N, 7·6%; As, 2·3%; W, 70·4%]. The analysis shows that the salt is anhydrous, and this is confirmed by the thermogravimetric analysis (Fig. 1) which reveals only the thermal decomposition of the product at 480°.

The pyridinium ion in this compound is exchangeable and the exchange reaction is found to be stoichiometric. The exchange isotherms are plotted in Figs. 2–4.

The order of adsorption on the exchanger is $Cs^+ > Rb^+ > Na^+ > Li^+ > K^+ > NH_4^+$ and $Cu^{2+} > Sr^{2+} > Ba^{2+}$. The compound seems to be highly specific towards Cs^+, Ag^+ and Tl^+, and an almost complete replacement of pyridinium ion occurs with silver and caesium. The slopes of the isotherms are quite different, showing that the exchanger can be used for the separation of these cations.

The sequence of cationic uptake is not the same as reported by other workers for heteropoly salts.[2,3] The adsorption seems to decrease with increasing atomic number or size of bivalent cations *viz.* Cu^{2+}, Sr^{2+} and Ba^{2+}. In the case of univalent cations no regular order is observed with respect to the size of the ion or the volume of the hydrated ion. On the other hand their sequence seems to follow the lyotropic number, which according to Bruins[4] and Voet,[5] holds true for ion-exchange processes, the species with a lower lyotropic number being adsorbed more strongly. Steric effects sometimes influence the selectivity order of adsorption of alkali metal ions and a reverse behaviour for alkaline earth cations has also been reported by Lefebvre and Gaymard.[6]

The X-ray studies of the heteropoly acids and their salts (summarized by Wells[7]) have shown that in such crystals

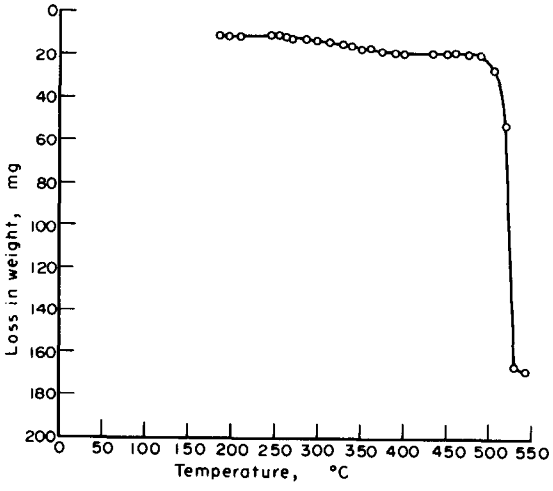

Fig. 1. TGA of pyridinium tungstoarsenate.

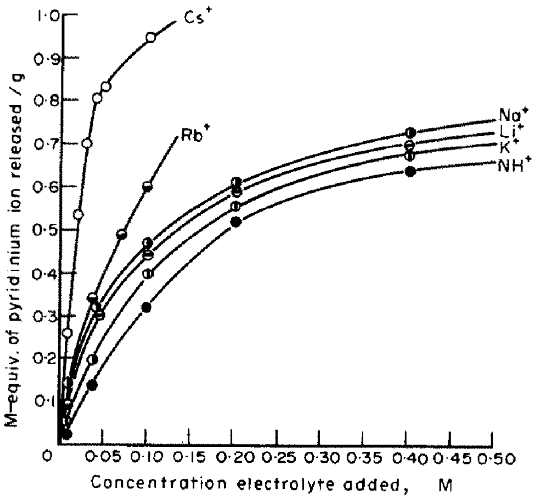

Fig. 2. Exchange isotherms of alkali metal ions and NH_4^+.

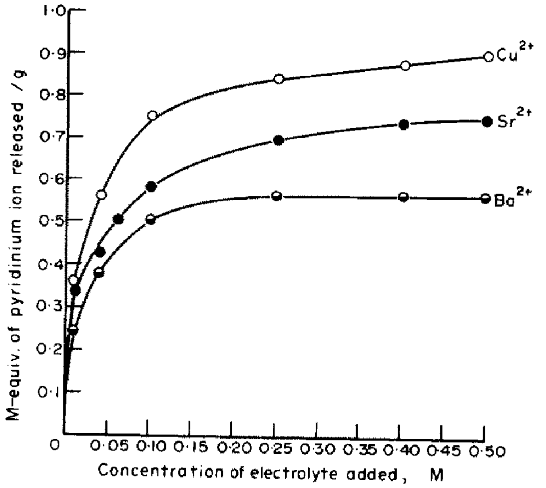

Fig. 4. Exchange isotherms of Cu^{2+}, Sr^{2+} and Ba^{2+}.

the cations with associated water molecules are fitted in between the large negative ions. Comparatively large cavities exist between these negative ions, allowing the accommodation of larger cations, even those of organic bases. Univalent cations such as Rb^+, Cs^+, Tl^+, Ag^+ and K^+, can be packed stably into the structure and lower the crystal energy sufficiently to give salts insoluble in water. In other cases, *e.g.*, lithium or sodium pyridinium heteropoly salts, their peculiar behaviour may be due to their solubility in the medium.

For the alkali metal ions and also for thallium and silver the logarithm of the selectivity coefficient (K') varies linearly with the saturation of the exchanger (Fig. 5) thus conforming to the empirical Kielland equation[8] established on theoretical grounds by Barrer and Falconer.[9]

$$\log K' = \log K + C(1 - 2\overline{X}_M)$$

where K' is the selectivity coefficient, K the thermodynamic equilibrium constant, $\overline{X}_M$ the fraction of exchanging sites occupied by the exchanging ion and

$$C = -\frac{E_\omega}{2{\cdot}303\,kT}\cdot\frac{N_A + N_B}{N}$$

N_A and N_B are the number of ions of the type A and B in the exchanger, N is the total number of available sites and E_ω is the interaction energy or the energy change in the crystal associated with pair formation, when two ions occupy adjacent sites.

Figure 5 shows the plot of log K' *vs.* $(1 - 2\overline{X}_M)$. The values of the thermodynamic equilibrium constant, K, free energy change, ΔG° and the energy of interaction between the adjacent ions on the surface, E_ω, are given in Table 1.

The smaller magnitude of E_ω suggests that the neighbouring ions on the exchanger surface are very little affected by adjacent ions. These values also indicate a

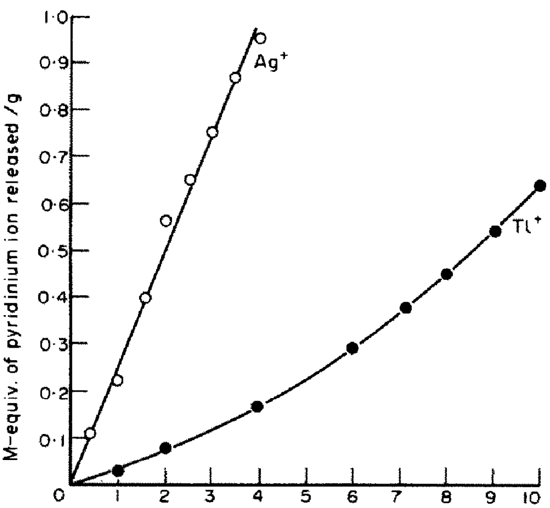

Fig. 3. Exchange isotherms of Ag^+ and Tl^+.

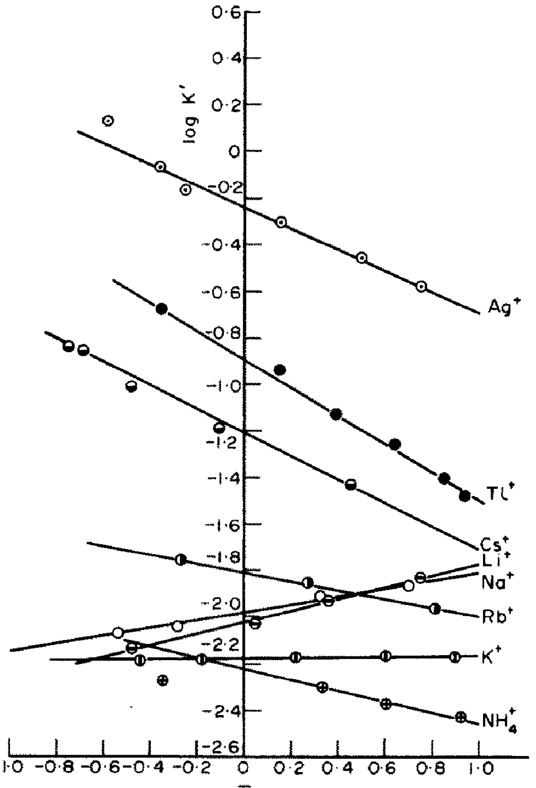

Fig. 5. Plot of logarithm of selectivity coefficients *vs.* $(1 - 2\overline{X}_M)$.

Table 1.

	Thermodynamic equilibrium constant	ΔG°, *kcal/mole*	E_ω, *kcal/mole*
K_{Py}^{Li}	0·0095	$2{\cdot}7_7$	−0·36
K_{Py}^{Na}	0·0104	$2{\cdot}7_2$	−0·23
$K_{Py}^{NH_4}$	0·0060	$3{\cdot}0_4$	0·29
K_{Py}^{K}	0·0067	$2{\cdot}9_8$	0·027
K_{Py}^{Rb}	0·0159	$2{\cdot}4_7$	0·28
K_{Py}^{Cs}	0·069	$1{\cdot}6_6$	0·69
K_{Py}^{Ag}	0·575	0·33	0·62
K_{Py}^{Tl}	0·129	1·22	0·83

strong preference for silver and the following affinity series can be written for this exchanger:

$$Ag^+ > Tl^+ > Cs^+ > Rb^+ > Na^+ > Li^+ > K^+ > NH_4^+$$

The magnitude of E_ω for various cations reflects that more work has to be done by Ag^+, Cs^+ and Tl^+ to occupy adjacent sites than by Rb^+ and K^+. On the other hand, it has been observed that it is easier to saturate the lattice with these three cations and these findings cannot be reconciled unless the exchange mechanism approaches very closely a chemical reaction between the almost dehydrated Cs^+, Ag^+, Tl^+ and pyridinium ions. Similar findings have been reported for ammonium molybdophosphate and phosphotungstate compounds.[10]

The replacement of the pyridinium ion of this salt with other organic cations *viz.* methylammonium, dimethylammonium and trimethylammonium has also been investigated. The studies show that the uptake of the ions is directly proportional to their size in the case of the first two compounds. The uptake of trimethylammonium ion is the least. The crystal lattice in pyridinium tungstoarsenate is perhaps too compact to allow the entry of the large trimethylammonium cation, but loose enough to permit the exchange of mono- and dimethylammonium ions.

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Summary—The exchange behaviour of pyridinium tungstoarsenate has been investigated with some uni and bivalent cations. The compound shows high specificity towards Cs^+ and Ag^+ and the exchange is complete even in the low concentration range. The slopes of the isotherms of various cations are widely different suggesting that separation of these ions on a pyridinium tungstoarsenate column is feasible. From a linear plot of Barrer's equation, the thermodynamic equilibrium constant, the energy of interaction between the ions on the surface and the free energy change of the process have been evaluated.

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LAPACHOL: A NEW ACID–BASE INDICATOR

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(*Received* 19 *August* 1975. *Accepted* 24 *September* 1975)

Lapachol [2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone] is easily available from the plants of *Bignoniaceae* and *Verbenaceae* in abundant quantity. Recently, we have isolated this compound from the petroleum-ether extracts of the heartwoods of *Tecomella undulata*,[1] *Tabebuia rosea*[2] and *Phyllarthron comorense*.[3]

Lapachol is a yellow crystalline solid, m.p. 139–140°. It gives a violet-red colour with ferric chloride and a red colour with magnesium acetate. It dissolves in aqueous sodium hydroxide, giving a deep red solution which turns light yellow on addition of sodium dithionite, and the red colour can be restored on shaking for some time in air.

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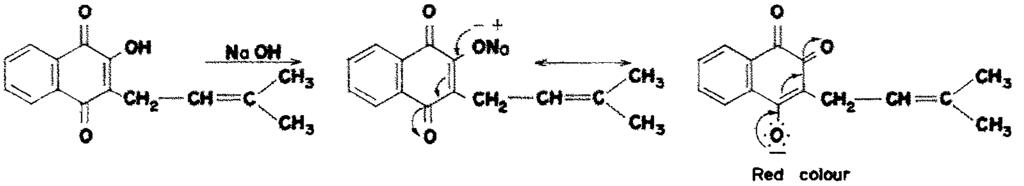

EXPERIMENTAL

Since it gave a blood-red colour with aqueous alkalies, we thought it worthwhile to examine its utility as an acid-base indicator. It gives no colour in acidic medium, probably because of protonation of the quinonoid oxygen atom suppressing its quinonoid nature, but has a red colour in alkaline medium, owing to its resonating forms.

The transition interval was determined by adding the indicator to a series of suitable buffers in test-tubes of equal colour and diameter, and found to be pH 4·8–5·8 when the indicator concentration is $10^{-3}\%$ in the test solution. The first perceptible colour is at pH 4·8, and the colour ceases to change at pH 5·8.

Lapachol is thus a suitable one-colour indicator for the titration of strong acids with strong or weak bases. The colour is fairly stable.

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Summary—Lapachol, a new one-colour acid-base indicator, is easily available from natural sources and gives a deep red colour with aqueous alkalies. Its transition range is found to be pH 4·8–5·8. It can be used for titration of strong acids with strong or weak bases.

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DETERMINATION OF SULPHIDE, SULPHITE AND THIOSULPHATE WITH THALLIC PERCHLORATE OR SULPHATE

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Department of Chemistry, University of Rajasthan, Jaipur, India

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Recently a review[1] describing analytical determinations of sulphide, sulphite and thiosulphate has appeared. It seems that there are contradictory reports about the iodimetric determination of sulphide. Kolthoff[2] has reported only partial oxidation of sulphide to sulphate in alkaline medium. Bethge[3] has reported that the iodimetric determination is not free from errors. Similarly difficulty has been encountered in the iodimetric determination of sulphite, particularly in alkaline medium, owing to air oxidation which can, however, be checked by addition of inhibitors.[4–6] Thiosulphate can, however, be determined[7,8] accurately iodimetrically both in acid and alkaline media.

The present paper describes the iodimetric determination of these substances with thallic perchlorate or sulphate and potassium iodide. The method is essentially a combination of iodometry and iodimetry. Thallium(III) liberates iodine from potassium and this iodine is subsequently used up by sulphide, sulphite or thiosulphate. The main advantage of the method is that it dispenses with the preparation of iodine solution (which does not have a constant titre) whereas thallic perchlorate or sulphate gives a standard solution stable over months and unaffected by air and light. Thallium(III) has already been used for the determination of thiourea, sulphite and thiosulphate, with *p*-ethoxychrysodine as indicator.[9] Apart from iodimetry, the present paper describes the use of indigo carmine indicator for the determination of sulphide, sulphite and thiosulphate.

EXPERIMENTAL

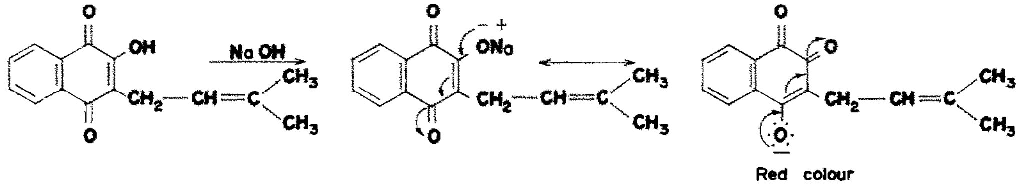
Reagents

Thallic oxide is added gradually to heated $\sim 5M$ perchloric or sulphuric acid until no more will dissolve. The solution is left overnight and then filtered. Alkali is added to the filtrate to precipitate thallic hydroxide, which is filtered off, washed, and dissolved in the appropriate acid. It is necessary to maintain about $0·5\,M$ acid concentration in the reaction mixtures and hence the acidity of the thallium(III) solutions is also determined by titration with caustic soda solution to the phenolphthalein end-point; it is necessary to add potassium bromide to complex thallium(III) to check its interference in the acid–base titration.

Solutions of sodium sulphide, sodium sulphite and sodium thiosulphate were prepared in doubly distilled water and standardized against an iodine solution. A 0·1% aqueous solution of indigo carmine was prepared.

Procedure

For iodimetric determination, a known quantity of sulphide, sulphite or thiosulphate was taken in an Erlenmeyer



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EXPERIMENTAL

Reagents

Thallic oxide is added gradually to heated ~5*M* perchloric or sulphuric acid until no more will dissolve. The solution is left overnight and then filtered. Alkali is added to the filtrate to precipitate thallic hydroxide, which is filtered off, washed, and dissolved in the appropriate acid. It is necessary to maintain about 0·5 *M* acid concentration in the reaction mixtures and hence the acidity of the thallium(III) solutions is also determined by titration with caustic soda solution to the phenolphthalein end-point; it is necessary to add potassium bromide to complex thallium(III) to check its interference in the acid–base titration.

Solutions of sodium sulphide, sodium sulphite and sodium thiosulphate were prepared in doubly distilled water and standardized against an iodine solution. A 0·1% aqueous solution of indigo carmine was prepared.

Procedure

For iodimetric determination, a known quantity of sulphide, sulphite or thiosulphate was taken in an Erlenmeyer flask and rendered about 0·5 M in acid with perchloric or sulphuric acid. For sulphide determination the acid concentration should not be less than 0·5M. Then 5 ml of 0·05M potassium iodide and some starch solution were added, and the solution titrated with thallium(III) solution with vigorous swirling. The titrant was added dropwise at intervals of 10–15 sec near the end-point.

In the direct determination using indigo carmine indicator, the end-point was marked by a colour change from blue to light green. Vigorous shaking is required in this case too. The end-point can be made sharper by the use of cobalt(II) sulphate along with the indicator. The colour change is then from blue to pink.

Results are given in Tables 1, 2 and 3.

Limitations

The method failed for amounts of sulphide larger than 10 mg, probably because hydrogen sulphide is formed in acid solutions and part of it escapes to the atmosphere. Cobalt(II) sulphate was not used in the case of sulphite because the colour of the indicator disappears within 2–5 min in its presence. Since sulphite solutions are known to decompose, the determinations were carried out also with solutions stabilized[12–15] by glycerol, sucrose and ethanol. The results were similar to those obtained without stabilization.

Determination of sulphide, sulphite and thiosulphate in admixture

Kurtenacker and Wollak[16] have carried out an iodimetric determination of the three in a mixture and the same method can be applied here, with thallium(III) solution substituted for iodine solution.Both iodimetric and indigo carmine methods are applicable for the mixtures. The results are given in Table 4.

Table 1. Determination of sulphide with thallium(III)

Iodimetric method Taken, *mg*	 Found, *mg*	Indigo carmine method Taken, *mg*	 Found, *mg*
2·45	2·43	2·45	2·44
3·25	3·22	3·25	3·21
4·35	4·31	4·35	4·34
6·55	6·51	6·55	6·55
8·42	8·35	8·42	8·41
9·25	9·21	9·25	9·23

Table 2. Determination of sulphite with thallium(III)

Iodimetric method Taken, *mg*	 Found, *mg*	Indigo carmine method Taken, *mg*	 Found, *mg*
0·65	0·65	1·26	1·28
1·26	1·27	6·30	6·31
2·50	2·45	7·55	7·52
2·90	2·92	12·50	12·51
3·50	3·51	17·55	17·53
4·85	4·90	25·35	25·32
5·45	5·42	31·50	31·55
7·60	7·45	44·20	44·30

Table 3. Determination of thiosulphate with thallium(III)

Iodimetric method Taken, *mg*	 Found, *mg*	Indigo carmine method Taken, *mg*	 Found, *mg*
1·25	1·25	2·95	2·95
2·50	2·51	7·45	7·46
3·75	3·76	9·95	9·92
6·20	6·22	12·40	12·45
8·75	8·77	14·85	14·84
9·35	9·37	22·35	22·37
10·55	10·58	24·85	24·90

Table 4. Determination of sulphide, sulphite and thiosulphate with thallium(III)

Taken, *mg* sulphide	 sulphite	 thiosulphate	Found, *mg* sulphide	 sulphite	 thiosulphate
1·25	2·52	2·48	1·22	2·50	2·44
1·55	2·85	3·72	1·51	2·82	3·69
2·55	3·45	6·21	2·52	3·41	6·20
3·15	4·75	2·25	3·05	4·54	2·21
3·75	5·40	3·25	3·68	5·37	3·22
4·15	7·55	8·67	4·10	7·51	8·56

DISCUSSION

The results of Tables 1, 2 and 3 are reasonable, the error being generally $< 1\%$. The errors are larger in the case of mixtures (Table 4), obviously because the determinations involve two operations, precipitation with $ZnCO_3$ and complexing with formadehyde.

The reactions of thallium(III) with sulphide, sulphite and thiosulphate are very fast in acid medium, that with sulphide being

$$\mathrm{Tl(III)} + \mathrm{H_2S} \rightarrow \mathrm{Tl(I)} + 2\mathrm{H}^+ + \mathrm{S}$$

The reaction of thallium(III) with iodide is still faster and the iodine so liberated reacts with sulphide, sulphite or thiosulphate, yielding iodide, and thus iodide acts as a catalyst through the operation of the I^0/I^- cycle. Although iodide may be regarded as a catalyst, it is not effective at lower concentrations because thallous iodide is precipitated and thus iodide is gradually removed from the solution during the titration. This thallous iodide adsorbs iodine, forming[11] $TlI.I_2$ and the bound iodine can be titrated only with difficulty and hence vigorous swirling is necessary.

Interferences

Mn^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} do not interfere in the iodimetric method, but Co^{2+} and Ni^{2+} interfere in the indicator method. Cu^{2+}, Fe^{3+}, As(III), As(V), Sb(III) and Sb(V) interfere in both the iodimetric and the indicator methods. Cl^-, Br^-, SO_4^{2-} and NO_3^- do not interfere.

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Summary—Sulphide, sulphite and thiosulphate can be determined separately or in admixture, with thallic perchlorate or sulphate in acid medium. A sample solution is rendered ~0·5*M* in acid, 5 ml of 0·05*M* KI are added and the solution is titrated to a starch end-point with thallium(III) solution. In another method an acid sample solution is titrated with thallium(III) or iodine solution in the presence of indigo carmine indicator. The end-point is improved in the presence of Co(II).

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DETERMINATION OF AZO COMPOUNDS WITH *N*-BROMOSUCCINIMIDE IN ACETIC ACID MEDIUM

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(*Received* 10 *April* 1975. *Revised* 20 *September* 1975. *Accepted* 7 *October* 1975)

Azo compounds have been determined quantitatively with reducing agents, *e.g.*, chromium(II),[1] tin(II),[2] titanium(III),[3] but these reagents readily undergo aerial oxidation, and the steps needed to prevent this are cumbersome. The reduction processes are slow at normal temperature and heating is required to complete the reaction. This paper describes the study of the reaction of *N*-bromosuccinimide with azo compounds and its analytical application to their determination. A 2–10 mg sample is reacted with a measured excessive volume of *N*-bromosuccinimide at room temperature and the excess of reagent is back-titrated iodometrically, The results generally show ±1% maximum deviation from the theoretical value.

STOICHIOMETRIC STUDY

The reaction of chrysoidine with *N*-bromosuccinimide has been studied as a representative reaction. Different known quantities of chrysoidine were reacted with excess of *N*-bromosuccinimide and the stoichiometry was calculated from the amount of *N*-bromosuccinimide consumed, and found to be 1:2 with respect to chrysoidine and *N*-bromosuccinimide.

A similar procedure has been followed for determination of the stoichiometry of reaction of other compounds with *N*-bromosuccinimide (Table 1).

The reaction mixtures were analysed for the end-products after the reaction was over. Succinimide has been isolated from the reaction mixture and identified from its melting point and mixed melting point. Different bromo-derivatives have also been isolated and similarly identified.

EXPERIMENTAL

Reagents

N-*Bromosuccinimide solution*, ca. 0·02*M*. *N*-Bromosuccinimide (0·3560 g) was dissolved in the minimum amount of lukewarm water and the solution diluted to the mark with cold distilled water in a 100-ml volumetric flask and standardized iodometrically.[4] The solution was prepared fresh before use.

Sample solutions. Stock solution of each sample (re-crystallized if necessary) was prepared by dissolving an accurately weighed amount in 15 ml of glacial acetic acid, except for the sodium salts of Congo Red and Methyl Orange, which were dissolved in water. The solutions were made up to volume with water in 100-ml volumetric flasks. Portions of the stock solution to give 2–10 mg of sample were used for each determination.

Potassium iodide solution, 15%.

Starch solution, 1%.

Sodium thiosulphate solution, ca. 0·02*M*. Standardized with a standard solution of copper sulphate.

Table 1. Stoichiometric ratio of azo compounds and *N*-bromosuccinimide

Compound	Observed molar ratio		
Chrysoidine G	2·004	2·031	1·988
Butter Yellow	2·004	1·986	1·992
Congo Red	2·014	2·014	1·973
Chrysamine G	4·027	3·983	3·999
Methyl Orange	5·001	4·985	5·018
Methyl Red	5·001	4·984	4·987

Procedure

A portion of solution containing 2–10 mg of the sample was placed in a 100-ml iodine flask, 5 ml of glacial acetic acid and 10 ml of *N*-bromosuccinimide solution were added, the flask was stoppered, and the reaction was allowed to proceed for 10 min at room temperature. After the reaction was complete, 5 ml of potassium iodide solution were added and the liberated iodine was titrated with standard sodium thiosulphate solution, with starch as indicator. A blank experiment was run under identical experimental conditions.

The amount of azo compound was calculated by means of the expression

Amount of azo compound

$$= [(B - A) \times M \times \text{M.W.}]/[2000n]$$

where B = ml of thiosulphate (0·02*M*) used for blank, A = ml of thiosulphate (0·02*M*) used for sample, M.W. = molecular weight of the sample, M = molarity of thiosulphate solution, n = stoichiometric ratio of *N*-bromosuccinimide to sample compound.

RESULTS AND DISCUSSION

Chrysoidine G was chosen as the model compound and was found to react quantitatively with *N*-bromosuccinimide (error generally < 0·5%). The method was also applied to Butter Yellow, Congo Red, Chrysamine G, Methyl Orange and Methyl Red. The error is generally <1%.

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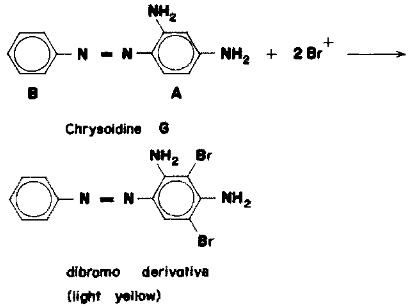
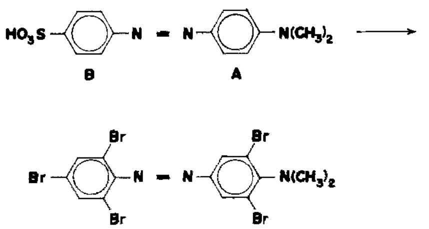


Hypotheses can also be advanced to account for the stoichiometry observed for the other reactions. For Methyl Orange, for example, the bromination proposed is



The *o*- and *p*-positions of nucleus A are activated by the $-N(CH_3)_2$ group and 2 atoms of bromine substitute at the free *ortho* positions. The nucleus B bears the electron-attracting $-SO_3H$ group and the electron density at positions *meta* to the $-SO_3H$ group increases, which facilitates the substitution at these two positions. Finally the $-SO_3H$ group is replaced by bromine. The pentabromo-derivative of Methyl Orange has been isolated and its structure identified and confirmed by infrared and NMR spectra.

Azo compounds are coloured but no difficulty has been experienced in detecting the end-point. However, it has been observed that azobenzene is not brominated with *N*-bromosuccinimide under the experimental conditions.

Because of the non-selectivity of the reagent, hydrazine, unsaturated compounds, amines, phenols, ascorbic acid, other azo compounds, *etc.* must be absent.

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POTENTIOMETRIC DETERMINATION OF n-BUTYL-1-BIGUANIDE WITH A LIQUID-STATE Cu^{2+}-SENSITIVE ELECTRODE

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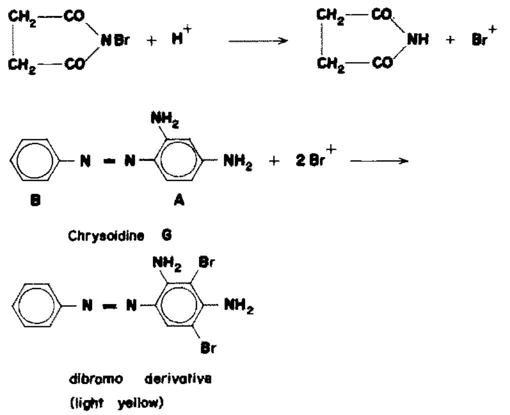
In the present paper we describe a new method for the determination of alkyl-1-biguanide, based on the use of a liquid-state Cu^{2+}-sensitive electrode. The construction and characteristics of the electrode have been described previously.[1–3] The method is based on the formation of complexes of the type $[Cu(Big)_2]X_2$ by the reaction between copper(II) ammine complexes with biguanides.[4]

There are a number of ways in which this method can be used for the determination of biguanides:

(*a*) use of an excess of copper(II) ammine in order to precipitate $[Cu(Big)_2]X_2$ and subsequent determination of the excess of Cu(II) in solution by potentiometric titration in presence of the Cu^{2+}-sensitive electrode;

(*b*) transformation of the biguanide salt into the free



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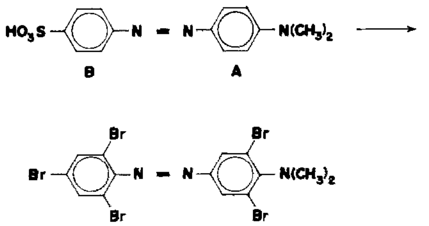

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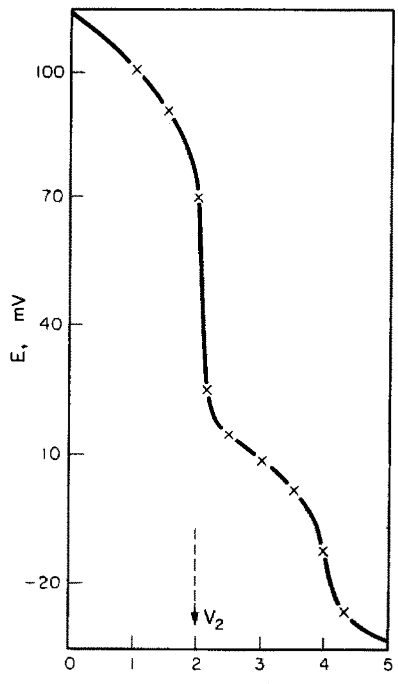

Fig. 1. Potentiometric titration curve of the ammoniacal mixture $[Cu(Big)_2]SO_4 + CuSO_4$ method (*a*).

base, which is then determined by direct potentiometric titration with an aqueous solution of $CuSO_4$, and use of the Cu^{2+}-sensitive electrode;

(*c*) separation of the water-insoluble complex and dissolution of a precisely known quantity in a suitable solvent and subsequent determination of Cu^{2+} in the solution by a convenient method.

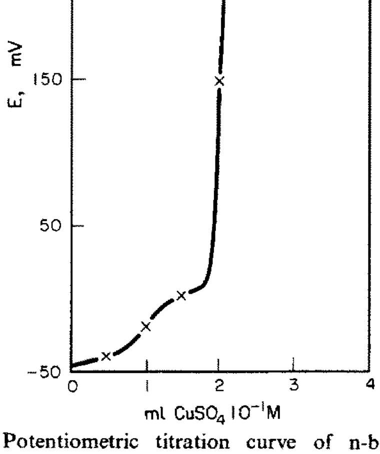

Fig. 2. Potentiometric titration curve of n-butyl-1-biguanide, method (*b*)

Table 1. Potentiometric determination of n-butyl-1-biguanide monohydrochloride

Taken, *mg*	Found, *mg*	Error, %
31·23	31·4	0·4
52·06	51·7	0·7
62·47	62·3	0·3
72·88	72·5	0·5
83·29	84·0	0·8
93·70	93·7	0·0
104·11	104·0	0·1

Methods (*b*) and (*c*) are more lengthy because a very accurate conversion of the biguanide salt into free base is needed. Also the filtration and drying are time-consuming and succeptible to errors.

In method (*a*) the $[Cu(Big)_2]SO_4$ complex is formed by adding an excess of ammoniacal $CuSO_4$ solution (with known titre) to an aqueous solution containing 30–100 mg of biguanide hydrochloride. The excess of Cu^{2+} is then determined by potentiometric titration with 0·1*M* EDTA, using the liquid-state Cu^{2+}-sensitive electrode.

We have studied the hydrochloride of n-butyl-1-biguanide which is the active component of the drug "Buformin". On the titration curve in Fig. 1 two potential jumps can be seen. They correspond to the excess of $CuSO_4$ and the complexed copper respectively. The quantity of n-butyl-l-biguanide monohydrochloride is given by

$$\text{n-butyl-1-biguanide.HCl} = 0{\cdot}03874(V_1f_1—V_2f_2)\text{g}$$

where V_1 is the total volume of 0·1*M* $CuSO_4$ solution added to precipitate $[Cu(Big)_2]SO_4$, f_1 is the factor of this solution, V_2 is the volume of 0·1*M* EDTA corresponding to the first potential jump (Fig. 1) and f_2 is the factor of this solution.

The application of the second method implies the quantitative conversion of n-butyl-1-biguanide hydrochloride into free base, by treatment with 0·1*M* NaOH of known titre; the n-butyl-1-biguanide is titrated potentiometrically with 0·1*M* $CuSO_4$. The potentiometric titration curve (Fig. 2) also shows two potential jumps.

The first of these is much smaller than the second, and corresponds to the formation of the 1: 1 soluble complex. The second jump ($\simeq$ 250 mV) is due to the formation of the insoluble complex $[Cu(Big)_2]SO_4$; 1 ml of 0·1*M* $CuSO_4$ corresponds to 0·03145 g of n-butyl-1-biguanide.

Tables 1 and 2 give the results of determinations by methods (*a*) and (b) respectively. The use of method (*a*) would have the advantage that the residual impurities remaining from the synthesis of the biguanide, such as dicyandiamide, n-butylguanidine, amines, *etc.* do not interfere in the determination.

The selectivity of the method has made possible the use of the electrode for the control of the synthesis of n-butyl-1-biguanide by following the concentration of the biguanide formed, directly in the reaction medium.

Table 2. Potentiometric determination of n-butyl-1-biguanide (free base)

Taken, *mg*	Found, *mg*	Error %
25·36	25·5	0·5
34·59	34·3	0·9
42·26	42·5	0·6
50·71	50·6	0·2
59·16	59·1	0·1
76·07	75·5	0·8

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Summary—Alkyl-1-biguanides are determined by titration with copper(II), or excess of copper(II) is added and the surplus determined by titration with EDTA, a liquid-state copper-sensitive electrode being used in both cases for potentiometric detection of the end-point.

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SPECTROPHOTOMETRIC DETERMINATION OF IMINODIACETIC ACID IN PRESENCE OF PRIMARY AMINO-ACIDS

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Several spectrophotometric and other methods[1–3] have been reported for the determination of amino-acids. None of them is, however, applicable to iminodiacetic acid, IDA, in presence of glycine and other primary amino-acids. The method proposed here is based on complex formation between IDA and ferric ions. Glycine also complexes ferric ion, but its interference can be eliminated by proper choice of pH and wavelength. Other primary amino-acids do not interfere.

EXPERIMENTAL

Reagents

Ferric alum was reagent grade. IDA was recrystallized from doubly distilled water. Fe(III)–IDA was prepared by mixing the requisite amounts of ferric alum and IDA, precipitated with alcohol and then recrystallized twice from doubly distilled water.

Procedure

To an aliquot of an unknown IDA solution, add a measured amount of ferric alum solution and dilute the solution to give a ferric alum concentration of $\sim 2{\cdot}5$–$3{\cdot}0 \times 10^{-4}M$, and an IDA concentration of ~ 1–$9 \times 10^{-5}M$ at pH 3·0–3·5. Measure the absorbance at 250 and 300 nm. The concentrations of iron(III) and IDA are chosen to give absorbances in the range 0·5–0·7.

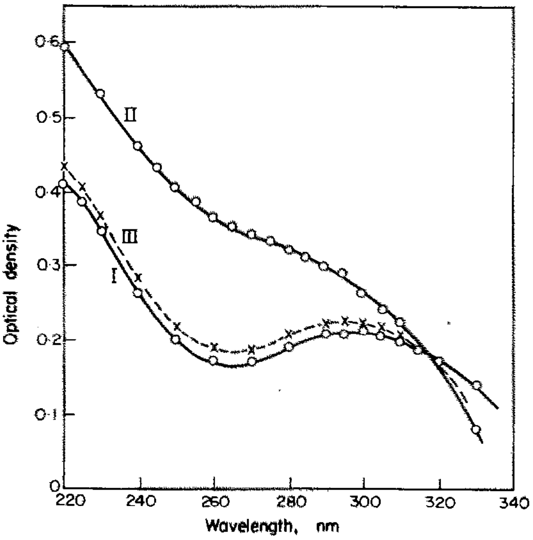

Fig. 1. Absorption spectra of (I), ferric alum; (II), (1:1) Fe(III)–IDA; and (III), (1:3) Fe(III)–GLY. pH = 3·0–3·5; $[Fe^{+3}] = 1 \times 10^{-4}M$.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of ferric alum, Fe(III)–IDA and Fe(III)–glycine complexes at pH 3·0–3·5. The ferric alum spectrum is characterized by a maximum at 300 nm and an identical absorbance at 250 nm. Fe(III)–glycine (1:3) also gives a similar, slightly more intense absorption spectrum. The spectrum of the Fe(III)–IDA (1:1) complex has no maximum but the absorbance at 250 nm is much higher than that at 300 nm.

All three systems obey Beer's law at the two selected wavelengths. Hence, if ϵ_1 and ϵ_2 are the molar absorptivities of Fe(III)–IDA at 250 and 300 nm respectively and A_{250} and A_{300} are the absorbances at 250 and 300 nm,

$$A_{250} - A_{300} = \Delta A = (\epsilon_1 - \epsilon_2)[\text{Fe–IDA}] = K[\text{IDA}] \qquad (1)$$

Thus a plot of ΔA *vs.* [IDA] serves as a calibration curve. K was found to be $1{\cdot}61 \times 10^3$ l. mole^{-1}. cm^{-1}. An IDA concentration as low as $\sim 10^{-5}M$ can be determined with a fair degree of accuracy.

The pH has an effect in the system, being optimum over the range 3·0–3·5. At pH greater than 3·5, the excess of iron(III) hydrolyses and at pH less than 3·0, ΔA for Fe(III)–IDA diminishes slightly. The accuracy of the method is further dependent upon the correct selection of the shorter wavelength such that there is automatic correction for the

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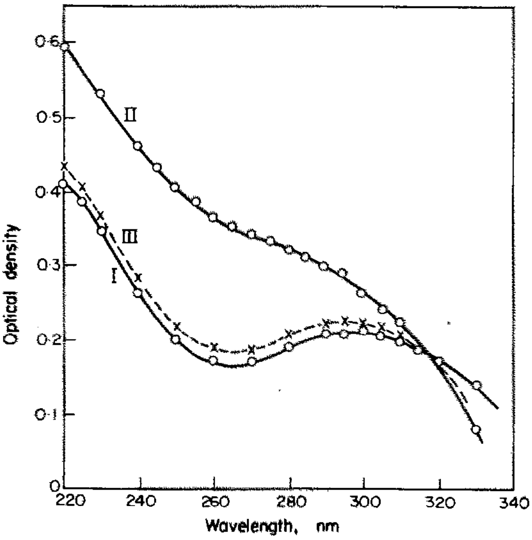

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Procedure

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All three systems obey Beer's law at the two selected wavelengths. Hence, if ϵ_1 and ϵ_2 are the molar absorptivities of Fe(III)–IDA at 250 and 300 nm respectively and A_{250} and A_{300} are the absorbances at 250 and 300 nm,

$$\begin{aligned} A_{250} - A_{300} &= \Delta A = (\epsilon_1 - \epsilon_2)[\text{Fe–IDA}] \qquad (1) \\ &= K\,[\text{IDA}]. \end{aligned}$$

Thus a plot of ΔA *vs.* [IDA] serves as a calibration curve. K was found to be $1\cdot61 \times 10^3$ l. mole^{-1}, cm^{-1}. An IDA concentration as low as $\sim 10^{-5}M$ can be determined with a fair degree of accuracy.

The pH has an effect in the system, being optimum over the range 3·0–3·5. At pH greater than 3·5, the excess of iron(III) hydrolyses and at pH less than 3·0, ΔA for Fe(III)–IDA diminishes slightly. The accuracy of the method is further dependent upon the correct selection of the shorter wavelength such that there is automatic correction for the

Table 1. Effects of primary amino-acids

Amino-acid added	Molar ratio, amino-acid:IDA	IDA taken, $10^{-6}M$	IDA found, $10^{-6}M$	Error, %
Glycine	1:4	80·0	80·0	±0·0
	1:2	80·0	80·5	+0·6
	3:4	80·0	80·6	+0·8
	1:1	80·0	82·0	+2·5
Alanine	1:4	80·0	81·0	+1·3
	1:2	80·0	82·0	+2·5
	3:4	80·0	80·8	+1·0
	1:1	80·0	81·0	+1·3

Table 2. Effects of various metal ions

Ion added	Molar ratio, metal ion:IDA	IDA taken, $10^{-6}M$	IDA found, $10^{-6}M$	Error, %
Ca(II)	1:3	90·0	90·0	±0·0
Ca(II)	1:2	80·0	82·0	+2·5
Ba(II)	1:3	90·0	92·0	+2·2
Ba(II)	1:2	80·0	81·0	+1·3
Cu(II)	1:3	90·0	92·0	+2·2
Cu(II)	1:2	80·0	82·0	+2·5
Co(II)	1:3	90·0	87·0	−3·6
Co(II)	1:2	80·0	82·0	+2·5
Ni(II)	1:3	90·0	88·0	−2·2
Ni(II)	1:2	80·0	81·0	+1·3
Cr(III)	1:3	90·0	91·5	+1·7
Cr(III)	1:2	80·0	80·5	+0·6

absorbance of the excess of iron(III) and of the iron(III)–glycine complex. This shorter wavelength was found to lie in the range 250 ± 2 nm. It should therefore be separately determined for each experimental arrangement.

Table 1 shows the effect of primary amino-acids, *e.g.*, glycine and alanine. The amino-acid:IDA mole ratio was varied from 1:4 to 1:1. It is evident from the results that the method is very promising in these cases too. Probably the metal complexes of the primary amino-acids are not stable at pH 3–3·5 or else ΔA then is negligible.

It is sometimes necessary to determine IDA in the presence of metal ions, so the effect of some chosen metal ions was also studied. Metal ion complexes of IDA which are not stable at the pH range used or from which the metal ion can be easily displaced by ferric ion, do not interfere. Table 2 shows some typical results; it is evident that the metal ions under study do not interfere seriously.

It can be claimed that the method is very simple, reproducible and is easily adaptable.

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Summary—Iminodiacetic acid down to $10^{-5}M$ is determined spectrophotometrically in the presence of primary amino-acids by complex-formation with iron(III) at pH 3·0–3·5. The method is simple, fairly accurate, rapid and free from interference from most common metal ions.

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ANALYTICAL CHEMISTRY OF UNUSUAL OXIDATION STATES: THE POLAROGRAPHY OF VANADIUM(IV) IN CYANIDE MEDIUM

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This paper, which reports the results of a continued investigation of the analytical chemistry of some unusual oxidation states,[1] is concerned with the polarography of vanadium(IV) in cyanide medium. Irreversible oxidative and reductive waves have been reported for vanadium(IV) in strongly alkaline medium.[2–4] Lingane and Meites[5] studied the polarography of several oxidation states of vanadium in a number of supporting electrolytes, and at different pH's. Vanadium(III) was found to give two rather poorly shaped waves with $E_{\frac{1}{2}}$ at −1·17 and −1·77 V *vs.* SCE, being reduced to an unknown species of vanadium(II). There are no previous reports of the polarography of vanadium(IV) in cyanide medium.

EXPERIMENTAL

Apparatus

A Sargent Model XVI polarograph was used together with a dropping mercury electrode (DME) and a saturated calomel electrode (SCE) in the measurement cell. The characteristics of the capillary were: $m = 2{\cdot}83$ mg/sec, $t = 3{\cdot}2$ sec, at 25° in 1*M* potassium cyanide with ionic strength adjusted to 3·0 by addition of sodium sulphate, and with height of column = 58 cm. Nitrogen was bubbled first through a solution of vanadium(II) to remove oxygen, then through a phosphate-buffered cyanide solution to saturate it with hydrogen cyanide in equilibrium with that pH, then through the solution under investigation.

Procedure

A stock solution of vanadium(IV) was prepared by dissolving $VOSO_4.5H_2O$ in 0·09*N* sulphuric acid. A suitable volume of this was taken, potassium cyanide was added, first to neutralize the acidity and then to give the desired cyanide concentration for the experiment. Sodium sulphate was added to adjust the ionic strength to 3·0 (or other value as required) and a drop of 1% gelatin solution to suppress a small maximum. Nitrogen was bubbled through the solution, and after 15–20 min the polarogram was recorded, with the polarograph and a potentiometer.

RESULTS

Effect of the vanadium concentration

Over the range 8×10^{-5}–$1{\cdot}5 \times 10^{-2}M$ for vanadium, the wave-height is strictly proportional to concentration, with a slope of 7·36 μA.l.mmole^{-1} (standard deviation 4%). The temperature coefficient is about 1%/deg. The proportionality to the square-root of the height of the mercury column confirmed that the electrode process was diffusion-controlled.

These results and their reproducibility, together with the good development of the waves and their broad diffusion range, allow us to propose a new polarographic method for the determination of vanadium, the recommended procedure being that used in this paper. The precision and accuracy are within the usual limits for classical polarography, and minimal for 10^{-5}–$10^{-2}M$ vanadium in >0·5*M* cyanide medium at 10–50°, the polarography being performed within an hour of the addition of cyanide. It is necessary to work at constant ionic strength.

An experiment involving coulometric reduction of the vanadium with repeated scanning of the polarograms between electrolyses revealed that two electrons were involved in the reduction. From this figure, and the capillary parameters already mentioned, the diffusion constant *D* in the Ilkovič equation was calculated to be $6{\cdot}2 \times 10^{-6}$ cm^2/sec.

Effect of the cyanide concentration

A $2 \times 10^{-3}M$ vanadium(IV) solution gave a wave-height increasing steadily from 14 μA in 0·5*M* cyanide to 15 μA in 1·5*M* cyanide, thereafter remaining constant (Table 1). In 0·2*M* cyanide the polarogram was ill-defined, and in 0·4*M* the wave-height was 11 μA. As the pH is quite high (10–11) it is likely that the vanadium(IV) is partially oxidized before the nitrogen is passed, when there is not much cyanide present, and in some of these solutions a turbidity suggested that the vanadium was precipitating.

The half-wave potential

Logarithmic plots of log $i/(i_d\text{-}i)$ against potential gave straight lines with slopes of about 90 mV, and $E_{\frac{1}{2}}$ values varying from −1·15 V in 0·5*M* cyanide to −1·10 V in 2·86*M* cyanide. Experimental values are tabulated in Table 2. The slopes suggested that the reduction was irreversible. Matsuda and Ayabe have deduced a general expression for the current–voltage curve for all reactions, reversible and irreversible,[6] and have shown how it can be used for the analysis of polarograms.[7] Over most of the wave, their expression simplifies to

$$E = (E_{\frac{1}{2}})_{\mathrm{irr}} - 2{\cdot}3\,\frac{RT}{\alpha nF}.\log\frac{i}{i_1 - i} \tag{1}$$

The factor α is termed the transfer coefficient for an irreversible electrode reaction. The variation of $(E_{\frac{1}{2}})_{\mathrm{irr}}$ with ligand concentration is given by

$$(E_{\frac{1}{2}})_{\mathrm{irr}} = 2{\cdot}3\,\frac{RT}{\alpha nF}\left[\log\frac{(k_f^0)f_N}{D_N} + \tfrac{1}{2}\log t - 0{\cdot}053 - \log\left(\frac{i_1}{i_d}\right) - (N - p)\log(f_X C_X)\right] \tag{2}$$

where (k_f^0) is the rate constant for the slow reaction at the electrode, *N* is the number of ligands bound to the

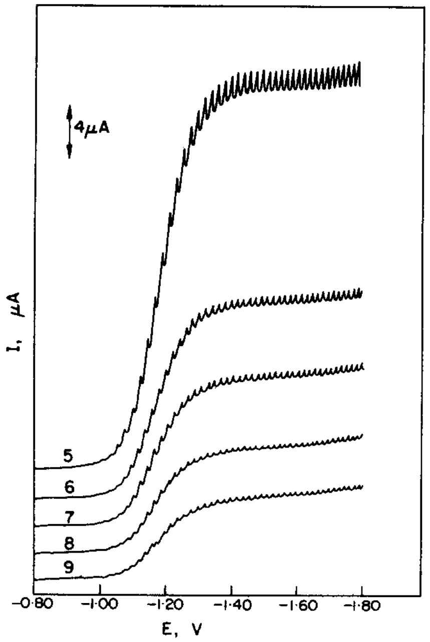

Fig. 1. Polarograms of $V^{(IV)}$ in cyanide 1·0*M* temperature 25°C, gelatine 0·05%, $V^{(IV)}$ concentration: (5)—$4 \times 10^{-3}M$; (6)—$2 \times 10^{-3}M$; (7)—$1{\cdot}5 \times 10^{-3}M$; (8)—$10^{-3}M$; (9)—$0{\cdot}8 \times 10^{-3}M$.

central ion in the species predominating in the solution and p the number in the species undergoing reduction after the dissociation step, f_N and D_N are the activity coefficient and diffusion coefficient respectively of the species MX_N and f_X and C_X are the activity coefficient and bulk concentration of the ligand X. The drop-time is denoted by t. As the limiting current is strictly diffusion-controlled in this case the term i_l/i_d becomes unity and its logarithm zero. From equation (1), assuming $n = 2$, we can solve to find α, which in this case is around 0·3 (see Table 2).

By combining equations (1) and (2) we get the simple relationship

$$N - p = \frac{\Delta \log \dfrac{i}{i_d - i}}{\Delta \log(f_X C_X)} \qquad (3)$$

Values for $(N - p)$ obtained by using this equation are also presented in Table 2. The considerable variation in these values makes it hard to come to any conclusion regarding the species involved in the reactions, though the figures do suggest that one cyanide ion is added to the complex species when reduction takes place in about 2*M* potassium cyanide solution.

Table 1. Influence of CN^- concentration on I_d

[KCN], *M*	I_d μA
0·20	5·8*
0·40	11·0
0·50	14·1
0·75	14·0
1·00	14·6
1·25	14·4
1·50	14·9
1·75	15·2
2·00	15·0
2·50	15·1
2·86	15·0

* Ill defined polarogram.

Table 2. Kinetic characteristics of the polarographic reduction of V(IV) in cyanide medium

$[CN^-]$, *M*	$\log f_x$	$-(E_{\frac{1}{2}})_{irr}$ *mV*	α	$(N - p)$*
0·50	−0·228	1149	0·31	
0·75	−0·228	1140	0·31	−0·48
1·00	−0·228	1135	0·30	−0·28
1·25	−0·228	1132	0·31	−0·23
1·50	−0·228	1130	0·29	−0·52
1·75	−0·228	1121	0·29	−0·85
2·00	−0·228	1115	0·31	−1·33
2·50	−0·228	1106	0·31	−0·86
2·86	−0·228	1100	0·31	−1·07

* Arithmetical mean of three measurements.

The rate constant k_f^0 for the reduction step can be found from equation (2), and takes the value $10^{-14{\cdot}2}$ cm/sec for 2*M* cyanide solution.

Two simple experiments were carried out to determine the formal potential $(E^0)_B$ for the V(IV)/V(II) system in cyanide solution. In the first, the potential was measured after mixing equal volumes of equimolar vanadium(II) and vanadium(IV) solutions in the presence of 2*M* cyanide, and in the second, vanadium(II) in 2*M* cyanide solution was titrated potentiometrically with hexacyanoferrate(III) solution. In both experiments, the formal potential was found to be −0·70 V *vs.* SCE. The difference between this and the $(E_{\frac{1}{2}})_{irr}$ of −1·1 V certainly indicates the highly irreversible nature of this reduction.

The rate constant $(k_O)_B$ of the overall process is given by

$$(K_G)_B = (k_f^0)_B \exp\left[-\frac{\alpha n F}{RT}(E^0)_B\right]$$

and has the value $10^{-6{\cdot}87}$ cm/sec, positive proof that the reduction is irreversible.

The literature on cyanide complexes of vanadium is not very extensive, and what there is contains many contradictions. Virtually all the facts relate to solid species, usually produced by precipitation from non-aqueous media, and statements concerning ionic species are largely hypothesis. So much faith is placed in spectroscopic observation and prediction, in spite of lack of confirmation by analytical data[8] that it has taken X-ray structure analysis in one case[9] to prove that the complex cyanide of vanadium(III) is in fact $V(CN)_7^{4-}$. Solid potassium hexacyanovanadate(II) $K_4V(CN)_6$ is well characterized[10] but reacts with water to give a brown precipitate. The heat of formation of a soluble vanadium(II) cyanide complex has been reported[11] but without any proof of the constitution of the species.

Rivenq found that a solution of vanadium(IV) titrated with cyanide gave a precipitate, with a cyanide to vanadium ratio of 2:1, which subsequently dissolved in an excess of cyanide.[12] He suggested the formula $VO(CN)_6^{4-}$ for this species, but this does not lie up with the formula $Cs_3VO(CN)_5$ reported for a blue crystalline salt described by Bennett and Nicholls.[13]

If the $N - p$ value of −1 means anything, it would fit the requirements for the reaction

$$VO(CN)_5^{3-} + 2e + H^+ \rightarrow V(CN)_6^{4-} + OH^-$$

between hypothetical ions predicted on the basis of two known solid compounds. A reduction of an oxo-species to a simple metal complex would be expected to be irreversible. But there is nothing to suggest why reduction should be to vanadium(II) instead of to vanadium(III).

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Summary—The polarographic reduction wave for vanadium(IV) in cyanide medium has been studied and the effect of cyanide concentration on the diffusion current and half-wave potential has been interpreted, using the theory of irreversible but diffusion-controlled reduction. Coulometric experiments suggest a two-electron transfer, and the shift of half-wave potential corresponds to the addition of one cyanide ion during the reduction step. The proportionality of wave-height to vanadium concentration in the used alkaline cyanide medium indicates a possible analytical unity. The half-wave potential is about −1·1 V.

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A REFINED CHEMICAL ANALYSIS OF $SnF_2.AsF_5$

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Studies of the systems MF_2–AsF_5–HF, where M is any bivalent metal, carried out in this laboratory, have resulted in the isolation of a number of compounds of the type $MF_2.AsF_5$. Compounds of this particular composition might be discussed either in terms of ionic formulations such as $M^{2+}F^-AsF_6^-$, $MF^+AsF_6^-$ or in terms of covalent, fluorine-bridged structures $FMF.AsF_5$. The true nature of the compounds can only ultimately be determined by a crystal structure investigation but so far, it has not been possible to isolate crystals suitable for crystallographic work.

However, by chemical analysis simple direct evidence for the presence of free fluoride on the one hand and hexafluoroarsenate on the other can be obtained, since both can be determined separately. Known methods of analysis are not directly applicable to this problem and we describe here the modifications made to the methods for chemical analysis of $SnF_2.AsF_5$, which was taken as the first test compound since on the basis of its vibrational spectra it was formulated as a salt of the fluorine-bridged polycation $(Sn–F)_n^{n+}$ with the AsF_6^- anion,[2] and more recently as $[Sn–F]^+[AsF_6]^-$.[1]

EXPERIMENTAL

Reagents and apparatus

Tetraphenylarsonium chloride solution, 6·7% *w/v*.
Cupferron solution, 5%.
Sodium hydroxide solution.
Ammonia solution.
Sulphuric acid, 75% *v/v*.
Thorium nitrate standard solution, 0·0125*M*.
Methylthymol Blue, 0·2% *solution in* 75% *methanol.*
TISAB buffer.
CBS buffer.

All reagents and standard solutions were of analytical-reagent grade. The fluoride content was also determined with a fluoride ion-selective electrode (Orion No. 94–09) in conjunction with a reference electrode (Orion No. 90–01) and digital pH-meter (Orion Model 801). The analytical methods employed were all checked against official standards.

Procedures

$SnF_2.AsF_5$ is a very sensitive material and rapidly hydrolyses in moist air. Samples were therefore weighed into air-tight Teflon containers in a dry-box. Before the hydrolysis in alkaline solution these were cooled to liquid-nitrogen temperature in order to moderate the violent reaction with water.

Total fluorine in the solution of the hydrolysed sample was determined by a modified distillation method.[3–5] The sample was decomposed by 75% sulphuric acid in the presence of silica sand within 6 hr in a distillation apparatus which permitted recycling of water vapour. The distillate containing sodium hexafluorosilicate was titrated with 0·0125*M* thorium nitrate in the presence of Methylthymol Blue indicator. The results obtained in several parallel determinations were within the permitted experimental error (see Table 1).

to a simple metal complex would be expected to be irreversible. But there is nothing to suggest why reduction should be to vanadium(II) instead of to vanadium(III).

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Summary—The polarographic reduction wave for vanadium(IV) in cyanide medium has been studied and the effect of cyanide concentration on the diffusion current and half-wave potential has been interpreted, using the theory of irreversible but diffusion-controlled reduction. Coulometric experiments suggest a two-electron transfer, and the shift of half-wave potential corresponds to the addition of one cyanide ion during the reduction step. The proportionality of wave-height to vanadium concentration in the used alkaline cyanide medium indicates a possible analytical unity. The half-wave potential is about $-1{\cdot}1$ V.

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A REFINED CHEMICAL ANALYSIS OF $SnF_2.AsF_5$

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Studies of the systems MF_2–AsF_5–HF, where M is any bivalent metal, carried out in this laboratory, have resulted in the isolation of a number of compounds of the type $MF_2.AsF_5$. Compounds of this particular composition might be discussed either in terms of ionic formulations such as $M^{2+}F^-AsF_6^-$, $MF^+AsF_6^-$ or in terms of covalent, fluorine-bridged structures $FMF.AsF_5$. The true nature of the compounds can only ultimately be determined by a crystal structure investigation but so far, it has not been possible to isolate crystals suitable for crystallographic work.

However, by chemical analysis simple direct evidence for the presence of free fluoride on the one hand and hexafluoroarsenate on the other can be obtained, since both can be determined separately. Known methods of analysis are not directly applicable to this problem and we describe here the modifications made to the methods for chemical analysis of $SnF_2.AsF_5$, which was taken as the first test compound since on the basis of its vibrational spectra it was formulated as a salt of the fluorine-bridged polycation $(Sn{-}F)_n^{n+}$ with the AsF_6^- anion,[2] and more recently as $[Sn{-}F]^+[AsF_6]^-$.[1]

EXPERIMENTAL

Reagents and apparatus

Tetraphenylarsonium chloride solution, 6·7% *w/v*.
Cupferron solution, 5%.
Sodium hydroxide solution.
Ammonia solution.
Sulphuric acid, 75% *v/v*.
Thorium nitrate standard solution, 0·0125*M*.
Methylthymol Blue, 0·2% *solution in* 75% *methanol.*
TISAB buffer.
CBS buffer.

All reagents and standard solutions were of analytical-reagent grade. The fluoride content was also determined with a fluoride ion-selective electrode (Orion No. 94–09) in conjunction with a reference electrode (Orion No. 90–01) and digital pH-meter (Orion Model 801). The analytical methods employed were all checked against official standards.

Procedures

$SnF_2.AsF_5$ is a very sensitive material and rapidly hydrolyses in moist air. Samples were therefore weighed into air-tight Teflon containers in a dry-box. Before the hydrolysis in alkaline solution these were cooled to liquid-nitrogen temperature in order to moderate the violent reaction with water.

Total fluorine in the solution of the hydrolysed sample was determined by a modified distillation method.[3–5] The sample was decomposed by 75% sulphuric acid in the presence of silica sand within 6 hr in a distillation apparatus which permitted recycling of water vapour. The distillate containing sodium hexafluorosilicate was titrated with 0·0125*M* thorium nitrate in the presence of Methylthymol Blue indicator. The results obtained in several parallel determinations were within the permitted experimental error (see Table 1).

It was found that the distillation residue could not be used for the determination of tin or arsenic because metastannic acid precipitated out of the solution during the distillation.

On a separate sample, hydrolysed in dilute sulphuric acid, AsF_6^- was precipitated by tetraphenylarsonium chloride.[6] The results obtained, however, were too high because tin was co-precipitated under these conditions. Attempts to mask tin with many of the known agents for tin[7] were not successful.

We found, however, that tin could be masked by using a mixture of sodium citrate and EDTA at pH 5–5·5. The results obtained were checked against determinations of AsF_6^- in the filtrates obtained after tin had been precipitated by ammonia. The AsF_6^- content in samples determined either way corresponded well with calculated values for $SnFAsF_6$.

Tin was determined gravimetrically by precipitation with both ammonia and cupferron.[8] As expected, the results of this standard method agreed well with the calculated value. In order to check whether the precipitation of tin is quantitative in the presence of fluoride and hexafluoroarsenate, a standard solution containing tin, potassium hexafluoroarsenate and ammonium fluoride was made. The determinations of tin content in this solution by the methods above gave results which were within the limits of experimental error.

Since the gravimetric method is rather time-consuming a considerable effort was applied to investigation of the applicability of complexometric determination of tin.[9–12] The results were discouraging. The presence of fluoride and perhaps also of hexafluoroarsenate interfered with the titration. If fluoride was removed by fuming with sulphuric acid, either deposits of metastannic acid were formed or tin was partly lost by volatilization.

In order to determine the free fluoride ion or fluoride bound as SnF^+ species in our samples, limiting cases were first examined. A number of standard solutions of suitable concentrations were made. One was a solution of tin difluoride in which the fluoride content was determined both by the distillation method and by ion-selective electrode.[13,14] In both cases the results were comparable. However, in a solution of potassium hexafluoroarsenate the ion-selective electrode could not detect free fluoride, whereas the distillation method gave the theoretical results. The hexafluoroarsenate ion is therefore stable and does not dissociate under the conditions of the measurement. Consequently, free fluoride can be determined quite easily in the presence of the hexafluoroarsenate species.

In the solutions of $SnF_2.AsF_5$ we were able to determine free fluoride with the ion-selective electrode and total fluorine content by the distillation method. The results of the analyses are presented for comparison in Table 1.

It is concluded that, in solution, the adduct $SnF_2.AsF_5$ should be regarded as either $[Sn]^{2+}[F]^-[AsF_6]^-$ or $[SnF]^+[AsF_6]^-$. This analytical information, in conjunction with vibrational spectroscopic data for the solid[1] suggests that the latter is the more likely formulation.

Acknowledgement—The samples of $SnF_2.AsF_5$ were kindly prepared by Mrs. D. Gantar. The author is indebted to Dr. B. Frlec for useful discussion and support. This work was financed through the Boris Kidrič Foundation.

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Table 1. Comparison of the results obtained

		% F			% AsF_6			% Sn		
			Found			Found			Found	
Sample	Formulation	Calcd.	Distillation	Ion-selective electrode	Calcd.	After masking	After pptn.	Calcd.	Cupferron	Dil. ammonia
SnF_2		24·25	24·5 24·3 ± 0·2	24·6 24·8 ± 0·1				75·75	75·4 75·4 ± 0·3	74·9 75·3 ± 0·3
$KASF_6$		49·99	49·7 49·9		82·85	82·2 82·5 ± 0·4				
$SnAsF_7$	SnF_2AsF_5	40·72 (total) 11·64 (free F^-)	40·1 40·5	6·0 5·8	52·03 calcd. as AsF_5			36·34	36·0 36·1	36·1 36·3
	$SnF^+AsF_6^-$	5·82 (free F^-)			57·84	58·0 58·0	58·2 57·9 ± 0·3			
Sn^{2+} + NH_4F + $KAsF_6$		51·35 (free F^-)		51·2 51·6	82·85	82·5	82·4 82·5	52·63	52·1 52·4	52·3 52·3

Summary—Combination of analyses using an ion-selective electrode and a distillation method make it possible to determine free fluoride in the presence of AsF_6^- in an adduct such as $SnF_2.AsF_5$, thus contributing to the structural information about the compound in solution. Other methods for the total analysis of the compound are described.

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ANALYTICAL DATA

SELECTIVE PYRIMIDINETHIOLS FOR PALLADIUM(II) DETERMINATION

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and

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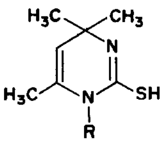
A large number of reagents have been proposed for the determination of palladium(II).[1–3] This study shows that 1-substituted-4,4,6-trimethyl-(1H,4H)-2-pyrimidinethiols (**I–VI**) are highly selective for Pd(II). In the presence of strong acids, the Pd(II) complexes are extractable into non-polar solvents without interference from large concentrations of other platinum-group metals. For simplicity and selectivity combined, the proposed method for determination of Pd(II) seems to be better than any other spectrophotometric procedure, but it does lack sensitivity.

(**I**) R = H
(**II**) R = C_2H_5
(**III**) R = n-C_4H_9
(**IV**) R = C_6H_5
(**V**) R = $C_6H_4OCH_3$(anisyl)
(**VI**) R = *p*-$C_6H_4NO_2$



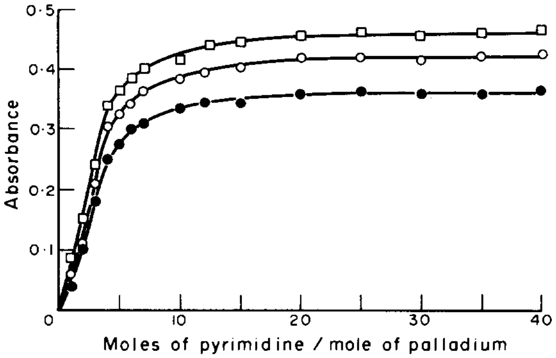


Fig. 1. Effect of excess of reagent. [Pd] $10^{-4}M$ + [Thiol] $10^{-4}M$–4·0 × $10^{-3}M$. ● Pyrimidinethiol when R = H. ○ Pyrimidinethiol when R = C_2H_5. □ Pyrimidinethiol when R = C_4H_9.

EXPERIMENTAL

Reagents

2-Pyrimidinethiols were prepared by the method of Mathes.[4] Their standard solutions (0·01M) were prepared by dissolving appropriate amounts in chloroform. Anhydrous $PdCl_2$ (Johnson Matthey) was dissolved in 1·0N hydrochloric acid and standardized gravimetrically. All other solutions were prepared with analytical grade reagents. Doubly distilled water was used throughout the work.

Spectral characteristics

Solutions of all the pyrimidinethiols except (**VI**) are virtually colourless. That of (**VI**) is light yellow. When a few drops of pyrimidinethiol solution (in any non-polar solvent such as chloroform, benzene or carbon tetrachloride) are added to acidic Pd(II) solution, an extractable yellow complex is formed. All the complexes have λ_{max} at 430 nm. At least a 20-fold molar excess of pyrimidinethiol is required for complete development of the colour (Figs. 1 and 2). The other characteristics of the complexes are summarized in Table 1. The data show that there is a slight increase in sensitivity with increase in molecular weight of the ligand in alkyl (**I–III**) or aryl (**IV–VI**) substituted compounds.

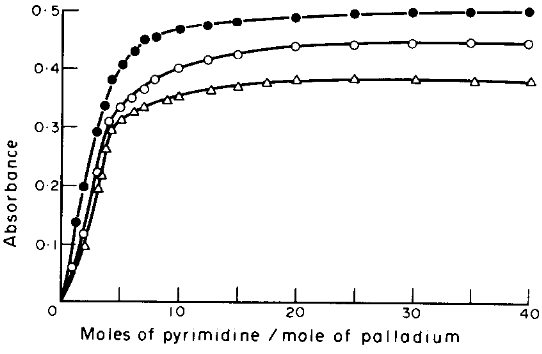


Fig. 2. Effect of excess of reagent. [Pd] $10^{-4}M$ + [Thiol] $10^{-4}M$–4·0 × $10^{-3}M$. △ Pyrimidinethiol when R = C_6H_5. ○ Pyrimidinethiol when R = $C_6H_4OCH_3$. ● Pyrimidinethiol when R = $C_6H_4NO_2$.

Table 1. Characteristics of palladium(II) complexes with 2-pyrimidinethiols

Characteristic	Pd(II)-complex with pyrimidinethiol					
	I	II	III	IV	V	VI
ϵ_{max}, *l. mole*$^{-1}$. *cm*$^{-1}$	$3{\cdot}7 \times 10^3$	$4{\cdot}2 \times 10^3$	$4{\cdot}6 \times 10^3$	$3{\cdot}85 \times 10^3$	$4{\cdot}4 \times 10^3$	$5{\cdot}0 \times 10^3$
Acid medium for max. extraction of the complex	3–6*N* HCl; 3–6*N* $HClO_4$; 3–6*N* HNO_3; 3–6*N* H_2SO_4	1–10*N* HCl; 1–4*N* $HClO_4$; 1–8*N* HNO_3; 1–22*N* H_2SO_4		1–10*N* HCl; 1–5*N* $HClO_4$; 1–8*N* HNO_3; 1–20*N* H_2SO_4		
Stability in chloroform, *hr*	5–6	5–6	5–6	1	1	1
Beer's law range, *ppm*	Up to 22·5	Up to 21·5	Up to 21·5	Up to 20·5	Up to 18·0	Up to 16·5
Accurate range of detn., *ppm*	5·3–20·0	5·3–16·0	5·3–16·0	5·1–15·0	4·6–15·0	4·0–14·8
Sandell sensitivity	0·028	0·024	0·022	0·028	0·024	0·021
Std. devn.* (8 samples)	0·0040	0·0048	0·0052	0·0065	0·0084	0·0078

* Of the absorbance for 10·7 ppm palladium.

Composition

The molar composition of the complexes was established by the methods of continuous variations and mole ratio. All the complexes contain palladium and pyrimidinethiol in a 1:4 ratio. This indicates that the ligands are probably acting as monodentate by complexation through the sulphur atom of the thiol group. The poor sensitivity of the ligands (Table 1) may also thus be explained.

Procedure

To a suitable aliquot of Pd(II) solution (Table 1), add 3–4 ml of 10*N* hydrochloric acid, dilute to 10 ml, add 10·0 ml of pyrimidinethiol solution (0·01*M* in chloroform) and shake for about 20 min. Allow to settle and remove the organic layer. Measure its absorbance at 430 nm against a reagent blank and calculate the metal concentration by comparing with a calibration graph.

Interferences

In determination of 10·7 ppm of Pd(II) with these thiols, at least 10^4 ppm of the following ions did not interfere: F^-, Cl^-, Br^-, NO_3^-, ClO_4^-, SCN^-, CH_3COO^-, SO_4^{2-}, $C_2O_4^{2-}$, tartrate, EDTA, BO_3^{3-}, PO_4^{3-}, citrate, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Fe^{2+} or Fe^{3+}. The presence of 5000 ppm each of Zn^{2+}, Cd^{2+}, Hg^{2+}, Sn^{4+}, V^{4+}, Mo^{6+}, Co^{2+} and Ni^{2+} could also be tolerated. Other platinum-group metals which could be tolerated are Ru^{3+}, Rh^{3+}, Ir^{3+} and Pt^{4+} (1100–1500 ppm) and Os^{8+} (100 ppm). Also 4000 ppm Cu^{2+}, 5 ppm Ag^+, 10 ppm Au^{3+} and 200 ppm NO_2^- were without interference. However, the anions I^-, CN^- and $S_2O_3^{2-}$ and also thiourea should be absent.

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Summary—Alkyl and aryl substituted 4,4,6-trimethyl-(1H,4H)2-pyrimidinethiols react selectively with palladium(II) in strong acids, forming yellow complexes (λ_{max} 430 nm) extractable into non-polar solvents. By an extractive spectrophotometric procedure, microgram amounts of palladium may be determined in the presence of milligram amounts of many species, including all the other platinum-group metals.

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PRELIMINARY COMMUNICATION

DYNAMIC SURFACE TENSION MEASUREMENTS FOR THE ASSESSMENT OF POTABLE WATER QUALITY

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The separation and identification of all individual surfactants is a difficult problem in water analysis.[1] Normally, pollution due to such materials is stated in terms of the equivalent concentration of a standard reference substance, which may differ chemically considerably from those substances actually present. On the other hand, it is important to note that different surfactants, at the same concentration, can affect the surface properties of water to a varying degree (even hundredfold differences are encountered). In our opinion this fact, which has heretofore been neglected in environmental studies, should be considered. In particular, we feel that the surface activity of substances present in water (that is, their capacity to change the excess surface free energy) can be a significant physical quantity in the assessment of the quality of water, in addition to the other chemical and physical quantities usually considered.

In this paper we have two aims: 1) to propose a parameter correlated with surface activity, which can be of practical use for the routine examination of potable water; 2) to reveal the significance of the surface activity in studies concerning pollution by surfactants.

EXPERIMENTAL

The concentration of anionic surfactants was determined according to the method of Longwell and Maniece,[2] of non-ionic surfactants according to the method of Greff et al.[3]

The dynamic surface tension of potable water samples was measured by a Langmuir apparatus with a recording electrobalance, following a procedure already described. Care was taken to avoid mistakes due to adsorption on the walls of the sample vessel.

RESULTS AND DISCUSSION

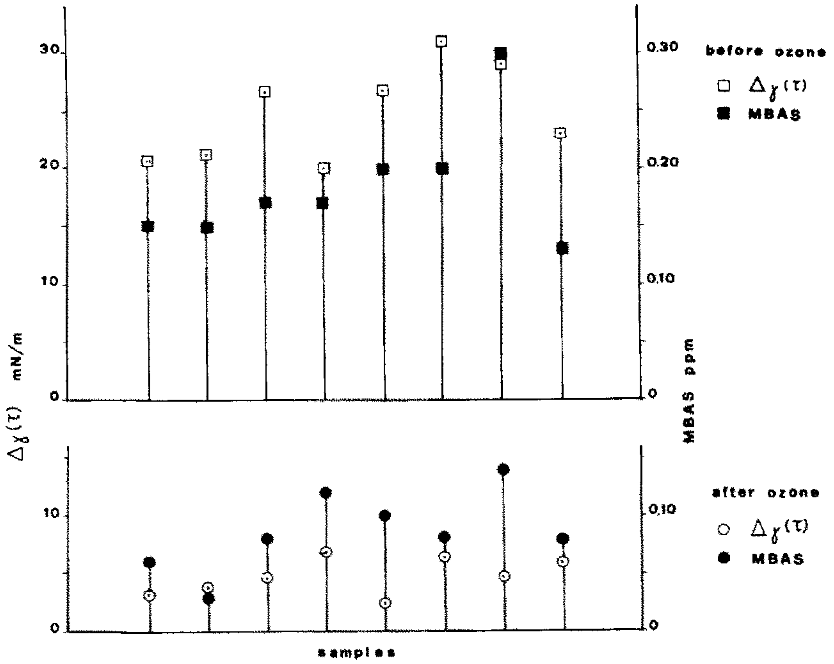
Parameter related to surface activity. The surface activity of a substance dissolved in water, defined as $-\lim d\gamma / dc$,[5] can be approximately determined for dilute solutions by the ratio $\Delta\gamma / c$, between the difference of the surface tension of the solution with respect to pure water and the concentration. The static surface tension is the appropriate quantity involved in this determination. However for potable water, in which the concentration of surfactants is normally very low ($c < 0.5$ ppm), the measurement of $\Delta\gamma$ (static) is not practical (a rigorous experimental procedure is required to obtain reproducibility and accuracy). Having in mind the importance of practicability in routine analysis, we take into consideration the dynamic surface tension, rather than the static one, for the investigation of the surface activity of substances present in water at very low concentratio levels. When the surface area of a solution of surfactants is decreased rapidly, there is a concomitant decrease of the surface tension, $\Delta\gamma$.[6] Following such a process, the value of $\Delta\gamma$ changes as a function of time. This function contains, among other quantities, the concentration and the surface activity.[7] Actually, for a given substance at various concentrations, the value of $\Delta\gamma(\tau)$, taken at a certain instant τ, increases roughly proportionally to c. Moreover, for different substances at the same concentration, the value of $\Delta\gamma(\tau)$ is a monotonically increasing function of the surface activity. Thus, we can take the ratio $\Delta\gamma(\tau)/\sum c_i$ as a parameter related to surface activity (SA), even if the latter cannot be determined from such a ratio. The most surface active substances are the predominant contributors to the value of SA, whereas those which are less so give negligible contributions.

Reproducibility of $\Delta\gamma(\tau)$ values is satisfactorily attained by standardization of sampling and measuring procedures.

Surface activity of substances in potable water. The figure shows values of $\Delta\gamma(\tau)$ and of MBAS (Methylene Blue Active Substances) relative to eight pairs of samples of potable water taken on different days from a municipal water treatment plant (fed from a river). Placing the respective segments on the same line, the figure also allows the visualization of the value of SA, that is, the parameter of surface activity (all samples were found to be free of non-ionic surfactants; therefore the value of MBAS was taken as the value of $\sum c_i$). The upper (lower) diagram concerns samples taken before (after) continuous flow treatment of the water with ozone.

As can be seen in both diagrams, for samples which have equal, or almost equal, MBAS values, the SA parameter can have values which are equal in some cases or very different in other cases (the differences quite exceed measurement errors). This means that, whereas the overall molar concentration of the surfactants is the same, the nature of the substances present, or, at least, the percentage concentration of each of them, varies

A comparison of the two diagrams shows that the MBAS values decrease by about 50 % following ozone treatment. If the nature of the substances remained the same, even though the concentration was halved, the same SA values would be expected before and after



ozone treatment. On the contrary, the SA values are drastically reduced. Thus ozone treatment, while reducing the molar concentration of the substances present, probably also changes to a large degree their chemical nature.

The above experimental results show that the SA parameter gives information concerning the nature of the substances present in water. Such information is additional to that given by the MBAS concentration parameter. On the basis of this consideration, we can conclude that the surface activity (or a parameter with relation to it) is a significant physical quantity in environmental studies. Moreover, pollution by surfactants can be more conveniently defined in terms of both the concentration and the peculiar property of these materials of modifying the excess surface free energy of water.

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DETERMINATION OF LANTHANIDES AND YTTRIUM IN ROCKS AND MINERALS BY ATOMIC-ABSORPTION AND FLAME-EMISSION SPECTROMETRY*

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Summary—The sensitivity of atomic-absorption and flame-emission determination of lanthanides and yttrium is improved by a factor of 2–5 when an absolute ethanol solution of the perchlorate of the metal (instead of an aqueous solution) is aspirated into a nitrous oxide–acetylene flame. Based on this, a method has been developed for accurate determination of small amounts of certain rare earths and yttrium. Lanthanum (1%) is used as a spectroscopic buffer to eliminate interferences and to enhance the sensitivities in certain determinations. Where the use of lanthanum is not practicable because of interferences (such as in the determination of praseodymium and samarium by flame emission), sodium (2000 ppm) is used as the spectroscopic buffer. Studies with synthetic solutions indicate that yttrium and most lanthanides can be directly determined in minerals without any chemical separation. With rock samples it is necessary to preconcentrate the traces of the rare earths by fluoride or oxalate precipitation with calcium as the carrier, followed by removal of calcium by hydroxide precipitation using mg amounts of iron as the carrier. The method developed has been applied to the determination of certain lanthanides and yttrium in a variety of rocks, including the Canadian reference rocks, syenites SY-1, SY-2 and SY-3, and some minerals such as britholite, cenosite, chevkinite, allanite, apatite and sphene.

Studies on the geochemistry of the rare earths by the Geological Survey of Canada required the determination of these elements in a variety of rocks and minerals. Owing to the similarity of chemical properties of the rare earths, separation of the individual elements before determination is very difficult and time-consuming. For this reason the trend in the determination of rare earths during the past two decades had been to separate them *en masse* by ion-exchange or co-precipitation with a carrier such as calcium, aluminium of iron before determination by emission spectrography[1–4] or X-ray fluorescence.[5–7] In neutron-activation analysis a post-irradiation ion-exchange separation of the rare earths is favoured.[8–10] Recently, when the usefulness of the nitrous oxide–acetylene flame in atomic-absorption and flame-emission determination of the refractory elements was discovered, the detection limits for various rare earths in these flames were studied and recorded.[11–16] Among others, the work of Hingle *et al.*,[14] which involved flame-emission studies of the perchlorates of the rare earths in ethanolic solution in a separated nitrous oxide–acetylene flame, appeared promising because of its ability to detect very low levels of the rare earths. But since the full potentiality of this method had not been explored, by use of atomic absorption, and no mention of its application to the analysis of rocks and minerals was found in the work of Hingle *et al.*, it was thought worthwhile to investigate this method. The present paper is the result of such an investigation.

Thus a method has been developed which allows the determination of ppm levels of most lanthanides and yttrium in rocks. Also the concentration of most rare earths in minerals can be determined by this method directly on the sample solution, obviating the necessity of separation from other common elements and from each other.

EXPERIMENTAL

Apparatus

A modified Yechtron AA-3 atomic-absorption spectrophotometer, equipped with an IM-5 amplifier–read-out unit, a Hamamatsu R-213 photomultiplier tube, a variable-flow nebulizer and a Teflon spray-chamber, was used. An uptake rate of 4 ml/min was maintained throughout the work. A Goguel-type[17,18] water-cooled ridge-slot burner head (slot length 7·4 cm) mounted on a Techtron AA-5 burner mounting was employed. For flame-emission measurements, a 285-Hz chopper was installed between the second lens and the monochromator slit, and a six-speed wavelength-scanning system was attached to the monochromator. All measurements were recorded on a photovolt Varicord Linear/Log Model 43 recorder. ASL and Westinghouse shielded hollow-cathode lamps were used for atomic-absorption measurements. A nitrous oxide–acetylene flame was used in both atomic-absorption and flame-emission studies. The nitrous oxide pressure was kept at 15 psig and the acetylene pressure and the burner position were varied to provide maximum signal (the "red feather" was never allowed to disappear from the flame).

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Table 1. Operating parameters and sensitivities for yttrium and certain rare earths in the nitrous oxide–acetylene flame

Element	Wave-length, *nm*	Spectral band-width, *nm*	Lamp current, *mA*	Sensitivity (ppm 1% absorption) This work	Jaworowski *et al*[11]	Van Loon *et al*[16]
Y	410·24	0·33	10	3·2	4†	1·8
Nd	492·45	0·17	5	9·4	20*	‡
Sm	429·67	0·17	10	7·6	20†	‡
Eu	459·40	0·33	10	0·35	1·5*	0·7
Dy	421·17	0·08	15	0·40	4†	1·0
Ho	410·38	0·08	15	0·67	‡	2·0
Er	400·80	0·17	10	0·46	2*	0·8
Tm	371·79	0·33	15	0·21	‡	1·0
Yb	398·80	0·33	5	0·07	‡	0·3

* Chloride in 80% ethyl alcohol.

† Chloride in 80% methyl alcohol.

‡ Not determined.

Operating parameters and sensitivities

Instrumental parameters and sensitivities for the rare earths are recorded in Table 1. The sensitivity data were obtained by spraying into the nitrous oxide–acetylene flame a perchlorate solution of the rare earth in absolute ethanol, the solution being buffered by 1% lanthanum. A comparison with other published sensitivity values (see Table 1) reveals the superiority of the present method. After this work was completed, a paper by Ooghe and Verbeek[19] came to the author's notice in which they reported spraying an 80% methanol solution of the rare earth chlorides (buffered with sodium or potassium) into the nitrous oxide–acetylene flame and obtaining much higher sensitivities than those reported by Jaworowski *et al.*[11] who used similar solutions without any spectroscopic buffer.

Reagents

Rare earth stock solutions. Dissolve an accurately weighed quantity of a spectroscopically pure rare earth oxide in dilute nitric acid and evaporate the solution to dryness on the steam-bath. Add a small quantity of perchloric acid and evaporate again to a moist residue. Cool in a desiccator charged with silica gel, dissolve the residue in absolute ethanol and dilute to a suitable volume. Transfer 1–2 ml of the stock solution, containing not more than 5 mg of rare earth oxide per ml, to a 10-ml weighed platinum crucible and leave at room temperature till evaporated to a moist residue. Carefully heat the bottom of the crucible with a small flame until the perchloric acid vapour is completely expelled. Ignite at 1000°, cool and weigh on a microbalance, using a similar platinum crucible as the tare Dilute an aliquot of the standardized stock solution to a definite volume with absolute ethanol so that the rare earth concentration in μg/ml is an integral number.

Lanthanum buffer. Dissolve, by heating, a sufficient quantity of lanthanum oxide (purity 5–9 s) in dilute hydrochloric acid to give an equivalent of 5·85 g of La_2O_3 per 100 ml of total final volume. Evaporate the solution to small volume, add 10 ml of 60% perchloric acid and evaporate to a moist residue. Cool, add 25 ml of absolute ethanol, break up the lumps with a glass rod to a fine powder and dissolve by stirring. Filter, if necessary, through a Whatman No. 40 filter paper and wash with absolute ethanol. Dilute to volume (100 ml for 5·85 g of La_2O_3) with absolute ethanol. Take a small aliquot in an ignited and weighed platinum crucible, evaporate and ignite to constant weight at 1000° to establish a correction factor for water and carbon dioxide, if any.

Sodium (10000 ppm) buffer. Dissolve $NaClO_4 \cdot H_2O$/ (6–12 g) in 100 ml of absolute ethanol and store in a polyethylene bottle.

Interference studies

Inter-element effects of the lanthanides and yttrium amongst themselves and in different matrices, as encountered in rare earth minerals, were studied by preparing synthetic solutions approximating the composition of some minerals such as britholite, cenosite, allanite and chevkinite. The synthetic solutions were prepared by mixing salt solutions of the common and the rare earth elements in such a way as to contain the equivalent of 100 mg of the mineral sample. The solutions were evaporated with

Table 2. Interference study in the atomic-absorption and flame-emission determination of yttrium and some lanthanides (synthetic solutions approximating the composition of certain minerals). Rare earth concentrations in *ppm*

Elements present in the synthetic soln * *ppm*	Sample concn, *mg/ml*	Y_2O_3† Taken	Found	La_2O_3‡ Taken	Found	Pr_6O_{11}‡ Taken	Found	Nd_2O_3† Taken	Found	Sm_2O_3‡ Taken	Found	Dy_2O_3‡ Taken	Found	Er_2O_3† Taken	Found	Yb_2O_3† Taken	Found
Allanite[20]																	
a) CaO = 100, MgO = 10, MnO = 30, Fe_2O_3 = 150, Al_2O_3 = 140, TiO_2 = 20·1, Ce_2O_3 = 124, ThO_2 = 21·2	1	27	28									5	6				
b) 2 × above concn	2			5·1 6·05	5·2 6·0												
Britholite[5]																	
a) CaO = 288, MgO = 2, Fe_2O_3 = 1·6, Na_2O = 2, Al_2O_3 = 48, CeO_2 = 166·4, ThO_2 = 56·4, P_2O_5 = 172	1	4	5 5			22	25 26	83	85 85	17	15 16	5	4 4	5	4·5 5	4	4·3 4·5
b) 2 × above concn	2			2·84	3·00 3·15												
Cenosite[6]																	
CaO = 175, Na_2O = 0·4, K_2O = 0·1, Fe_2O_3 = 6, Al_2O_3 = 12·2, TiO_2 = 0·3	1	183	185 187									32	32 32	36	36 36		
Chevkinite[21]																	
CaO = 25, MgO = 4, Fe_2O_3 = 100, Al_2O_3 = 20, MnO = 6, TiO_2 = 200·5, Ce_2O_3 = 248, ThO_2 = 21·2, P_2O_5 = 0·4	1	20	21 21			22	25 26	152	152 152								

* Plus specified amounts of rare earths.

† Determined by atomic absorption in 1% lanthanum buffer.

‡ Determined by flame emission in 2000 ppm sodium buffer (no buffer used in the case of lanthanum).

60% perchloric acid to a moist residue in order to convert the salts into perchlorates. After cooling in a desiccator, the salts were dissolved in absolute ethanol and the solution was diluted to 25 ml. From this stock solution three sets of solutions were prepared, all in absolute ethanol and containing 1 mg of sample/ml, the first having no spectroscopic buffer, the second containing 1% lanthanum and the third 2000 ppm of sodium as spectroscopic buffers. The rare earths and yttrium were determined in these solutions by atomic-absorption and flame-emission spectrometry. In order to test the recovery the calibration curves were prepared by use of mixtures of pure rare earth perchlorates in absolute ethanol and containing the spectroscopic buffer, where necessary. The results are given in Table 2.

Lanthanum was determined by flame emission from the first solution containing no spectroscopic buffer since sodium (2000 ppm) interfered at the most sensitive lanthanum line (550·13 nm). The use of strontium perchlorate buffer did not improve the sensitivity for lanthanum. Lanthanum (1%) buffer was found to interfere at the most sensitive lines of samarium (429·67 nm) and praseodymium (495·14 nm) during their flame-emission determinations. Therefore, the flame-emission determination of these two elements was completed in the sodium buffer medium. The results in Table 2 indicate that the lanthanides and yttrium can be directly determined in the mineral sample solutions without any chemical separation.

As most rocks contain minor or trace amounts of the rare earths, it is not possible to determine them without preliminary concentration. The bulk amount of the matrix elements such as calcium, iron, aluminium, titanium and magnesium (from a 2–10 g sample) must also be removed to reduce the salt concentration in the final small volume of solutions to be used for atomic-absorption and flame-emission determination of the rare earths. The disadvantage of ion-exchange separation of the bulk of the common elements from 5–10 g rock samples is the need to use big columns, a large volume of wash solutions and subsequent time-consuming evaporation steps. Separation of major amounts of iron by mercury cathode electrolysis from samples such as magnetite and limonite gossan before rare earths determination has been used with success in this laboratory. Tests also showed that if a sample contained a small amount of calcium, hydrofluoric acid attack would co-precipitate small amounts of rare earths with calcium fluoride; these could be converted into perchlorates, dissolved in ethanol and quantitatively determined by the method above. However, in the presence of large amounts of calcium, the separation of the rare earths with calcium as the oxalates, followed by removal of calcium by precipitation of the rare earth hydroxides in the presence of a small amount of aluminium hydroxide or ferric hydroxide as the carrier is generally favoured. Since the final rare earth concentrate obtained by this method contains aluminium or iron as the carrier element, it was necessary to investigate the effect of these two elements on the atomic-absorption and flame-emission determination of the lanthanides and yttrium. The results of this investigation, as given in Table 3, show that the rare earths can tolerate a concentration of 0·8 mg of Fe_2O_3 per ml in the sample solution. The presence of the aluminium carrier causes slightly lower results (*cf.* Table 3). Therefore, ferric hydroxide carrier was used in this work in the co-precipitation of small amounts of the rare earths.

Recommended procedures

Flow-sheets outlining the analytical schemes are given in Figs. 1 and 2.

Determination of lanthanides and yttrium in rare earth minerals (Fig. 1). Take the sample (0·1–0·2 g) in a 50-ml platinum dish and heat gently to drive off moisture and any carbonaceous material. Treat with 5 ml of hydrofluoric acid and 10 ml of nitric acid, cover and digest on the steam-bath. Add more hydrofluoric acid, if necessary, to complete the decomposition.

If the sample does not contain phosphate, evaporate the solution to dryness on the steam-bath, add 5 ml of nitric acid and evaporate to dryness again. Add 5 ml of 60% perchloric acid and evaporate to a moist residue.

If the sample contains major amount of phosphate (as in britholite, monazite, *etc.*), evaporate the solution to dryness on the steam-bath. Add 25 ml of hydrofluoric acid to the residue and heat on the steam-bath for 1 hr with occasional stirring. The fluorides of rare earths and calcium are completely precipitated. Allow the precipitate to settle, filter it off on a Whatman No. 40 filter paper and wash with hot water. Transfer the precipitate to the original platinum dish and decompose the paper with nitric acid (steam-bath). Evaporate to dryness, add 5 ml of perchloric acid (60%) and evaporate to a moist residue.

After cooling in a desiccator, dissolve the residue in absolute ethanol and dilute to 25 ml (volumetric flask) with the same solvent. Transfer aliquots of this stock solution into two volumetric flasks to prepare solutions containing 1 and 3 mg of sample per ml, respectively. Add sufficient lanthanum buffer to have a final 1% lanthanum concentration and dilute to volume with absolute ethanol. Determine, by atomic-absorption, the major rare earths with the 1-mg/ml solution and the minor rare earths with the 3-mg/ml solution. Determine lanthanum by flame-emission from a 2-mg/ml sample solution in absolute ethanol (no spectroscopic buffer). Prepare calibration curves by aspirating the blank (1% La) and standard solutions of the rare earths (containing 1% La) into the flame immediately before and after the sample solutions.

Determination of lanthanides and yttrium in rocks and other minerals containing small amounts of these elements (Fig. 2). Depending on the rare earth content, take 2–10 g of sample in a 100-ml platinum dish, add 30 ml of hydrofluoric acid, cover and heat on the steam-bath with occasional stirring with a platinum rod. After decomposition is complete, evaporate the solution to dryness on the steam-bath. Add 40–50 ml of hydrofluoric acid, break the lumps with the platinum rod, cover and digest on the steam-bath for 1 hr. Allow the precipitate to settle and filter it off on a Whatman No. 40 filter paper in a polyethy-

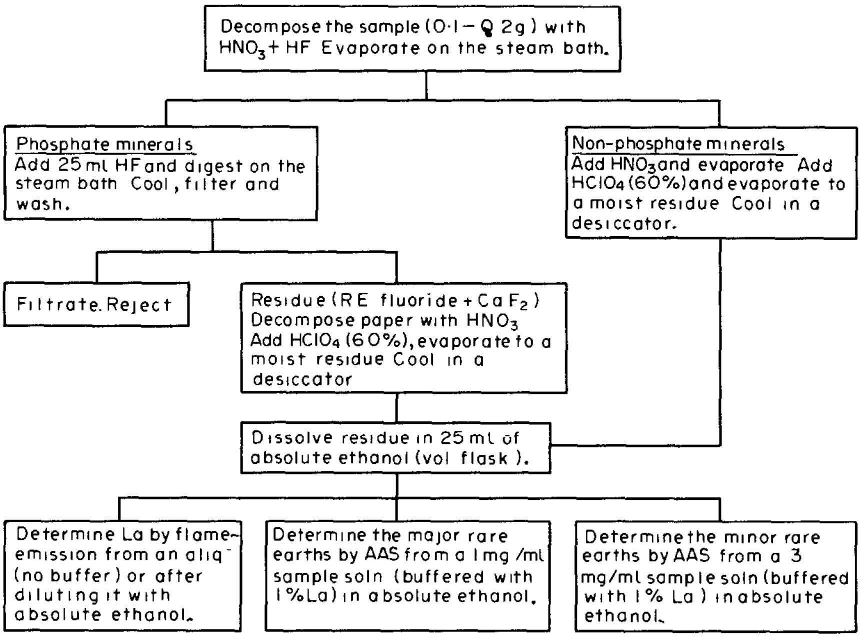
Table 3. Interference study in the atomic-absorption and flame-emission determination of trace amounts of yttrium and certain lanthanides in the presence of aluminium and iron carriers (rare earth concentrations in *ppm*)

Carrier present	Y_2O_3*		La_2O_3†		Pr_6O_{11}†		Nd_2O_3*		Sm_2O_3†		Eu_2O_3*		Dy_2O_3†		Ho_2O_3*		Er_2O_3*		Yb_2O_3*	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
Al_2O_3	60	48			55	42	52	32	56	47	15	12	30	26	2	2	15	12		
(16 mg/10 ml)		60‡																		
Fe_2O_3	60	58	74	75	55	50	52	48	56	58†	15	15	30	33	2	2	15	15	5	5
(8 mg/10 ml)			294	290					75	75*									10	10
									149·4	150*										

* Determined by atomic-absorption in 1% lanthanum buffer.

† Determined by flame-emission in 2000 ppm sodium buffer (no buffer used in the case of lanthanum).

‡ Determined by atomic-absorption in 2000 ppm sodium buffer.



Decompose the sample (0·1 – 0·2 g) with HNO_3 + HF Evaporate on the steam bath.

Phosphate minerals
Add 25 ml HF and digest on the steam bath Cool, filter and wash.

Non-phosphate minerals
Add HNO_3 and evaporate Add $HClO_4$ (60%) and evaporate to a moist residue Cool in a desiccator.

Filtrate. Reject

Residue (RE fluoride + CaF_2) Decompose paper with HNO_3 Add $HClO_4$ (60%), evaporate to a moist residue Cool in a desiccator

Dissolve residue in 25 ml of absolute ethanol (vol flask).

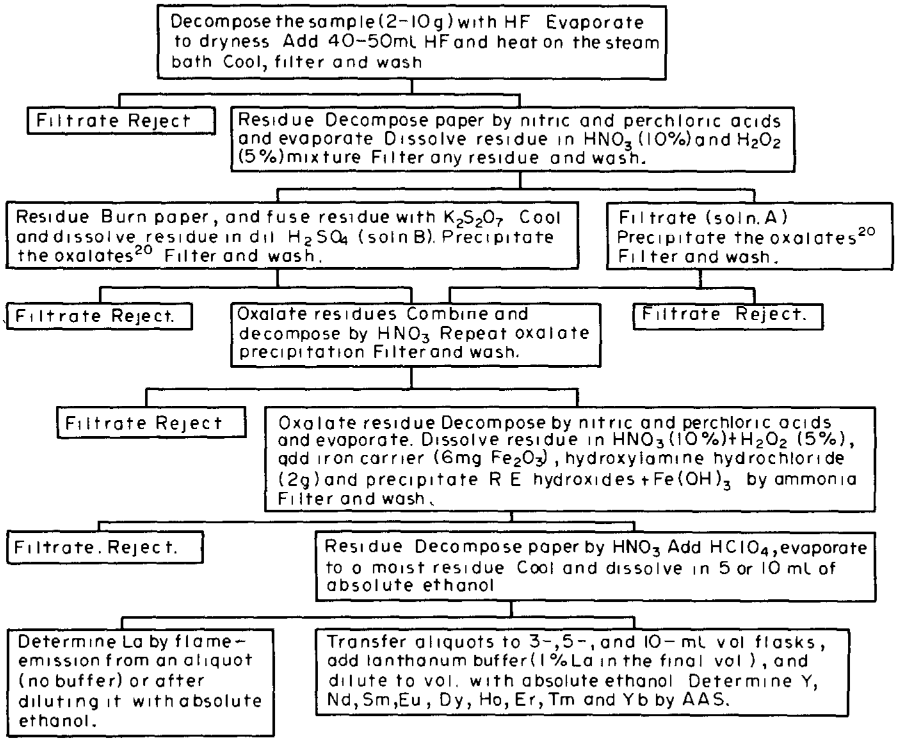
Determine La by flame-emission from an aliq (no buffer) or after diluting it with absolute ethanol.

Determine the major rare earths by AAS from a 1 mg/ml sample soln (buffered with 1% La) in absolute ethanol.

Determine the minor rare earths by AAS from a 3 mg/ml sample soln (buffered with 1% La) in absolute ethanol.

Fig. 1.

lene funnel and wash the residue with hot water. Reject the filtrate. Transfer the precipitate to the original platinum dish, add 25 ml of concentrated nitric acid, cover and digest on a warm water-bath (60–70°) until the paper is decomposed. Evaporate to dryness, add 25 ml of nitric acid and repeat the evaporation to dryness (steam-bath). Add 5 ml of nitric acid, 10 ml of 60% perchloric acid and heat cautiously on a sand-bath. Withdraw from the heat if a vigorous reaction starts, and cover. After the reaction subsides, evaporate to a moist residue. Dissolve this in 10% nitric acid containing 5% hydrogen peroxide, filter off any small insoluble residue and wash thoroughly with the same solvent. Reserve the filtrate (solution A). Take the residue in a platinum crucible, burn the paper at 400° and heat to 600°. Fuse the residue with potassium pyrosulphate, cool and dissolve in hot dilute sulphuric acid (solution B). Precipitate the oxalates of the rare earths and calcium separately from solutions A and B following the method



Decompose the sample (2–10 g) with HF Evaporate to dryness Add 40–50 ml HF and heat on the steam bath Cool, filter and wash

Filtrate Reject

Residue Decompose paper by nitric and perchloric acids and evaporate Dissolve residue in HNO_3 (10%) and H_2O_2 (5%) mixture Filter any residue and wash.

Residue Burn paper, and fuse residue with $K_2S_2O_7$ Cool and dissolve residue in dil H_2SO_4 (soln B). Precipitate the oxalates[20] Filter and wash.

Filtrate (soln. A) Precipitate the oxalates[20] Filter and wash.

Filtrate Reject.

Oxalate residues Combine and decompose by HNO_3 Repeat oxalate precipitation Filter and wash.

Filtrate Reject.

Filtrate Reject

Oxalate residue Decompose by nitric and perchloric acids and evaporate. Dissolve residue in HNO_3 (10%) + H_2O_2 (5%), add iron carrier (6 mg Fe_2O_3), hydroxylamine hydrochloride (2 g) and precipitate R E hydroxides + $Fe(OH)_3$ by ammonia Filter and wash.

Filtrate. Reject.

Residue Decompose paper by HNO_3 Add $HClO_4$, evaporate to a moist residue Cool and dissolve in 5 or 10 ml of absolute ethanol

Determine La by flame-emission from an aliquot (no buffer) or after diluting it with absolute ethanol.

Transfer aliquots to 3-, 5-, and 10-ml vol flasks, add lanthanum buffer (1% La in the final vol), and dilute to vol. with absolute ethanol Determine Y, Nd, Sm, Eu, Dy, Ho, Er, Tm and Yb by AAS.

Fig. 2.

of Carron *et al.*,[22] using ammonia instead of sodium hydroxide for adjusting the pH to 3·8. Filter and wash the precipitate with 0·1% ammonium oxalate. Combine the two oxalate precipitates and decompose them by heating with 25 ml of concentrated nitric acid. Evaporate to a moist residue after adding 5 ml of perchloric acid. Dissolve the residue in water and dilute to 50 ml. Repeat the oxalate precipitation, followed by filtration and destruction of the filter paper and oxalates by nitric acid and perchloric acid as above. Dissolve the perchlorate residue in a solution containing 10% nitric acid and 5% hydrogen peroxide. Add a measured quantity of ferric chloride or nitrate solution to give the equivalent of 6 mg of Fe_2O_3, and 2 g of hydroxylamine hydrochloride, and precipitate the rate earth hydroxides and ferric hydroxide by adding enough ammonia to raise the pH to > 10 (pH paper). Filter off, and destroy the paper by nitric and perchloric acids as usual. After transferring the solution to a 10- or 20-ml beaker, evaporate to a moist residue of the perchlorates. Cool in a desiccator, dissolve in absolute ethanol and dilute to 5 or 10 ml in a volumetric flask (stock solution). According to the concentration of yttrium and the lanthanides expected, transfer aliquots of this stock solution to 3-, 5- and 10-ml volumetric flasks, add the required quantity of lanthanum buffer to each flask to yield 1% La in the final solution, and dilute to volume with absolute ethanol. Determine Y, Nd, Sm, Eu, Dy, Ho, Er, Tm and Yb in these lanthanum buffered solutions by atomic-absorption, using scale expansion up to 12·5 ×, if necessary. Determined lanthanum by flame-emission from the original stock solution, or from a diluted solution (no buffer). Determine the concentration of the unknown elements from the calibration curves prepared by aspirating the blank (1% La) and standard solutions of the rare earths (containing 1% La) in the flame immediately before and after the sample solutions. Although Table 3 shows that the determination of yttrium and lanthanides in the presence of 0·8 mg of Fe_2O_3 per ml is possible, it is perhaps better to add to the standards the amount of iron (as perchlorate in absolute ethanol) expected in the unknown sample solution, to increase the precision and accuracy.

RESULTS AND DISCUSSION

In order to test the effectiveness of the proposed method in actual sample analysis, two previously analysed rare earth minerals, britholite and cenosite, and three syenite reference samples, SY-1, SY-2 and SY-3 from the Canadian Certified Reference Materials project, were chosen. The results of analysis of britholite and cenosite as well as two other minerals, allanite and chevkinite, by the proposed method are given in Table 4. The X-ray fluorescence analyses of the rare earth concentrates from britholite and cenosite are also included in Table 4 for comparison.

Table 4. Determination* of certain lanthanides and yttrium in some rare earth minerals and comparison with previously published X-ray fluorescence values, where available (all results, average of 2–6 determinations, are given as %)

	Britholite		Cenosite		Allanite†	Chevkinite¶
Oxides	This work	Hughson & Sen Gupta[5]	This work	Pouliot *et al*[6]	This work	This work
Y_2O_3	0·44	0·4	26·2	25·27	0·20	0·30
La_2O_3	5·9	5·6			4·75	4·00
Nd_2O_3	7·5	8·0	0·20	0·19	1·80	1·30
Sm_2O_3	1·3	1·5	0·22	0·27	‡	1·00
Eu_2O_3	0·29	**	0·13	**	0·07	0·05
Dy_2O_3	0·22	**	3·06	3·10	‡	‡
Ho_2O_3	0·04	**	1·07	**	0·10	0·01
Er_2O_3	0·03	**	2·65	3·53	‡	‡
Tm_2O_3	0·006	**	0·45	**	‡	‡
Yb_2O_3	0·012	**	2·33	2·71	<0·05	<0·05

* Yttrium and rare earths were determined by atomic-absorption; lanthanum was determined by flame-emission.

** Not determined.

† From Picanoe river, north of Otter lake, Quebec, Canada.

‡ Not detected.

¶ From Pitt prospect, Pontiac county, Quebec, Canada.

Table 5. Results (%) of replicate determinations of minor rare earths in britholite by atomic-absorption spectrometry

Oxide	Found in this work
Y_2O_3	0·44,* 0·44,*
	0·43,† 0·43,†
	0·44,‡ 0·44,‡
Er_2O_3	0·03,* 0·03,*
	0·03,† 0·03,†
	0·03,‡ 0·03,‡
Ho_2O_3	0·05,* 0·05,*
	0·03,†
	0·03,‡ 0·03,‡
Tm_2O_3	0·006,* 0·006,*
Dy_2O_3	0·24,* 0·24,*
	0·21,†
	0·20,‡ 0·23,‡
Yb_2O_3	0·012,* 0·011,*
	0·011,† 0·013,†
	0·013,‡ 0·013,‡
Eu_2O_3	0·29,* 0·29,*
	0·29,† 0·29,†
	0·28,‡ 0·29,‡
Sm_2O_3	1·25,* 1·28,*
	1·22,† 1·23,† 1·33,†
	1·13,‡ 1·13,‡

* Directly determined after phosphate separation.

† Determined after separation by oxalate and hydroxide precipitation (without any carrier).

‡ Determined after separation by oxalate and hydroxide precipitation (with iron carrier).

The cenosite specimen (from Bancroft, Ontario) analysed in this work was not exactly the same as that analysed by Pouliot *et al.*[6] The grains were handpicked under a microscope by the donor at a different time. Consequently there is a possibility of slight variation in the composition. This may be the reason for small differences in the results for yttrium and erbium obtained by the two methods, although the agreement between the results for other rare earths is good (see Table 4).

As the X-ray fluorescence data for the minor rare earth contents of britholite are not available, the comparison is restricted to the values reported.[5] There is a minor difference in the neodymium values, but the results for yttrium, lanthanum and samarium are comparable. The advantage of the atomic-absorption method is shown by its ability to determine small amounts of Eu, Dy, Ho, Er, Tm and Yb in britholite. The results of replicate determinations of the minor rare earths in britholite are included in Table 5, which also gives comparative data on three ways of determination, *viz.* direct determination after phosphate separation, determination after separation by oxalate and hydroxide precipitation without using any carrier, and determination after separation by oxalate and hydroxide precipitation using iron as a carrier.

The rare earth values obtained by the proposed method on the reference rocks SY-1, SY-2 and SY-3, and three other samples (limonite gossan, apatite and

Table 6. Determination* of certain lanthanides and yttrium in rocks and some minerals containing small amounts of these elements and comparison with other values, where available (all results, average of two determinations, are given as *ppm* in the sample)

Element	Syenite rock-1**		Syenite rock-2**		Syenite rock-3**		Limonite Gossan¶	Apatite¶¶	Sphene¶¶
	This work	Reported median or values[23,24]	This work	Median of other values[25]	This work	Median of other values[25]	This work	This work	This work
Y	425	450	120	140	600	710	79	1260	1890
La	200	220	88	88	1250	1400	1023	1961	597
Nd	260	302	75	<100†	700	840	–***	2744	2058
Sm	70	<100,245	17	17,<20‡	108	80,130‡	–***	517	604
Eu	9	8,15	2.3	2	14	15	43	78	104
Dy	76	100,135	21	<80†	118	110†	26	261	436
Ho	18	2,21	7	?	22	?	–***	61	105
Er	48	42,57	13	?	52	?	–***	131	219
Tm	9.6	5	2.5	?	10.5	?	–***	20	38
Yb	55	70	16	16	55	62	<9	88	176

* Yttrium and rare earths were determined by atomic-absorption; lanthanum was determined by flame-emission.
** Spectroscopy Society of Canada standard reference material.
*** Not detected.
† Single result only from one source.
‡ Two results only from two sources.
¶ From Springiron lake, British Columbia, Canada.
¶¶ From Turners island, Ontario, Canada.

sphene) are given in Table 6. In the case of the syenite rocks the results are found to be close to other reported values or their medians, obtained by spectrographic or neutron-activation methods. Although the author was able to determine Ho, Er and Tm in SY-2 and SY-3 by the present method, no other laboratory has yet reported data for these elements.

Table 2 shows that the determination of praseodymium is possible by flame-emission. However, no praseodymium was detected in the samples reported on in Tables 4 and 6. Cerium, thorium and gadolinium were found to be very insensitive in both flame atomic-absorption and flame-emission. Perhaps flameless atomic-absorption should be tried for these elements to increase the sensitivity. Otherwise, in a composite scheme of analysis, these elements can be determined in a fraction of the concentrate by other methods[26] such as emission spectrography, X-ray fluorescence, colorimetry and titrimetry.

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ON THE OPTIMUM CONDITIONS FOR THE REDUCTION OF NITRATE TO NITRITE BY CADMIUM

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Summary—The variables of direct importance in the reduction of nitrate to nitrite by a metallic reductant such as cadmium used in a reductor column are discussed with special reference to the determination of nitrate as nitrite in very dilute solutions, *e.g.*, natural waters. As a result of these considerations the effect of flow-rate (expressed as bed-volumes/min), pH, temperature, chloride concentration and various types of reductor cadmium on the yield of nitrite is investigated. The effect of dissolved oxygen in the sample solution on pH and cadmium concentration in the reduced solution is demonstrated. At constant pH a maximum yield of nitrite is obtained at a certain flow-rate, which is explained as the result of a rapid formation and simultaneously proceeding slow reduction of nitrite. With increasing pH this maximum is shifted to lower flow-rates, and grows broader whilst the yield at maximum approaches 100%; at pH 9·5 a yield of 99·9 ± 0·1% is obtained. The temperature has little effect on the reduction rate in the interval 20–30° but at 10° the reduction is noticeably slower. Chloride ions have a strongly retarding effect on the reduction rate but the yield at maximum is not affected. Electrolytically precipitated cadmium, filings of pure cadmium or amalgamated pure cadmium all give practically the same yield at maximum though some differences in reduction rate are observed. Impure cadmium or copper–cadmium and silver–cadmium, owing to the formation of galvanic cells with higher reducing power, give a high reduction rate, which also applies to nitrite, causing a poorer yield at maximum. The practical consequences of the results are thoroughly discussed.

For the determination of nitrate at very low concentrations, for instance in natural waters, it has for some time been customary to make use of the reaction

$$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$$

followed by determination of nitrite according to one of the many modifications of the Griess-Ilosvay reaction. If the sample contains nitrite as well as nitrate the former is directly determined by the same colour reaction and deducted from the sum. The determination of nitrite seems at present to be a satisfactory procedure. The reduction step, however, has obviously presented difficulties, which often originate from a tendency to over-reduction. Reducing agents in solution, as well as metallic reductants, have been used. The most promising results have been obtained by using cadmium,[1–4] amalgamated cadmium[5–7] or copper–cadmium[8,9] as reductants. The present state concerning the use of these reductants is summarized in the following quotation:[10] "However, which kind of reductor to use and how to prepare it, as well as how to control the different conditions governing the reduction process, are matters of very different opinion. What seems to be a suitable procedure in one laboratory does not always function in another. For these reasons it seems for the present impossible to distinguish one recommendable method from the great number of existing modifications."

This situation is due to the fact that the factors governing the reduction process and their interdependence have in no case been systematically studied. The aim of the present paper is to remedy this lack of knowledge to some extent and so facilitate the selection of a method. The aim is not to present a method ready for use on different kinds of samples; it must always be the province of the analytical chemist responsible to adapt a method to a particular kind of sample. To do that it is, however, indispensable to know how the method functions in its basic form, that is in absence of substances not essential for the reaction.

PRELIMINARY CONSIDERATIONS

Variables of obvious importance in the reduction of nitrate to nitrite by a metallic reductant used in a reductor column relate partly to such properties of the reductant as the reduction potential and the surface area per unit of volume, and partly to such properties of the solution as the pH and presence of substances influencing the reaction. If over-reduction can occur these combined properties would result in a certain optimum time of contact which might also be dependent on the temperature. Quite apart from the study of how these parameters affect the yield, some existing nitrite determination method must be adapted to the properties of the reduced solution. The investigation reported here has been guided by the following considerations.

The reduction potential

The standard reduction potential for the Cd/Cd^{2+} couple is $-0{\cdot}403$ V. If the cadmium contains metals of lower reduction potential, its reduction power will increase. This may, however, also occur through formation of local cells if the metallic impurities have a positive reduction potential. This effect has been artificially brought about by treatment of cadmium preparations with a copper sulphate solution;[8] copper is precipitated and partly adheres to the cadmium as a porous layer. A galvanic cell is produced with the copper as the cathode. As the standard reduction potential of the Cu/Cu^{2+} couple is $+0{\cdot}337$ V the emf of the cell under standard conditions will be 0·740 V and its reducing power much higher than that of cadmium alone.

It has also been proposed to amalgamate the cadmium by treatment with a mercuric chloride solution.[5] The surface layer of the cadmium particles will then be covered by a layer of solid cadmium amalgam and a small decrease of the reduction power may be expected.

Whether "copperizing" or amalgamation is used, a change of the active surface area may also occur. The influence of the specific surface area will be discussed in connection with the time of contact.

The properties of the solution

From the equations

$$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$$

$$HNO_2 + 5H^+ + 4e^- = NH_3OH^+ + H_2O$$

$$HNO_2 + 7H^+ + 6e^- = NH_4^+ + 2H_2O$$

it is evident that the hydrogen-ion concentration has a strong influence on the reduction process. A certain hydrogen-ion concentration is necessary for the quantitative reduction of nitrate to nitrite; too high a concentration will cause a further reduction of the nitrite formed. Most earlier authors have probably been aware of this fact but no systematic experiments at different pH-values have been published and statements on the proper pH to use are sometimes contradictory. Thus, for instance, several authors (*cf.* Elliott and Porter)[4] recommend a pH of 9·6. Grasshof[6] states, "Die quantitative Reduktion zur Stufe des Nitrites ist von der Einhaltung eines bestimmten pH-Wertes abhängig, der etwas unterhalb des Neutralpunktes liegt. Steigender pH bewirkt eine unvollständige, fallender eine weitergehende Reduktion." but uses an ammonium–ammonia buffer having a pH which can be calculated to be about 8·1. Henriksen and Selmer-Olsen,[9] using a buffer of pH 8·6, state, "The pH of the ammonium chloride buffer used could be varied between 5·0 and 10·0 without effect on the reduction of nitrate to nitrite.".

A second requirement for the solution is that it must prevent precipitation of cadmium hydroxide on the surface of the cadmium particles, which would seriously lower the efficiency of the reductor. Several authors have considered this problem but no one seems to have been aware of the fact that the production of cadmium ions in the reductor is very much larger than that caused by the nitrate reduction alone. As earlier established,[11] dissolved oxygen is very rapidly and quantitatively reduced according to

$$2Cd + O_2 + 4H^+ = 2Cd^{2+} + 2H_2O$$

thus producing an equivalent amount of cadmium ions. Around the neutral point only insignificant amounts of cadmium ions are produced by reduction of hydrogen ions. Dilute water solutions in equilibrium with air contain about 0·5 mg-atm of oxygen per litre corresponding to a cadmium concentration of about 0·5 m*M*. This concentration is further increased by the nitrate reduction but only by an amount of a lower order of magnitude. The solubility of cadmium hydroxide in pure water is about 0·01 m*M* and its solubility product about 6×10^{-15}. At a cadmium-ion concentration of 0·5m*M* precipitation of hydroxide is calculated to begin at about pH 8·5 if no ionic strength or complexing effects are considered. The risk of precipitation should be higher in fresh water than in sea-water, in which the complexing effect of chloride ions should be noticeable.

As seen from the reaction equation the reduction of oxygen will remove two hydrogen ions for every atom of oxygen. This corresponds to addition of 1 meq of base per litre of solution: a considerable increase of pH in unbuffered solutions will therefore occur.

From these considerations the following conclusions may be drawn. An investigation of the pH-dependence of the reduction is necessary. The buffer solutions to be used should have capacity enough to allow the addition of 1 meq of base per litre without a greater change of pH than a few tenths of a unit; they should if possible be used at their maximum buffer capacity. At higher pH-values the buffer solutions should contain a substance, preferably the buffer substance itself, able to form soluble complexes with cadmium ions, sufficiently stable to prevent precipitation of cadmium hydroxide at the pH of the buffer.

The time of contact

The reduction of nitrate and a simultaneously proceeding slow reduction of the nitrite formed would result in an optimal time of contact between metal and solution for a maximum yield of nitrite. Though the process may be performed by shaking the finely divided metal with the solution,[4] only the reduction in a reductor column is considered here as the generally most practical method. The optimal time of contact is a function of the surface area of the metal per unit of volume, its bed volume in the reductor and the flow-rate, as well as of the properties of the solution and the reduction potential of the metal previously discussed. If the flow-rate is expressed in bed-volumes/min (henceforth abbreviated bv/min), for roughly equal bed-diameters the optimal time of contact for a certain cadmium preparation and solution would be determined by the flow-rate only. The usual procedure for manual analysis has been to use an open reductor with a reservoir for the solution at its upper end, and an adjustment of the flow-rate with a stop-cock. This does not give rise to a constant flow-rate, but only a constant time for passage of a certain added volume. It therefore seems to be a better procedure, even for manual analyses, to use closed reductors and to pump the solution through them at a constant flow-rate, as is done in the flow systems for automatic analysis.

The nitrite determination

The most promising method for the determination of nitrite seems to be Bendschneider and Robinson's[12] modification of the method proposed by Shinn.[13] The nitrite is made to react with sulphanilamide, forming a diazonium salt which is coupled to *N*-(1-naphthyl)ethylenediamine. The resulting aminoazo compound has a molar absorptivity of about $5 \times 10^4\,\text{l.mole}^{-1}.\text{cm}^{-1}$ at 543 nm, the wavelength of its absorption maximum. Though the method seems to be fairly free from interferences the following precautionary measures should be taken when trying to utilize its full intrinsic precision. To avoid errors on account of minute variations of the absorptivity due to variations of, *e.g.*, temperature and composition of the solution, the nitrite standard should be made up to the same concentration as the sample as regards the buffer, added salts *etc.* and be processed simultaneously with the sample. The neutralizing effect of the buffer on the diazotizing reagent should be considered. Rather than measurement of the absorbance, its deviation from that of a nitrite standard corresponding to a 100% yield of nitrite should be determined by differential spectrophotometry.

EXPERIMENTAL

Equipment

To obtain a constant and adjustable flow-rate a peristaltic pump (Gilson "Minipuls II") with 2·6 mm i.d. Tygon tubing was used. With this dimension the maximum flow-rate was 10 ml/min. By use of two tubes connected to a T-tube before the reductor, the flow-rate could be doubled.

The reductor tubes were straight glass tubes of 1·0 cm^2 inner cross section, at the inlet end narrowed down to 4 mm o.d., at the outlet end closed with a ground joint or a rubber stopper with an outlet tube of 4 mm o.d. The cadmium bed (for bed length, see the tables) was enclosed between Pyrex wool plugs. To fill the reductors, the inlet end was connected to the pump, allowing buffer solution of pH 6·9 (see later on) to be pumped into the tube and the level of the solution to be raised or lowered at will. The cadmium was introduced in portions, the tube being continuously tapped to facilitate packing, and solution being kept above the cadmium level to avoid entrapped air. Small stray air bubbles are without consequence but can easily be removed by slowly pumping deaerated buffer solution through the reductor. The reductor was used in the vertical position with the inlet end at the bottom. Each day before the first series of reductions 25 ml of 0·05*M* sulphuric acid were passed through to remove any cadmium hydroxide which might possibly have formed, followed by buffer solution of pH 6·9 until the effluent was neutral. When not in use the reductors were kept filled with the buffer solution, and the inlet and outlet tubes closed with glass rods.

Cadmium preparations

Electrolytically precipitated cadmium (abbreviated e.p. cadmium). Prepared as described in an earlier paper;[11] the suggested method of storage, *i.e.*, keeping the cadmium crystals in the dry state, was employed. The material consists of fine dendritic needles and is fairly voluminous. About 11·5 g are needed to form a 10-cm^3 bed, the interstitial volume thus being about 85% of the total. Due to the method of preparation the percentage of foreign metals should be low.

Cadmium filings. The starting material was "Cadmium Sticks Reagent" from Matheson, Coleman & Bell with stated maxima of Cu 0·005, Fe 0·001, Pb 0·02 and Zn 0·1%. The burrs were removed from a brand-new rasp by rasping 20–30 g of cadmium. The filings thereafter obtained were washed with acetone, 2*M* hydrochloric acid, water and methanol, dried *in vacuo* and kept over silica gel in a desiccator. About 23 g are needed for a 10-cm^3 bed; the interstitial volume is about 74% of the total.

From these filings *"copperized" cadmium* was prepared by shaking 10 g with 25 ml of 0·08*M* copper sulphate. The product was washed with buffer solution of pH 6·9 and directly used for filling the reductor. In an analogous way *"silverized" cadmium* was prepared from 10 g of filings and 40 ml of 0·05*M* silver nitrate. In both cases precipitated copper or silver not adhering to the cadmium particles was removed by the washing. *Amalgamated cadmium* filings were prepared by shaking the filings with a solution of mercuric chloride in 0·1*M* hydrochloric acid, calculated to give amalgams of 1, 2 or 4% of mercury. The amalgams were treated as above.

Granulated cadmium. Merck's "Cadmium grob gepulvert, zur Füllung von Reduktoren" was passed through sieves and the 0·5–1 mm fraction washed and dried as described for the filings. About 10 g are needed for a 2-cm^3 bed, the interstitial volume being about 55% of the total.

Solutions

Buffer solutions were prepared from reagent grade chemicals in the concentrations given in Table 1. The imidazole in the pH 9·3 buffer was added as a complexing agent for cadmium ions ($\beta_4 \sim 7{\cdot}5$). Its complexing effect is not significantly influenced by an excess of calcium or magnesium ions. The solubility of cadmium hydroxide in the buffer solutions of pH 8·0 and 9·3 was determined. A small amount of e.p. cadmium was added to the solution and the mixture stirred in the presence of air until turbid from the precipitation of cadmium hydroxide. After filtration, and removal of the chlorides by evaporation with a small excess of sulphuric acid, the cadmium concentration was determined by potentiometric titration with EDTA.[11] The

Table 1. Buffer solutions used

Buffer *pH*	Moles of constituents used to make up 1 litre of stock solution	Dilution for use
5·4	0·150 tris(hydroxymethyl)aminomethane, 0·100 succinic acid	1:10
5·7	1·00 imidazole, 0·95 HCl	1:100
6·9	1·00 imidazole, 0·50 HCl	1:100
8·0	1·00 tris(hydroxymethyl)aminomethane, 0·50 HCl	1:100
9·3	1·00 NH_3, 1·00 NH_4Cl, 1·00 imidazole	1:100
5·1	1·00 NH_4Cl	1:10

solubility found in buffer of pH 8·0 was 1·22m*M*, in buffer of pH 9·3 1·18m*M*. The latter buffer without imidazole gave a solubility of only 0·56m*M* which was considered too close to the calculated minimum permissible value of 0·5m*M*. In this connection it may be mentioned that the solubility in a synthetic ocean-water of 3·5% salinity was found to be 0·48m*M*.

Standard solutions of 0·02*M* potassium and sodium nitrates were prepared from reagent grade chemicals dried at 110°. The solutions were stored in dark brown bottles. The nitrogen contents of both preparations were determined by reduction to ammonia with Devarda's alloy, distillation and titration.[14] No difference >0·05% relative was established. Dilutions of these solutions to 20µ*M*, containing buffer and other additions if any, were freshly prepared each day.

The diazotizing reagent. Sulphanilamide (2·50 g) and 50 ml of hydrochloric acid (1 + 1) were dissolved in water and diluted to 250 ml. For use in solutions with an excess of base >0·01*M*, the acid concentration was appropriately increased.

The colour developer. N-(1-Naphthyl)ethylenediamine dihydrochloride (0·250 g) was dissolved in water and diluted to 250 ml. The solution was kept in the dark in a refrigerator. Small portions were withdrawn and brought to room temperature before use.

Procedure

If not otherwise stated, the experiments were carried out at room temperature (20–23°).

In each series of experiments the flow-rate was varied and a sample taken for each flow-rate for the determination of nitrite. To minimize increases in concentration by evaporation at low flow-rates it was necessary to seal the vessels connected to the pump and reductor with rubber stoppers with capillary holes for equalizing the pressure. Before each series of experiments about 25 ml of 0·05*M* sulphuric acid were pumped through the reductor at the maximum flow-rate, followed by buffer solution of pH 6·9 until the effluent was neutral. The flow-rate was then adjusted to the highest value intended, the intake of the pump connected to the solution to be reduced, and a volume of about 4 times the free volume in the tubing and reductor pumped through the system. A sample allowing 10 ml to be pipetted out was then collected in a test-tube which was immediately thereafter sealed with a rubber stopper. Without the pump being stopped, the flow-rate was adjusted to the next value and a volume of about 1·5 times the free volume of the system was passed through before the next sample was collected, and so forth. On conclusion of the reductions the system was washed out and filled with buffer solution of pH 6·9.

Without undue delay, 10-ml portions of the collected samples as well as of a nitrite standard having the same concentration as the nitrate solution (even with regard to buffer and other additions if any), were pipetted into long-necked 25-ml flasks. With an "Oxford sampler" 200 µl of the diazotizing reagent were added and mixed by swirling, and after 5 min 200 µl of the colour developer were added in the same way. After a further 15 min the difference in absorbance at 543 nm of sample and nitrate standard was determined in a Beckman B spectrophotometer connected to a stabilized power supply, 1-cm cells being used, with the sample solution as zero.

The validity of Beer's law was confirmed. For each nitrite standard differing in composition, the absorbance was determined by using the same solution, without nitrite, as blank. The absorbance showed only minute variations for different buffers. The absorbance obtained from the 20 µ*M* nitrite solution used was ~0·97. Thus a deviation of 0·001 in absorbance corresponds to ~0·1% in yield of nitrite. The reproducibility of measurement of simultaneously developed 20 µ*M* standard solutions was better than 0·001 absorbance units.

As the same buffer *etc.* were used in both the nitrate and the nitrite standards, a blank caused by nitrite in the buffer *etc.* will cancel out if nitrite is not decomposed in the process. A blank caused by nitrate will, however, show and this was determined by reducing a solution containing only buffer *etc.* at the flow-rate found as optimum and measuring it against the unreduced solution. The absorbance of this blank, usually <0·001 and never >0·005, was applied as a correction.

RESULTS

The pH-dependence of the nitrite yield

In strongly acidic solution, ~5*M* sulphuric acid, nitrate is quantitatively reduced to ammonia by iron ($E^\circ = -0{\cdot}44$ V). On the other hand, the same reduction can be carried out in strongly alkaline solution by using a powerful reducing agent such as Devarda's alloy (Cu, Al, Zn). According to the author's experiments, the details of which will not be described in this paper, nitrate is rapidly reduced by cadmium at low pH (1–3) to hydroxylamine and small amounts of ammonia. In the pH interval 3–5 the velocity of this reaction decreases fairly rapidly and the reduction tends to stop at the formation of nitrite. The following experiments were intended to determine the yield of nitrite in the pH interval 5·4–9·3.

Solutions 20µ*M* in regard to KNO_3 and containing buffers in the dilutions given in Table 1 were reduced at different flow-rates in a reductor containing e.p. cadmium. This material was preferred as a representative of pure cadmium on account of the satisfying results obtained with it for other purposes, *cf.* Nydahl.[11] In this connection a study was also made of any simultaneously proceeding reduction of nitrite, starting with buffered 20µ*M* $NaNO_2$ solutions. Further details and the results are given in Tables 2 and 3.

As far as the increase in pH during the reduction is concerned, the following observation can be made. On reduction of the dissolved oxygen the concentration of base is increased by about 1 meq/l. while, in the present case, the reduction of nitrate contributes only about 0·04 meq/l., an amount which may be neglected in the following discussion. In the buffers

Table 2. The increase in pH on reduction. Solutions 20 µ*M* in regard to KNO_3, and containing buffers in the dilutions given in Table 1, were passed through e.p. cadmium. Bed dimensions: 5·2 cm × 0·96 cm^2 = 5·0 cm^3. Flow-rate 0·5 bv/min

Buffer *pH*	pH found	
	before redn.	after redn.
5·4	5·39	5·61
5·7	5·73	6·26
6·9	6·92	7·16
8·0	8·03	8·32
9·3	9·32	9·47
5·1	5·14	7·52

Table 3. Reduction of 20 μM nitrate or nitrite solutions by e.p. cadmium as a function of pH and flow-rate. Bed dimensions: 5·2 cm × 0·96 cm^2 = 5·0 cm^3.

Flow-rate, *bv/min*	Yield or recovery of nitrite, %, found by reduction using buffers (*cf.* Table 2) of pH						
	5·4	5·7	6·9	5·1	8·0	9·3	9·3*
				Reduction of nitrate			
4	77·2	86·1		57·4	—	—	
2	90·0	95·1	90·0	78·8	—	—	—
1	92·3	97·7	97·0	92·9	96·3	93·9	93·6
0·5	86·8	96·8	98·9	98·7	99·2	98·3	98·9
0·2	70·5	91·6	98·5	99·8	99·7	99·9	99·8
0·1	—			—	99·5	100·1	99·8
0·05	—	—	—	—	99·4	99·9	99·7
0·025	—	—	—	—	—	—	99·8
				Reduction of nitrite			
4	98·4	99·5	—	—	—	—	—
1	92·8	98·1	99·5	—	—	—	—
0·5	—	—	—	—	100·0	100·0	—
0·2	69·5	90·9	98·4	99·7	—	—	99·9
0·1				—	99·6		—
0·05	—	—	—	—	—	99·8	99·8

* Bed dimensions: 11·0 cm × 0·91 cm^2 = 10·0 cm^3.

of pH 6·9 and 8·0, 0·005*M* in regard to base and corresponding acid, used at their maximum buffer capacity, the increase of pH was about 0·3, and in the twice as concentrated buffer of pH 9·3, half that amount.

According to an earlier paper[11] the reduction of the dissolved oxygen proceeds very rapidly. Even at a flow-rate of 33 bv/min, 98·5% of the oxygen is reduced. As the reduction of nitrate seems to proceed at less than 1/30 of this rate it is obviously the pH determined in the reduced solution that has been predominant during the reduction and that consequently has determined the course of the reaction. This is clearly evident in the series of experiments with the unbuffered 0·1*M* NH_4Cl which shows an increase of pH from 5·1 to 7·5 but a yield of nitrite intermediate between those obtained in solutions of final pH 7·2 and 8·3. This series, moreover, shows the influence of the chloride concentration, which will be discussed in a later section, and is therefore not discussed in the following.

If the pH is kept constant during the reduction of nitrate, a maximum yield of nitrite is obtained at a certain flow-rate. At flow-rates higher than the optimal the reduction is incomplete, at lower flow-rates the yields closely follow the recoveries obtained by the direct reduction of nitrite. This is particularly evident at a flow-rate of 0·2 bv/min.

With increasing pH the maximum is shifted to lower flow-rates, and grows broader whilst the yield approaches but does not reach 100%. Even at a final pH of 9·5 a slight reduction of nitrite occurs.

In its initial stage the reduction of nitrite at a constant pH increases almost linearly with the residence time in the reductor, as illustrated in Fig. 1, where the loss in recovery is plotted against the inverse of the flow-rate. Accordingly, the product *K* of loss (%) and flow-rate (bv/min), signifying the loss of nitrite at a flow-rate of 1 bv/min when reducing a nitrite solution, is nearly constant and, *ceteris paribus*, a measure of the reduction rate at the selected pH. Thus *K* is ~7 at a final pH of 5·6 and ~0·01 at a final pH of 9·5.

Table 4. Effect of temperature on the reduction of 20μM KNO_3 solutions by e.p. cadmium. Buffer of pH 8·0. Bed dimensions: 5·2 cm × 0·96 cm^2 = 5·0 cm^3. The approximate values of *K* are calculated from the losses at the flow-rate of 0·1 bv/min

Temp., °C	Yield of nitrite, %, at a flow-rate, *bv/min*, of						*K*, approx.
	2	1	0·5	0·2	0·1	0·05	
30·0	97·5	99·4	99·7	99·5	99·0	—	0·1
20·0	96·6	99·5	99·7	99·5	99·4	99·0	0·06
10·0	93·6	98·0	99·6	99·8	99·7	99·6	0·03

No specific influence of the different buffers can be gathered from these results.

The investigation was not extended to pH values above 9·5 on account of the expected difficulty of avoiding precipitation of cadmium hydroxide and also hydroxides or carbonates of other metals possibly present, when using the method in practice. From the latter point of view the buffer of pH 8·0 may well be preferred though the yield is slightly lower than that obtained with buffer of pH 9·3. On this account most of the following experiments were performed with use of the buffer of pH 8·0. An additional reason was that tendencies to deviations of the yield are larger and thus more easily observed than at a higher pH.

The effect of temperature on the rate of reduction

Reductions were performed with reductor and inlet tubing immersed in a thermostat. Further details and results are given in Table 4. In the interval 20–30° the temperature has little effect on the rate of reduction of nitrate. At 10° the reduction is noticeably slower, causing a shift of the maximum to the next lower flow-rate. As is evident from the values of *K*, the rate of reduction of nitrite is approximately doubled for a 10° increase of temperature. However, owing to the low values of *K*, the yields at the maxima vary only within experimental error.

Effect of salt concentration

For the determination of nitrate in sea-water it is of obvious interest to investigate the effect of the sodium chloride concentration on the yield. The results

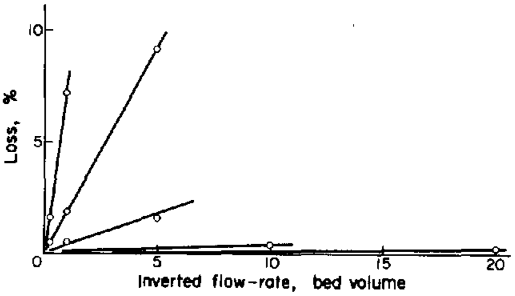

Fig. 1. Loss in recovery of nitrite at different pH values, plotted against the inverted flow-rate.

Table 5. Effect of the NaCl or Na_2SO_4 concentration on the reduction of 20μM KNO_3 solutions by e.p. cadmium. Bed dimensions: 11·0 cm × 0·91 cm² = 10·0 cm³

Buffer *pH*	NaCl, *M*	Yield of nitrite, %, at a flow-rate, *bv/min*, of 1	0·5	0·2	0·1	0·05	0·025
6·9	0*	97·0	98·9	98·5	—	—	
	0·1	79·0	93·6	99·0	98·4	96·7	—
	0·5	—	80·1	96·6	98·6	97·7	—
8·0	0*	96·3	99·2	99·7	99·5	99·4	—
	0·1	75·3	92·1	99·5	99·8	99·5	—
	0·5	—	81·2	97·4	99·7	99·7†	99·5
9·3	0*	93·6	98·9	99·8	99·8	99·7	99·8
	0·1	77·3	86·8	98·8	99·9	99·9	99·6
	0·5	—	75·8	95·9	99·7	100·1§	99·9
	Na_2SO_4, *M*						
8·0	0·05	92·2	99·0				
	0·1	88·4	98·1				

* Values from Table 3 inserted for comparison.

† The reduction of a 20μM $NaNO_2$ solution gave 99·7% recovery.

§ The reduction of a 20μM $NaNO_2$ solution gave 99·9% recovery.

of such experiments are given in Table 5. The concentration of 0·5M NaCl approximately corresponds to that of ocean-water while 0·1M NaCl may be considered as equivalent to Baltic sea-water.

Sodium chloride has a strongly retarding effect on the rate of the nitrate reduction, an effect which increases with the chloride concentration and causes the maxima to be shifted to lower flow-rates. The reduction rate of nitrite is also retarded though the effect is not so drastically noticeable as in the case of nitrate. The maximum yield remains unchanged within experimental error.

For comparison a few experiments were carried out in the presence of sodium sulphate. It was found that the dye formed by the colour reaction was not sufficiently soluble at the sulphate concentrations used but began to precipitate before the measurement was ended. The reduced solution was therefore diluted 5 times before the colour development and the absorbance determined in a 5-cm cell. A comparison of these results with those obtained in the presence of sodium chloride shows that the retardation is mainly caused by the chloride ions. Considering the reaction equation for the reduction, the reducing power of cadmium should increase when the concentration of cadmium ions decreases, in this case by complex formation with the chloride ions, and the reduction should be accelerated instead of retarded. However, the chloride ions might in some way interfere with the reaction mechanism.

The results obtained with the 0·1M NH_4Cl solution previously mentioned (Table 3) show about the same retardation as obtained with a 0·1M NaCl solution.

Effect of various cadmium and metal–cadmium preparations

Reduction experiments were carried out in the same way as before, using various commercial forms of cadmium, with or without copper treatment, or treatment with silver or mercury solutions. The results are given in Table 6. The different reduction properties are characterized by stating the maximum yield, the flow-rate at the maximum and the approximate value of K.

Table 6. Reduction of 20μM KNO_3 solutions by various cadmium or metal–cadmium preparations. Buffer pH 8·0

Preparation	Bed dimensions	At the maximum: yield, %	flow-rate, *bv/min*	*K*, approx.
E.p. Cd§	*	99·7	0·2	0·04
Cd filings	*	99·6	0·05	0·02
Granulated Cd	†	97·7	2	3
Cd filings + Cu	†	95·9	5	12
Cd filings + Cu‡	†	98·5	2	1·2
Cd filings + Ag	†	95·4	5	12
Cd filings, 1% Hg	*	99·8	0·4	0·08
Cd filings, 2% Hg	*	99·8	0·5	0·06
Cd filings, 4% Hg	*	99·7	1	0·3
Granulated Cd, 1% Hg	†	98·0	2·5	2·3

* 4·9 cm × 1·02 cm² = 5·0 cm³.

† 2·1 cm × 0·97 cm² = 2·0 cm³.

§ Values from Table 3 inserted for comparison.

‡ In 0·5M NaCl solution.

Filings obtained by rasping pure cadmium gave, within experimental error, the same yield as e.p. cadmium but at a quarter the flow-rate, which may be ascribed to some form of passivity or, simply, a considerably smaller specific surface area. In this connection it may be mentioned that the first 20–30 g of filings obtained by using a brand-new rasp gave a higher reduction rate, probably on account of contamination by burrs from the rasp.

The granulated cadmium had an unexpectedly high rate of reduction, also with respect to nitrite, and consequently with a poorer yield at the maximum. Analysis of this material indicated Cu < 2 ppm, Zn ~ 10 ppm but also a residue, insoluble in HCl or HNO_3, of 0·1%, at least partly consisting of graphite. By forming local cells this residue is probably the cause of the increased reduction power.

Copperizing the filings brought about, as expected, an appreciable increase of the reducing power. The rate of reduction of nitrite is high, and the yield at maximum poor. If the reduction is carried out in 0·5M NaCl solution the retarding effect of the chloride ions will cause a somewhat better yield. These series of experiments are also illustrated by the curves of Fig. 2 showing the possibility of errors when using copperized cadmium without due attention to chloride contents and flow-rate.

Silverizing the cadmium brought about approximately the same results as copperizing.

Amalgamation of the cadmium filings brought about a considerable increase of the reduction rate, whilst retaining the same yield as that obtained with untreated filings or with e.p. cadmium. This fact indicates that the reduction potential has remained practically constant whereas a hypothetic passivity might have been removed or the specific surface area increased. Actually, the amalgamated filings under the microscope at 100× magnification showed a rough, grainy surface unlike the bright one of the untreated

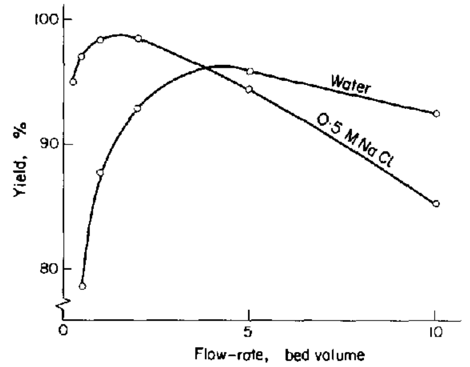

Fig. 2. Reduction of nitrate by copperized cadmium. Effect of chloride ions on the rate of reduction. Buffer pH 8·0.

filings. Varying the percentage of mercury brought about only minor variations of the reduction properties. Amalgamation of the granulated cadmium had little influence on the effect of its impurities. Amalgamation of e.p. cadmium led to a breakdown of its dendritic structure with the formation of lumps, causing difficulties in producing a homogeneous reductor bed. These experiments were therefore not pursued.

DISCUSSION AND CONCLUSIONS

The reductor cadmium

Every new sample of cadmium or metal–cadmium should be tested for its reducing power under the proper conditions by determining the yield of nitrite at the optimum flow-rate as previously described. Provided that these parameters are known it seems obvious that each type of reductor filling might be used for the determination of nitrate if allowance is made for the reduction of the nitrite formed as well as of that which might be originally present in the sample, depending on the error which can be tolerated.

A high rate of reduction of nitrite, as for instance with copper–cadmium in the reductor, results in a narrow optimum range of flow-rate, the location of which varies with the chloride concentration and probably also with the temperature. The correction for nitrite reduction (when copper–cadmium is used, amounting to 1·5–4% of the expected yield, depending on the chloride concentration) will therefore suffer from larger errors than at a low reduction rate. From this point of view the use of pure cadmium or amalgamated pure cadmium is to be preferred. The nitrite correction then amounts to only a few tenths of 1%, and at pH 9·5 to about 0·1%, within a far broader range of flow-rate. If, however, larger errors may be tolerated, the copper–cadmium, or an impure form of cadmium such as the granulated cadmium tested in this paper, can be used to advantage, as the time for reduction is considerably shortened. This gain of time should be especially valuable for the analysis of sea-water since it counteracts the retarding effect of the chlorides. Another advantage is that the purity of the cadmium used as starting material is of little or no consequence.

The special procedure, unsupported by experimental evidence, used by Wood *et al.*[8] for the preparation of copper–cadmium in order to avoid contact with air, seems not to serve any useful purpose since the metal is still allowed to react with the oxygen contained in the washing solution. Incidentally, the same observation applies to the procedure used by Koroleff[7] for the preparation of amalgamated cadmium.

The amount of copper remaining on the filings after the washing may be significant for the reduction rate as the copper functions as a cathode and its surface area consequently should have an influence on the time of contact.

E.p. cadmium and amalgamated pure cadmium filings both give a very low rate of reduction of nitrite. Which reductor filling to use is partly a matter of availability. If cadmium filings or granulated cadmium of sufficient purity and proper size were commercially available their use would be convenient since the amalgamation is easily carried out. It might also be possible to use these reductor metals without amalgamation after depassivation or enlargement of the surface area by etching. The manual tooling of a cadmium stick with a rasp is laborious and involves the risk of contamination. E.p. cadmium is easily prepared, and since nobler metals are removed with the anodic slime there is no risk of the formation of local cells. Precipitation of cadmium from a cadmium sulphate solution by zinc[1] is said to give easily clogged columns,[4] and also involves risk of formation of local cells by the nobler metals which might be present in the zinc and in this case are not removed.

If a reductor contains particles of different sizes, the smallest ones, at least partly packed in the interstices between the larger particles, are used up first and the surface area of the reductor bed is consequently lowered. This may have been a contributory cause of the gradually decreasing efficiency of the reductor observed by several authors. Another cause, and probably the main one, may have been the precipitation on the cadmium particles of hydroxides *etc.* as previously mentioned, or of such substances as humic matter, soil colloids or micro-organisms. This source of error should not be neglected but the reductor checked as to its reduction power at appropriate intervals. Concerning the e.p. cadmium used for the experiments on pure solutions in this paper, no decrease in efficiency in the optimum range has been observed. In this connection, and as a conceivable remedy against precipitated matter, it may be mentioned that amalgamated pure cadmium as well as e.p. cadmium can be washed with hydrochloric acid of 4*M* or even higher concentration without appreciable hydrogen evolution or change of efficiency at the optimum flow-rate.

Samples containing metals precipitated by cadmium will contaminate the reductor with these metals and, depending on the degree of contamination, have an effect on its reducing power. Thus a blackening was observed on the inlet end of the cadmium bed after the passage of several litres of solution through the reductor. This blackening was caused by the copper content of the distilled water, about 30 μg/l., but has so far not caused any significant increase in efficiency. The proposed use of copper wool[7,10] for enclosing the reductor bed should, however, be avoided. Probably a copper–cadmium reductor might be used to advantage for samples containing significant amounts of precipitable metals.

pH and buffer solutions

The higher the pH, the lower is the nitrite correction and the broader the optimum range of flow-rate. A lower pH than that necessary to avoid precipitation in the reductor should therefore not be used. A pH below 8 should rarely be needed. If larger errors are tolerated the demand for a predetermined and constant pH naturally decreases. Thus Table 3 shows that at a flow-rate of 0·5 bv/min a final pH varying between 6·3 and 9·5 causes the yield of nitrite to vary between 97 and 99%. The following discussion, however, presupposes a striving for minimal errors.

The buffer concentrations used in the present investigation appear sufficient for unbuffered sample solutions. However, the pH and buffer capacity of a sample solution may be such that addition of acid or base or the use of a more concentrated buffer solution is needed. This must be considered in each individual case.

The introduction of imidazole into the buffer of pH 9·3 might be avoided by using the buffer at a higher concentration. Its ability to complex cadmium ions is then increased and a higher buffer capacity is gained. To avoid higher chloride concentration the ammonium chloride might be replaced by ammonium acetate.

The use of an unbuffered ammonium chloride solution will cause a pH which varies with the actual oxygen content, pH and buffer capacity of the sample. The use of the tetrasodium salt of EDTA (2m*M*) as complexing agent for cadmium ions without addition of any buffer[8] will also cause pH variations depending on the actual composition of the sample solution.

Any significant increase of the buffer concentration should be compensated for by a corresponding increase of the concentration of hydrochloric acid in the diazotizing reagent in order to keep the pH constant during diazotation and colour development.

Reduction and nitrite determination

The use of a peristaltic pump in order to facilitate the attainment of a sufficiently constant flow-rate is a prerequisite. Such pumps designed for the simultaneous running of several samples are commercially available.

In the present investigation the absorbance was determined in a 1-cm cell and a sample volume of 10 ml was sufficient for rinsing and measurement. In practice, on account of low concentrations, it will sometimes be necessary to determine the absorbance in 5- or 10-cm cells requiring a sample volume up to 50 ml. When several successive reductions are run, and assuming that the system is to be rinsed with two times its free volume between samples, the time, *t*, in minutes, required for each sample, is obtained from the equation

$$t = (1/F)(V_s/V_b + 2V_f/V_b)$$

where F is the flow-rate in bv/min, V_s the sample volume, V_b the bed volume and V_f the free volume of the system. The approximate flow-rate to use being known, the appropriate bed volume in relation to the required sample volume can be estimated, as well as the required pump capacity.

The effect or removal of interfering substances is not considered in this paper because this will be a problem particular for every new kind of sample. The vital point is of course to reveal such interferences by appropriate experiments and then do something about it.

If a high degree of accuracy is desired, as for instance in determination of nitrate in commercial fertilizers, the differential spectrophotometric method is recommended. In that case the sample concentration can usually be chosen sufficiently high and near that of the standard solution. Regarding samples of natural waters, the demand for accuracy is considerably lower and their nitrate contents so widely varied and sometimes so low that differential spectrophotometry does not present any significant advantages. A calibration curve may then be applied in the usual way. In principle the calibration should be run with the same composition, temperature *etc.* in the standard nitrite solutions as for the sample. Sufficient experience will show to what extent deviations from this rule may be permitted.

The question may arise whether the analysis might not be performed in a wholly empirical way by establishing the relation between nitrate concentration and absorbance, thus omitting the calibration with nitrite standard solutions. This is, of course, possible if nitrite is absent from the sample or present only in such amounts that the correction for its decomposition is insignificant. Yet the need for checking this relation at appropriate intervals remains.

The running of reagent blanks as well as frequent checking of the cell correction is, of course, the more important the lower the concentrations to be determined.

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AN INTERLABORATORY STUDY OF POTASSIUM DETERMINATION IN ROCKS AND MINERALS*

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Summary—Seven laboratories took part in this interlaboratory study which was part of an investigation of the flame-spectrometric determination of potassium in rocks and minerals suitable for potassium–argon age-measurement. Three of these laboratories determined potassium in the following five international reference rocks: tonalite T-1, basalt BCR-1, andesite AGV-1, granite G-2, and granodiorite GSP-1. The other five samples (with the number of laboratories analysing them in parentheses) were: a chlorite rock (7), an altered basic igneous rock (5), an altered basaltic andesite (5), a biotite (6) and a potassium feldspar (7). Details of sample preparation and methods of analysis are given; no laboratory used exactly the same method as any of the other six laboratories. Results have been examined by analysis of variance; larger relative between- and within-laboratory variations occurred for the two samples containing less than 0.1% potassium than for seven of the eight other (higher potassium) samples; between-laboratory variations for the basalt BCR-1 and, to a lesser extent, the andesite AGV-1, were high and of similar magnitude to those for the samples containing less than 0.1% potassium. The causes of any poor interlaboratory agreement in the present study are considered.

This interlaboratory study was part of an investigation[1] of the flame-spectrometric determination of potassium in the many types of rocks and minerals[2] suitable for potassium–argon age-determination. The whole investigation was aimed at improving the reliability of potassium–argon age-determinations, by minimizing errors in the flame-spectrometric determination of potassium. The poor interlaboratory agreement of potassium results for the biotite B-3203 has been discussed by Pinson[3] who considered it to be "one of the great curiosities of modern analytical chemistry that it is possible to analyse for argon, which occurs to the extent of about 0.01 to 0.001 cc of gas per gram in a sample, to a much greater accuracy and with more confidence than it is possible to analyse for one of the major elements, namely potassium". The great majority of results reported for the biotite B-3203 involved flame emission measurement of the sample solution.

Results of previous interlaboratory studies of potassium determination are summarized in Table 1. The best interlaboratory agreement in Table 1 was obtained for the muscovite P-207: in this sample the between-laboratory relative standard deviations of results for potassium and potassium–argon age were 1.3 and 2.6% respectively.[7] Such agreement, while adequate for many age-determinations, is not adequate in many stratigraphic studies where, according to Cooper,[5] the total relative analytical error in a potassium–argon age-determination should not exceed 0.5%.

Ingamells[14] has found that poor interlaboratory agreement for the biotite B-3203 and the muscovite P-207 is largely due to sample inhomogeneity. It is very likely that sampling errors were eliminated in the present study by fine grinding as described later in this paper. Thus the variation of results observed in the present study can be confidently regarded as due to analytical errors as distinct from sampling errors.

The aims of the present interlaboratory study were:

(*i*) to compare between-laboratory variations with those in previous studies (Table 1);

(*ii*) to see whether between-laboratory variations are significantly greater than within-laboratory variations, and thus to indicate systematic errors in the methods of at least some of the participating laboratories.

As shown in Table 2, three laboratories in Australia and one in each of New Zealand, Russia, South Africa and U.S.A. took part in this study. These laboratories are all engaged in rock and mineral analysis and five of them in potassium–argon age-determination. Henceforth in this paper, the laboratories are identified by letters of the alphabet.

All participating laboratories were requested to:

· (*i*) determine potassium twice in each sample and not to do the second analysis concurrently with the first;

(*ii*) determine hygroscopic moisture in each sample at the time of each analysis;

(*iii*) check the accuracy of standard potassium solutions;

(*iv*) report the potassium content in the sample, as received, to 3 or 4 significant figures, to give an apparent precision of 0.1%;

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Table 1. Results of previous interlaboratory studies of potassium determination

Sample	References	No. of labs.	Mean K %	Relative std. devn. of laboratory means, %
Biotite, B-3203	3–6	13	7.58	1.9
Muscovite, P-207	7	22	8.54	1.3
Amphibole (Libby, Mont. 16948)	8	4	1.60	13.2
Granite, G-1	9, 10	34	4.55	2.6
Granite, G-2	10	30	3.74	4.8
Granite, R117	11	12	3.89	3.3
Tonalite, T-1	12	14	1.03	7.0
Lunar soil sample 12070	13	14	0.196	9.1

(*v*) give details of standard compound used;

(*vi*) give details of dissolution and flame methods used.

Ten samples, with potassium contents between 0.05 and 10%, were used in this study. These samples were numbered from NSWMD-1 to NSWMD-10 in order of increasing potassium content. Five of the samples were international reference rocks, namely the tonalite T-1 from Tanzania,[12] and the basalt BCR-1, the andesite AGV-1, the granite G-2 and the granodiorite GSP-1 from the United States Geological Survey.[15] The other five samples were from New South Wales and had previously been analysed at this laboratory; these samples were as follows.

NSWMD-1. Foliated chlorite rock containing minor amounts of talc, quartz and albite; from Cow Flat Talc Mine *via* Bathurst, New South Wales; University of Sydney Geology Department Catalogue No. 46264; collected by Dr. B. J. Barron, New South Wales Department of Mines.

NSWMD-2. Medium-grained, altered basic igneous rock containing relict diopside, and a suite of alteration minerals including chlorite, tremolite and pla-

Table 2. Participating laboratories and analysts

Laboratory	Analyst(s)
Research School of Earth Sciences, The Australian National University, Canberra, Australia 2600	R. Maier
The Australian Mineral Development Laboratories, Frewville, South Australia 5063	J. C. Watts and A. W. Webb
United States Geological Survey, Branch of Analytical Laboratories, Menlo Park, California 94025	L. B. Schlocker
Geochronological Laboratory, Institute of Ore Deposits Geology (IGEM), U.S.S.R. Academy of Sciences, Staromonetny 35, Moscow, U.S.S.R. 109017	L. L. Shanin
Department of Scientific and Industrial Research, The Institute of Nuclear Sciences, Lower Hutt, New Zealand	W. J. McCabe and R. G. Ditchburn
National Chemical Research Laboratory, The South African Council for Scientific and Industrial Research, Pretoria, South Africa	F. W. E. Strelow and A. H. Victor
Chemical Laboratory, N.S.W. Department of Mines, Sydney, Australia 2000	T. D. Rice

Table 3. Methods used in the present study

Laboratory	Summary of method	Standard K compound
A	HF–H_2SO_4 decomp. in Pt dishes. Na buffered, Li int. std. FE measurement on Baird Atomic instrument in propane–air flame. For samples NSWMD-1, -2, -3, prelim. IE sepn. similar to that of Lab. E.	K_2SO_4, Analar, Hopkin and Williams, Batch 20676, heated to constant weight at 500°
B	HF–H_2SO_4 decomp. in Pt dishes. Aliquots buffered with Merck Suprapur Cs_2SO_4 and K measured by AAS (Varian Techtron AA-5 instrument) in acetylene–air flame.	$KHC_8H_4O_4$ dried at 120° for 24 hr
C	Subsamples (100.0 mg) fused with $LiBO_2$ (700.0 mg) in graphite crucibles at 950° for 15 minutes and dissolved in 100.00 ml of 4% v/v HNO_3. A 1:10 dilution was made before aspirating into a direct reading (Li int. std.) IL 343 flame photometer with propane–air flame.	(Note 1)
D	100-mg subsamples decomp. in Pt dishes with HF–$HClO_4$. After addn. of 2.5 g of pure $MgCl_2$ (as buffer), solutions diluted to 50.00 g with water. FE measurement on a "high sensitivity diffraction grating flame spectrophotometer built in the laboratory", in gas (mostly methane)–air flame.	KCl dried at 105°
E	HF–HNO_3 decomp. and ultrasonic dispersion of solid particles in 100-ml Teflon beakers. Evapn. to dryness on water bath. Further HF–HNO_3 treatment and evapn. to dryness. Residue dissolved by adding 0.5 ml of HNO_3 and 10 ml of satd. H_3BO_3, warming and dilg. with H_2O to about 60 ml. K in this solution sepd. by IE on Dowex 50W-X12 resin, 200–400 mesh. K eluted with 0.75*M* HNO_3 collected in weighed glass flask, and measured by FE (propane–air flame and water-cooled burner).	$KHC_8H_4O_4$, Analar, BDH, dried at 120°
F	HF–HCl–$HClO_4$ decomp. in 100-ml Teflon beakers. After heating to $HClO_4$ fumes, contents of beaker dissolved in 10 ml of 1*M* HCl and transf. to a 150-ml Pyrex beaker to be diluted to about 0.2*M* in acid. After addition of 0.10% H_2O_2, K sepd. by IE on Bio-Rad AG 50W-X8 resin, 200–400 mesh. K measured by AAS (Perkin-Elmer 303 instrument, propane–butane–air flame and specially designed flat water-cooled burner).	KCl, Merck "*pro analysi*", dried at 150°
G	$LiBO_2$ fusion of 500-mg subsamples in 30-ml Pt crucibles for 15 min at 900°. Melt dissolved in dilute HNO_3 and an aliquot diluted gravimetrically and buffered with 1.20 mg of Merck Suprapur CsCl per g. K separated from another aliquot by IE on Dowex 50W-X8 resin, 100–200 mesh; K fraction (containing some Na) buffered with Cs as above. Polyethylene-ware used exclusively. K measured by AAS (Varian Techtron AA-5 instrument with digital read-out) in acetylene–air flame. Reported	KCl, "Specpure", heated at 550° for 4 hr

Table 3—continued

Laboratory	Summary of method	Standard K compound
	results are means for both types of measurement solution; individual results are given in Table 9.	

Notes. 1. Laboratory C used analysed samples (of well-established K contents and proven homogeneity) as standards. These were prepared by the same technique as the other samples. Sierra quartz was used for setting instrument to zero; the French biotite BIO-R (7.305% K) and an amphibole (0.758% K) were used to calibrate the instrument.

2. Int std. = internal standard; FE = flame-emission spectrometry; AAS = atomic-absorption spectrometry; IE = cation-exchange chromatography.

gioclase; from Woods Reef *via* Barraba, New South Wales; University of Sydney Geology Department Catalogue No. 47624; collected by Mr. R. Glen, New South Wales Department of Mines.

NSWMD-3. Porphyritic clinopyroxene-rich, altered basaltic andesite also containing phenocrysts (which were probably olivine but have been altered to chlorite) in a matrix of chlorite, carbonate, albite, epidote and sphene; from breccia pipe at Sofala, New South Wales; University of Sydney Geology Department Catalogue No. 46120; collected by Dr. B. J. Barron, New South Wales Department of Mines.

NSWMD-9. Biotite separated manually from host rock which also contained quartz, fluorite and minor amounts of sphalerite; from Torrington, New South Wales; supplied by Mr. D. R. Pinkstone, New South Wales Department of Mines.

NSWMD-10. Impure potassium feldspar containing microcline, some albite and a small amount of quartz; from 13 km SE of Broken Hill, New South Wales.

Because of scarcity of several samples, there was enough of only two samples to be sent to all seven laboratories; the potassium feldspar NSWMD-10 is the only sample of which an appreciable amount (8 vials) remains for distribution to other interested laboratories.

EXPERIMENTAL

Preparation of samples

In order to overcome sampling errors and errors due to segregation of particles on storage,[16] the five samples from New South Wales were ground to pass a 200-mesh sieve; these samples were ground in a 50-ml capacity Siebtechnik tungsten carbide mill. Since the possibility of contamination of low-potassium samples with minerals high in potassium is best avoided,[17] samples were crushed and sieved in order of increasing potassium content.

One jar of each of the five international reference rocks was available. These samples were not further ground or sieved because they were already at least 98% 200-mesh.[15]

Samples were distributed in clear polystyrene vials with polyethylene snap-on caps. These containers, from new stock, were initially washed with tap-water and a brush, followed by washing with demineralized water and drying at 60°C for 24 hr.

Vials to hold a particular sample were numbered and placed, in numerical order, in a row. The sample was thoroughly mixed by being rolled in a large polystyrene jar for 30 min on a rolling machine, and was then added in equal increments, by means of a small nickel spatula, to each vial in turn. This was continued until each vial had its full complement of sample–ranging from 2.7 g for sample NSWMD-7 to 9.0 g for sample NSWMD-10.

Methods used

Table 3 summarizes the methods used and gives details of the standard compounds used. No laboratory used exactly the same method as any of the other six laboratories. All laboratories brought the samples into solution by either hydrofluoric acid attack or lithium metaborate fusion, and subsequently measured potassium concentration by either flame emission or atomic-absorption spectrometry.

Three laboratories (E, F and G) separated potassium by cation-exchange chromatography. Laboratory A did so only for the low-potassium samples, NSWMD-1, NSWMD-2 and NSWMD-3.

Laboratory F filtered off the residues of samples NSWMD-1 and NSWMD-2 after the acid treatment (described in Table 3) and dissolved them with a mixture of phosphoric, perchloric and hydrofluoric acids.[18]

RESULTS AND DISCUSSION

Table 4 summarizes the results for the international reference rocks and also lists the "usable values" of Abbey[19] and, except for the tonalite T-1, results[20] obtained by Laboratory E on initial lots of samples (from United States Geological Survey) different from those used in this study. The right-hand double column of Table 4 summarizes the results of analysis of variance for each sample.

Analysis of variance showed that the results of Laboratories A, D and G in Table 4 agreed well with one another only for the granite G-2. The agreement between the results of these three laboratories was worst for the basalt BCR-1, although the overall mean for this sample agreed very well with the result of Laboratory E—which could indicate that the "usable value" for the basalt BCR-1 is low by about 1.7% relative. For the remaining three international reference rocks, one laboratory reported results consistently lower than those of the other two laboratories.

Results reported in Table 4 for the tonalite T-1 indicate that its "usable value" is high by 1.5–2% relative.

Table 4. Results for international reference rocks

	% K (dry basis)			% Rel. std. devn. of mean of duplicate[a] results of labs. A, D and G	
Sample	"Usable value"	Lab. E[e]	Labs. A, D and G overall mean	Between-lab.	Within lab.
MRT Tonalite T-1	1.03[f]	—	1.008 (0.998–1.014)[b] (0.04–0.15)	0.86[d]	0.62
USGS Basalt BCR-1	1.40	1.429 ± 0.005	1.426 (1.399–1.457) (0.75–1.02) (80/9)	2.02[c]	0.17
USGS Andesite AGV-1	2.43	2.456 ± 0.003	2.430 (2.383–2.458) (0.70–1.35) (11/4)	1.71[c]	0.13
USGS Granite G-2	3.75	3.760 ± 0.013	3.732 (3.725–3.743) (0.11–0.32) (23/21)	0.25	0.28
USGS Granodiorite GSP-1	4.59	4.630 ± 0.015	4.575 (4.541–4.594) (0.05–0.18) (18/12)	0.64[d]	0.28

[a] Labs. A, D and G each reported the results of two separate determinations (carried out at least six days apart) per sample.

[b] The top set of figures in brackets for each sample gives the range of laboratory mean results for potassium; the set below this gives the range of laboratory mean results for hygroscopic moisture; in the lowest brackets for the USGS samples are the Split/Position numbers.

[c] Greater than within-laboratory standard deviation at 99% confidence level.

[d] Not greater than within-laboratory standard deviation at 95% confidence level.

[e] On initial lot of sample different from that analysed by Labs. A, D and G. Each result of Lab. E is the mean of 12 complete determinations ± the 99% confidence limit of the mean.

[f] This "usable value" and subsequent ones are as reported by Abbey.[19].

The result in Table 4 from Laboratory E for a different initial jar of the granodiorite GSP-1 is appreciably higher (by 1.2% relative) than the overall mean result in Table 4; this is probably due to the inhomogeneity of sample GSP-1 which has been noted by Ingamells and Switzer.[17]

Table 5 is rather similar in structure to Table 4 but concerns the five samples from New South Wales. Instances of poor agreement between duplicate analyses can be isolated by examination of tables of individual results for these samples. (Tables of individual results for all samples in the present study can be supplied on request.)

Table 6 gives results of analysis of variance when such instances are excluded. Exclusion of poorly agreeing duplicate analyses before analysis of variance is justified by the fact that, where more than two laboratories have analysed a given sample (as in the present study), the methods of all laboratories must be of the same precision for the conclusions from analysis of variance to be strictly valid.[21]

Low within-laboratory standard deviations in Table 6 of between 0.1 and 0.2% relative indicate the best precision attainable with flame-spectrometric instrumentation; such precision has been well documented elsewhere.[17] However, multiple instrumental readings of sample and standard solutions are necessary for such good precision; the methods of all laboratories in the present study involved such multiple readings. The attainment of flame-spectrometric precision of 0.1–0.2% relative standard deviation, by taking fewer than six sets of individual readings of a given sample solution and appropriate pair of standard solutions, awaits further improvements in nebulizer-burner and gas-control systems.[1]

The emphasis of the remaining discussion in this paper is on problems of accuracy of flame methods for determining potassium in rocks and minerals, rather than precision.

Results of previous interlaboratory studies

Comparison of between-laboratory relative standard deviations in Tables 4 and 5 with those of previous studies in Table 1 shows that only for the basalt BCR-1, the andesite AGV-1, and the low-potassium samples NSWMD-1 and NSWMD-2 does the between-laboratory relative standard deviation exceed 1.3%, which was obtained[7] for the muscovite P-207 and is the lowest figure in Table 1.

Table 5. Results for samples from New South Wales

Sample	No. of labs.	Overall mean % K (dry basis)	% Rel. std. devn. of mean of duplicate[a] results	
			Between-lab.	Within-lab.
Chlorite rock NSWMD-1	7	0.0570 (0.0553–0.0611)[b] (0.14–0.37)	3.59[c]	1.57
Altered basic rock NSWMD-2	5	0.0739 (0.0722–0.0760) (0.19–0.47)	1.89	1.91
Altered andesite NSWMD-3	5	0.3002 (0.297–0.303) (0.40–0.90)	0.86[c]	0.36
Biotite NSWMD-9	6	7.603 (7.48–7.67) (0.15–0.59)	0.89[c]	0.32
Feldspar NSWMD-10	7	9.794 (9.71–9.90) (0.12–0.53)	0.67[c]	0.26

(Analysis by the author of the low-potassium samples gave: %SiO_2 26.5, 55.5, 45.0; Al_2O_3 20.3, 14.5, 9.17; TiO_2 0.17, 0.46, 0.71; ZrO_2 0.02, 0.02, 0.01; Fe_2O_3 3.11, 0.32, 1.61; FeO 22.6, 8.48, 9.31; MnO 0.58, 0.12, 0.26; MgO 15.2, 4.18, 15.0; CaO 0.22, 7.68, 9.84; SrO 0.005, 0.05, <0.005; BaO 0.01, <0.01, 0.01; Na_2O 0.02, 5.93, 1.27; K_2O 0.06, 0.09, 0.36; P_2O_5 0.06, 0.06, 0.19; H_2O (+105°C) 11.0, 2.19, 4.58; H_2O (−105°C) 0.18, 0.16, 0.60; CO_2 0.09, 0.32, 1.68; S 0.01, <0.01, 0.04; Total 100.1, 100.1 and 99.6 for samples NSWMD-1, NSWMD-2 and NSWMD-3 respectively.)

[a] Each laboratory reported the results of two separate determinations (carried out at least six days apart) per sample.

[b] The upper set of figures in brackets for each sample gives the range of laboratory mean results for potassium; the lower set gives the range of laboratory mean results for hygroscopic moisture.

[c] Greater than within-laboratory standard deviation at 95% confidence level.

Sampling problems

The suitability of the procedure used in the present study for allocating samples to vials has been confirmed[1] by analysing replicate 500-mg subsamples from three vials of sample NSWMD-1 and replicate 100-mg subsamples from four vials of sample NSWMD-10. The potassium contents of NSWMD-1 and NSWMD-10 were found to be 0.0560 ± 0.0002 and 9.81 ± 0.02% respectively, in all vials studied. Hence it is reasonable to assume that the observed potassium content of a given sample in the present study is independent of the particular vial used.

Results for hygroscopic moisture, $H_2O(-105°)$

As indicated in Tables 4 and 5, there were frequent instances of poor interlaboratory agreement of hygroscopic moisture results. In the foregoing statistical study of potassium results converted onto a dry basis

Table 6. Results of analysis of variance before and after exclusion of instances of poor within-laboratory agreement

Sample	No. of labs.	Overall mean % K (dry basis)	% Rel. std. devn. of mean of duplicate results		Is between-lab std. dev. greater than within-lab std. dev. at 95% confidence level?
			Between-lab.	Within-lab.	
NSWMD-2	5	0.07391	1.89	1.91	No
	4	0.07383	2.17	0.78	Yes
	3[a]	0.07395	2.62	0.09	Yes[b]
NSWMD-9	6	7.603	0.89	0.32	Yes
	5	7.627	0.47	0.18	Yes
NSWMD-10	7	9.794	0.67	0.26	Yes
	4	9.799	0.50	0.09	Yes[b]

[a] Labs. E, F and G.

[b] Also at 99% confidence level.

(as recommended[19]), interlaboratory variations of hygroscopic moisture results have been assumed to be due to differences in geographical location of the laboratories, and not due to major inaccuracies in some laboratories' methods for hygroscopic moisture.

Methods of sample dissolution

Work reported elsewhere[1] has shown that, for samples NSWMD-1 and BCR-1, solutions prepared after fusion with lithium metaborate for 15 min at 900° give the same potassium results as solutions prepared by hydrofluoric acid attack in both open and sealed vessels. Hence it is reasonable to assume that errors in the various dissolution procedures listed in Table 3 are negligible provided sufficient care is taken to avoid contamination and mechanical losses.

Choice of standard compound

Analytical-reagent grade potassium chloride, potassium hydrogen phthalate and bisulphate-free potassium sulphate have been found[1] to be suitable standard compounds; *i.e.*, readily obtainable at least 99.8% pure after appropriate heating. Any significant systematic error from this source is therefore very unlikely.

Accuracy of standard solutions

Accuracy of standard solutions, besides depending upon the use of a suitable standard compound, also depends upon other factors such as calibration of balances (and of volumetric glassware if this is used instead of gravimetric dilution) and freedom of interaction of the potassium in the standard solutions with container walls. It was impossible to establish whether these factors were sufficiently considered by all laboratories in the present study. Therefore inaccurate standard solutions could have made a significant contribution to the lack of interlaboratory agreement in some instances in the present study.

Contamination from glassware

High between-laboratory variations for the low-potassium samples NSWMD-1, -2 and -3 are at least partly due to contamination from reagents, surroundings, or vessels. As shown in Table 6 except for sample NSWMD-2, Laboratories E, F and G obtained very good within-laboratory agreement for these samples; this suggests that contamination from glassware (not accounted for by blank runs) or adsorption onto walls of polyethylene vessels (Laboratory G) occurred. The latter possibility has been excluded by the finding[1] that the polyethylene vessels used by Laboratory G do not adsorb potassium from acidified solutions.

It is worth noting that the glassware of Laboratories E and F was preconditioned by soaking in 0.75*M* nitric acid and in hot 1:1 nitric acid, respectively. Such treatment has been stated[22] to be likely to sensitize the glass surface so that it will retain adsorbed ionic films. This is presumably because of replacement, by hydrogen ions, of cations such as calcium, sodium and potassium previously bound to the surface of the glass. The acid-treated glass surface, when attacked by very dilute hydrofluoric acid resulting from hydrolysis of complex fluorides[23] in the sample solutions of Laboratories E and F, would thus cause less contamination by potassium than a glass surface not acid-treated. (However such contamination by potassium from acid-treated glassware would not occur if, after nitric acid treatment, no potassium remained on or near the surface in sites accessible to attack by very dilute hydrofluoric acid; negative errors could then arise because of adsorption

Table 7. Comparison of results of Laboratories E, F and G for low-potassium samples

		Mean K *ppm*			Between-lab. difference, K *ppm*		
Sample	Ca, %	Lab. E	Lab. F	Lab. G	E − F	E − G	F − G
PCC-1	0.38	13.2 (±1.2)	30.9 (±0.8)	—	−18	—	—
DTS-1	0.1	10.5 (±1.0)	14.0 (±1.9)	—	−3	—	—
NSWMD-1	0.16	565	583	560	−18	+5	+23
NSWMD-2	5.49	737	760	722	−23	+15	+38
NSWMD-3	7.03	3025	—	3001	—	+24	—

Notes. 1. Laboratory E made 10 and 9 complete determinations on samples PCC-1 and DTS-1, respectively.[20] Laboratory F made 4 complete determinations on these two samples.[24]

2. Results of Laboratories E and F for samples PCC-1 and DTS-1 are ± the standard deviation of a single determination.

3. In Reference 10, three laboratories obtained the following potassium results (on the USGS samples) by neutron activation analysis:

Sample PCC-1; 11.5, 11, 9.0 ppm K
Sample DTS-1; 8.8, 9, 7.9 ppm K

4. Laboratory C has reported 9 ± 2 ppm K for sample DTS-1.[17] This is the mean of six complete determinations ± the standard deviation of a single determination and agrees well with the neutron activation results.

by acid-treated glassware of potassium in sample solutions.)

Table 7 gives results of Laboratories E, F and G for low-potassium samples in the present study; results[20,24] of Laboratories E and F for the USGS reference rocks, PCC-1 and DTS-1, are also included. Note 3 of Table 7 gives results of three other laboratories[10] which have analysed samples PCC-1 and DTS-1 by neutron activation; these results are appreciably lower than the flame-spectrometric results of Laboratories E and F. The good agreement of the result of Laboratory C for sample DTS-1 (Note 4, Table 7) with the neutron-activation results, indicates that contamination from glassware is less likely when solutions are prepared by lithium metaborate fusion rather than by hydrofluoric acid treatment.

Interlaboratory differences in Table 7 vary from sample to sample, and are more pronounced for samples with higher calcium contents (also given in Table 7). The question of the possibe effect of calcium upon the extent of potassium contamination from glassware arises because calcium has the widest range of composition of all the major elements in the five samples in Table 7.

When samples high in potassium are analysed by the methods of Laboratories E and F, the results in Table 7 show that contamination from glassware does not cause an appreciable error; an absolute positive error not exceeding 0.004% potassium (38 ppm) is indicated; this represents a relative error of 7% for sample NSWMD-1, and of only 0.04% for sample NSWMD-10 which contains 9.8% potassium.

The occurrence of contamination from glassware, during analysis of samples low in potassium, requires further investigation.

Flame-spectrometric method and technique

Procedures involving flame measurement are susceptible to small systematic errors due to any of the following: (*a*) inaccurately diluted standard and sample solutions, (*b*) contamination by airborne potassium (*e.g.*, in smoke), (*c*) failure to maintain standard and sample measurement solutions at the same temperature, (*d*) large variations in hydrostatic head between sample and standard measurement solutions,[25] and (*e*) slight non-linearity of instrument response. It has been shown[1] that such errors can be avoided.

Table 8. Results of Laboratory A for samples NSWMD-1 to NSWMD-3, with and without cation-exchange separation of potassium

	% K (dry basis)	
Sample	With separation	Without separation[a]
NSWMD-1	0.0548	0.0737
	0.0557	0.0671
		0.0707
		0.0701
NSWMD-2	0.0772	0.0819
	0.0713	0.0745
		0.0821
		0.0822
NSWMD-3	0.2989	0.3127
	0.2976	0.3135

[a] No correction made for bias[26] due to iron.

Table 9. Results of Laboratory G with and without cation-exchange separation of potassium

		% K (dry basis) Type of AAS measurement solution[b]		
Sample	Run[a]	NO	Cs	IE
NSWMD-1	1	0.0555	0.0556	0.0569
	2	0.0553	0.0554	0.0559
NSWMD-2	1	0.0752[c]	0.0721	0.0720
	2	0.0749	0.0720	0.0724
NSWMD-3	1	0.2998	0.2991	0.2999
	2	0.3021	0.3012	0.2999
T-1	1	1.011	1.011	1.021
	2	1.013	1.009	1.013
BCR-1	1	1.444	1.426	1.424
	2	1.433	1.418	1.423
AGV-1	1	2.468	2.458	2.460
	2	2.502	2.459	2.455
G-2	1	3.773	3.738	3.715
	2	3.724	3.713	3.732
GSP-1	1	4.594	4.610	4.600
	2	4.590	4.579	4.587
NSWMD-9	1	7.59	7.61	7.59
	2	7.60	7.58	7.58
NSWMD-10	1	9.86	9.84	9.77
	2	9.86	9.80	9.82

[a] Run 2 was done about 2 months after run 1.

[b] NO = no buffer other than lithium from flux. Cs = buffered with 1.20 mg of CsCl per g. IE = K fraction from ion-exchange separation, buffered with 1.20 mg of CsCl per g.

[c] High probably because of ionization interference by large excess of sodium over potassium in sample NSWMD-2.

The need to separate potassium from other constituents in the sample before flame measurement seems to depend upon the type of flame measurement: the lithium internal-standard, propane–air flame emission method of Laboratory A gave high results for the low-potassium, ferromagnesian samples NSWMD-1, -2 and -3 when potassium was not separated (Table 8); however, the atomic-absorption, acetylene–air flame method of Laboratory G for unseparated solutions buffered with caesium always gave results which agreed well with results for separated solutions (Table 9).

CONCLUSIONS

The results of the present interlaboratory study are good enough to support the conclusion[1] that—provided sampling errors are overcome and sufficient attention is paid to detail at all stages of the analytical procedure—a between-laboratory variation in flame-spectrometric potassium results of less than 0.5% relative standard deviation is attainable. Greater precautions to avoid losses and contamination during preparation of sample solutions, and stricter measures to avoid interferences and other errors in the flame measurement step would yield better interlaboratory agreement than that observed in some instances in the present study.

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RELATIVE SENSITIVITY COEFFICIENTS FOR THE ANALYSIS OF STEEL BY SPARK-SOURCE MASS-SPECTROMETRY

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Summary—Quantitative analysis by spark-source mass-spectrometry requires the knowledge of so-called sensitivity coefficients for the elements being determined. Five series of analyses have been carried out on five different steel standard reference materials (NBS-SRM 661–665), using photoplate detection. The relative sensitivity coefficients (S_R) of Ti, V, Cr, Mn, Co, Ni, Cu, As, Zr, Nb, Mo, Sn, Sb, La, Ta and W were determined *vs.* iron as an internal standard. The S_R values were independent of the elemental concentration. A relative standard deviation of about 15% was obtained. The accuracy as confirmed by comparing the results for a pure iron sample with those obtained by neutron-activation analysis was within the same limits.

Spark-source mass-spectrometry is increasingly being used for trace analysis in metals and alloys. This technique has the advantage of being capable of determining almost all elements at the sub-ppm level, and down to the ppM (parts per milliard) level in favourable conditions, but suffers from poor precision with a coefficient of variation of 20–30%.[1,2] When the method is used on an absolute basis, *i.e.*, without standards, inaccurate results are obtained. The mass-resolved ion-beams reaching the detector are not representative of the true composition of the sample, as a result of selective evaporation, non-uniform ionization efficiency and selective transmission through the analyser.[3,4] For each element a concentration level is measured which differs from the true concentration, and the ratio of these values is called the sensitivity coefficient or sensitivity factor.

Honig[4] defined the "absolute overall yield" $Y_0(x)$ of component x as

$$Y_0(x) = I_d(x)/A(x) = Y_s(x).f_t(x).f_d(x)$$

where

$I_d(x)$ = number of ions detected
$A(x)$ = number of sample atoms vaporized
$Y_s(x) = I_s(x)/A(x)$, "source yield" or the ratio of number of ions produced to the number of sample atoms vaporized
$f_t(x)$ = instrumental transmission factor
$f_d(x)$ = detector response factor.

In a typical double-focusing mass spectrometer $Y_0(x)$ lies between 10^{-7} and 10^{-8}.

In practical quantitative analysis the most important parameter is the ratio $Y_0(x)/Y_0(y)$ where y represents the matrix element, or more generally, an element, present in the sample at known concentration, which is used as an internal standard. This parameter is called the relative sensitivity coefficient of component x.

In the literature various kinds of "sensitivity factors" or "sensitivity coefficients" are frequently encountered. In this paper the relative sensitivity coefficient (S_R) for element x is defined as $S_R\,(x/y)_z$ = ratio of the concentrations of elements x and y in the matrix material z as determined by mass spectrometry, divided by the ratio of the true concentrations of elements x and y. This can be expressed as

$$S_R(x/y)_z = [(C_x/C_y)_{\text{determined}}/(C_x/C_y)_{\text{true}}]_z. \quad (1)$$

Only singly-charged ions are considered and corrections are made for variation in background and line-width. The definition proposed by Farrar[5] includes a correction for the influence of the ion-mass on the detector response. This correction is not made in this work, since there is no unanimity in the literature about the exact value of this correction factor,[6] which depends on the nature of the ion-sensitive plate.

From the definition of S_R it is obvious that all values are calculated with respect to an element y having an arbitrary value of unity. In the steel standards analysed in this work, the sensitivity coefficient of iron is set equal to unity thus: $S_R(\text{Fe/Fe})_{\text{steel}} = 1$.

For the experimental determination of sensitivity coefficients, standard reference materials are required. A large number of experimentally measured sensitivity coefficients can be found in the literature,[5,7–9] but agreement is rather poor. The data are often difficult to compare because of differences in the definition of S_R or because they are calculated with respect to different elements. In addition, the sensitivity coefficients may depend on the characteristics of the instrument used and on a number of experimental parameters, such as spark conditions, spark geometry with respect to entrance slit, width of various slits, and accelerating voltage. Several authors have observed matrix effects.

Another approach is to calculate relative sensitivities of elements in a radiofrequency spark, from their physical and chemical properties.[3,5] For analytical work, such calculated values may be of interest when no suitable standards are available.

The purpose of the present work is to determine the relative sensitivity coefficients of a number of elements in steel under well-specified experimental conditions. The effect of varying various experimental parameters is reported.

EXPERIMENTAL

Apparatus

The experiments were performed with a double-focusing instrument with Mattauch–Herzog geometry (JMS-01 BM-2, JEOL, Tokyo). The instrument incorporates a spherical electric field to reduce the beam spread in the *z*-direction, and is equipped with a radiofrequency spark source. Ilford Q-2 ion-sensitive plates were used as the detector. These plates were read with a scanning microdensitometer JEOL JMD-2C interfaced to a JEOL JEC-6 computer (8K, 16-bit words; magnetic drum memory of 8K). The computer program (JEOL JMA-1340) has been discussed in a recent paper.[10]

Samples

Four low-alloy steels and one electrolytic iron, available from the National Bureau of Standards, Washington, D.C. (NBS-SRM 661–665) were chosen as standard reference materials covering a large concentration range for as many elements as possible. These materials have the reputation of excellent homogeneity.

Table 1 lists the certified concentrations for a number of elements; the only elements indicated are those for which a certified concentration is available for at least 4 standards and with interference-free mass-lines. According to the certificate, these values are not expected to deviate from the "true" concentration by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5 The values in brackets were obtained by a single method of analysis

In addition, a so-called high-purity iron sample, prepared for the "Verein Deutscher Eisenhüttenleute" was analysed. The analysis of this sample by neutron activation has been studied exhaustively.[11]

Sample preparation

As the standards were in rod form (diam. 3·2 mm), they were cut to the proper length. The sparking surfaces were ground flat to minimize changes in interelectrode self-shielding. After etching with nitric acid of *pro analysi* quality the electrodes were mounted in the sample holders in such a way that sparking would occur preferentially between the flattened portions of the electrodes.

Mass spectrometric procedure

The electrodes were positioned as shown in Fig. 1 in order to minimize the effects of irreproducible spark position[12] and were aligned so as to obtain maximum transmission

The width of the slits was as follows, object slit 30 μm, α slit (in front of the electrostatic field) 0·7 mm and β slit (energy-defining slit—behind the electrostatic field) 1·0 mm.

The "Variac" setting which controlled the input to the radiofrequency oscillator was set at 4 kV, this corresponds to a spark-source voltage of about 65 kV. The other spark conditions were as follows, pulse length 20 μsec, repetition frequency from 10 to 3000/sec, and ion-accelerating voltage 30 kV.

A series of graded exposures was made on each plate, ranging from 3×10^{-13} to 2×10^{-7} C in steps of about $10^{1/2}$. All samples were pre-sparked for at least 5 min

RESULTS AND DISCUSSION

Reproducibility of experimental sensitivity coefficients for standard NBS-SRM 661

Standard sample NBS-SRM 661 was analysed eight times in sequence. The average value of the experimentally determined concentrations is indicated in

Table 1. Composition of standard samples, % w/w

Element	NBS-SRM 661 AISI 4340 steel	NBS-SRM 662 AISI 94B17 steel	NBS-SRM 663 Cr-V steel	NBS-SRM 664 High-carbon steel	NBS-SRM 665 Electrolytic iron
Ti	0·020	0·084	0·050	0·24	0·0006
V	0·011	0·04$_1$	0·31	0·10$_5$	0·0006
Cr	0·69	0·30	1·31	0·06$_5$	0·007$_2$
Mn	0·66	1 04	1·50	0·25$_5$	0·0057
Fe	95·6*	95·3*	94·4*	96·7*	99·9*
Co	0·030	0·30	0·048	0·15	0·007$_0$
Ni	1·99	0·59	0·32	0·14$_2$	0·041
Cu	0·042	0·50	0·09$_8$	0·24$_9$	0·0058
As	0·017	0·09$_2$	0·010	0·05$_2$	(0·0002)
Zr	0·009	0·19	0·049	0·068	<0.00001
Nb	0·022	0·29	0·049	0·15$_7$	<0·00005
Mo	0·19	0·06$_8$	0·030	0·49	0·0050
Sn	0·01$_1$	0·016	(0·095)	(0·005)†	<0 0005
Sb	0·004$_2$	0·012	0·001$_6$	(0·035)	<0·00005
La	0·0004	0·0004	0·0006	0·00007	<0·000005
Ta	0·020	0·20	(0·053)	0·11	<0·00005
W	0·01$_5$	0·21	0·04$_5$	0·10	<0·0001

* By difference

† Approximate value

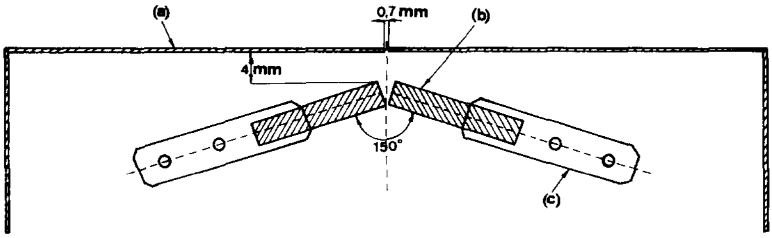

Fig. 1. Electrode position. (a) Accelerating slit (tantalum), (b) sample electrode, (c) sample holder (tantalum).

column 3 of Table 2, iron being used as the internal standard. The relative standard deviation, shown in column 4, is defined as

$$s_{\%} = \frac{100}{\bar{C}}\sqrt{\frac{(C_i - \bar{C})^2}{n-1}} \qquad (2)$$

where C_i is an individual concentration, $\bar{C}$ is the mean concentration and n is the number of analyses.

The average value of $s_{\%}$ for all elements is 15%. The relative sensitivity coefficient S_R (column 5 of Table 2) is in accordance with equation (1), where $S_R(\mathrm{Fe/Fe})_{\mathrm{steel}} = 1{\cdot}00$ and can be calculated by using the data in Table 1 (column 2). Significant differences can be observed among the tabulated S_R values and there is a correlation between these values and the properties of the elements concerned.

Sensitivity coefficients as a function of concentration: analysis of standards NBS-SRM 661–665

From the analytical point of view it is important to show whether the S_R values vary with the concentration of the element in a given matrix. This information can be extracted from a study of all the available steel standards, since the elemental concentrations span one or more orders of magnitude. Therefore the standards NBS-SRM 662–665 were analysed five times and the average concentrations were used to calculate the S_R values given in Table 3.

The errors of the certified values (Table 1) differ widely, and the specified uncertainty was interpreted as being twice the standard deviation. The standard deviation indicated with each relative sensitivity coefficient in Table 3 was obtained from

$$s = \frac{a}{b}\sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2}$$

where a refers to the concentration determined by mass spectrometry and b to the certified concentration.

Table 3 also gives the weighted average of the S_R values derived from all the standards and its relative standard deviation calculated from

$$\bar{S}_R = \frac{\Sigma(S_{R_i}/s_i^2)}{\Sigma(1/s_i^2)}; \quad s_{\%} = \frac{100}{\bar{S}_R}\cdot\frac{\sqrt{N}}{\Sigma(1/s_i^2)}$$

Table 2. Results of eight analyses of NBS-SRM 661 (AISI 3440 steel)

Element	Isotopes used	Mean concentration, % w/w	Relative standard deviation, %	Relative sensitivity coefficient
Ti	47,48	0·036	10	1·8
V	51	0·0140	5	1·27
Cr	52,53	1·06	8	1·5
Mn	55	1·8	12	2·7
Fe	54,57	95·6	—	1·00
Co	59	0·024	15	0·78
Ni	60,61,62	1·3	14	0·63
Cu	63,65	0·041	7	0·97
As	75	0·033	17	1·9
Zr	90,91	0·011	23	1·2
Nb	93	0·017	11	0·78
Mo	92,95,96,97,98,100	0·12	11	0·64
Sn	116,117,118,119,120,122	0·027	21	2·5
Sb	121,123	0·011	21	2·5
La	139	0·0013	22	3·4
Ta	181	0·010	20	0·48
W	182,183,184,186	0·006	26	0·41

Overall average standard deviation = 15%

Table 3. Experimentally determined S_R values for five NBS steel standards

Element	S_R values experimentally determined					Average for all standards	Relative standard deviation, %
	SRM 661	SRM 662	SRM 663	SRM 664	SRM 665		
Ti	1·8 ± 0·2	2·1 ± 0·3	1·2 ± 0·3	1·7 ± 0·3	1·1 ± 0·2	1·5	15
V	1·27 ± 0·09	1·4 ± 0·3	1·0 ± 0·2	1·44 ± 0·06	1·3 ± 0·2	1·4	8
Cr	1·5 ± 0·1	1·49 ± 0·08	1·4 ± 0·1	1·6 ± 0·1	1·5 ± 0·1	1·5	7
Mn	2·7 ± 0 3	2·7 ± 0·2	2·3 ± 0·2	2·5 ± 0·2	2·8 ± 0·4	2·7	7
Fe	1·00	1·00	1·00	1·00	1·00	1·00	—
Co	0·8 ± 0·1	0·74 ± 0·04	—*	0·7 ± 0·1	0·6 ± 0·1	0·74	10
Ni	0·63 ± 0·09	0·66 ± 0·03	0·74 ± 0·09	0·6 ± 0·1	0·7 ± 0·1	0·66	9
Cu	0·97 ± 0·07	1·06 ± 0·06	1·02 ± 0·08	1·0 ± 0·2	1·2 ± 0·3	1·03	8
As	1·9 ± 0·3	1·8 ± 0·6	1·7 ± 0·4	2·4 ± 0·5	—	1·9	21
Zr	1·2 ± 0·3	1·3 ± 0·2	1·0 ± 0·2	1·0 ± 0·2	—	1·1	18
Nb	0·78 ± 0·09	0·9 ± 0·1	0·8 ± 0·1	0·64 ± 0·05	—	0·72	11
Mo	0·64 ± 0·07	0·64 ± 0·04	0·55 ± 0·09	0·53 ± 0·07	0·6 ± 0·1	0·60	9
Sn	2·5 ± 0·8	2·6 ± 0·7	(2·0 ± 0·4)	—	—	2·3	25
Sb	2·5 ± 0·6	2·3 ± 0·6	2·3 ± 0·7	(2·4 ± 0·6)	—	2·4	25
La	3·4 ± 0·8	3·5 ± 0·9	2·5 ± 0·6	3·7 ± 0·9	—	3·0	25
Ta	0·47 ± 0·09	0·5 ± 0·1	(0·37 ± 0·08)	0 39 ± 0·08)	—	0·42	21
W	0·4 ± 0·1	0·4 ± 0·1	0·29 ± 0·08	0·27 ± 0·06	—	0·31	27
average r.s.d.	16%	17%	18%	16%	16%		15%

* Interference of $^{118}Sn^{2+}$

The overall mean relative standard deviation of 15% is to be compared with the corresponding standard deviation for the NBS 661 sample, which is 16%. It can thus be concluded that over the impurity concentration range studied there is no evidence that S_R is a function of the composition. Figure 2 shows the S_R values measured for chromium, vanadium, cobalt, nickel, molybdenum and tantalum, plotted as a function of concentration. It is possible, by linear regression analysis, to calculate the slopes of the straight lines and their uncertainty. A systematic survey for all the elements studied shows no evidence that the slope differs significantly from zero, as is apparent from Table 4.

Precision and accuracy

From Tables 2 and 3 it is apparent that the precision of the experimentally determined S_R values is of the order of 15%. This can be compared with the corresponding figures obtained by other authors, which are summarized in Table 5.

This precision gives an indication of the accuracy with which similar steel samples can, in principle, be analysed, relying on the experimentally determined S_R

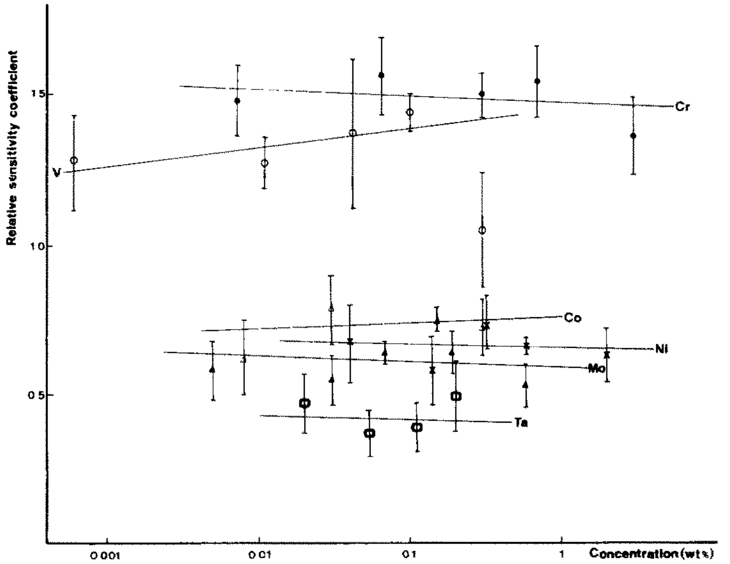

Fig. 2. Effect of concentration on the relative sensitivity coefficients of some elements in steel standards. ● Cr; ○ V; △ Co; × Ni; ▲ Mo; □ Ta.

Table 4. Relative sensitivity coefficients *vs.* concentration for steel standards. Slopes of the straight lines obtained by the least-squares method

Element	Slope (change in S_R per unit logarithmic concentration interval)	Concentration range, % *w/w*
Ti	0·27 ± 0·10	0·0006–0·24
V	0·065 ± 0·065	0·0006–0·31
Cr	−0·025 ± 0·067	0·0007–1·31
Mn	−0·12 ± 0·18	0·0057–1·50
Co	0·039 ± 0·074	0·007–0·30
Ni	−0·013 ± 0·083	0·041–1·99
Cu	0·050 ± 0·075	0·0058–0·50
As	0·39 ± 0·61	0·010–0·09
Zr	0·087 ± 0·26	0·009–0·19
Nb	−0·080 ± 0·10	0·022–0·29
Mo	−0·020 ± 0·054	0·0050–0·49
Sn	−0·65 ± 0·80	0·01–0·095
Sb	−0·0031 ± 0·63	0·002–0·035
La	−1·1 ± 1·2	0·00007–0·0006
Ta	−0·016 ± 0·13	0·020–0·20
W	−0·050 ± 0·13	0·01–0·21

Table 5. Precision of experimentally derived S_R values in steel or iron

Matrix	Investigator	Overall relative standard deviation %
Iron alloys	Short and Keene[13]	37
NBS steels	Ito and Yanagihara[7]	36
NBS steels	McCrea[14]	18
NBS steels	Jaworski and Morrison[9]	15

Table 6. Analysis of trace impurities in iron: comparison of results obtained by NAA and SSMS

Element	Mass used for SSMS	Concentration, *ppm*		Deviation, %
		NAA	SSMS	
V	51	2·52 ± 0·15	2·5 ± 0·1	−1
Cr	52	6·2 ± 1·0	6·4 ± 0·5	+3
Mn	55	10·7 ± 0·3	10 ± 2	−6
Co	59	80·4 ± 1·1	64 ± 3	−21
Ni	60	864 ± 5	800 ± 100	−10
Cu	63	41·0 ± 1·0	39 ± 5	−6
As	75	8·55 ± 0·35	11 ± 2	+24
Mo	92,95,96,97 98,100	64·2 ± 1·0	70 ± 10	+13
Sb	121,123	0·39 ± 0·02	0·52 ± 0·08	+32
			average r.s.d.: 12%	average: 13% (absolute value)

Table 7. Precision of the measurement of the exposures

Exposure, *C*	Number of lines measured	Relative standard deviation of the measured intensities, %	
		pulse length, 20 *μsec*	pulse length, 20, 40 or 80 *μsec*
3×10^{-9}	25	4·8	6·9
10^{-9}	23	5·5	6·0
10^{-10}	9	7·5	6·4
10^{-11}	5	11	15
10^{-12}	4	23	24

Table 8. Range of estimated errors in certified values of the standards used

Standard	Number of elements used*	Range of uncertainty, %	Average uncertainty, %
NBS 661	16	0·5–45·5	10·7
NBS 662	16	1·0–25·0	6·0
NBS 663	14	0·7–31·3	6·7
NBS 664	14	1·5–14·3	5·8
NBS 665	8	1·7–16·7	6·9

* The values from a single method of analysis are excluded.

values. To confirm this the high-purity iron sample was analysed and the results are compared with those obtained by neutron-activation analysis,[11] in Table 6.

Various experimental parameters control the precision. *High frequency spark.* Systematic fluctuations in the spark plasma are now considered to be insignificant in comparison with random variations.[15] These variations are averaged out to some extent. *Densitometer and photoplate.* The errors originate from nonuniformities of the emulsion and also from the measurement of the line and background optical densities. We have found that with the automated densitometer the precision of the measurements is 2–5%.[10] This is consistent with results obtained by Franzen and Schuy[16] and Skogerboe, Kashuba and Morrison.[15] *Exposure measurements.* The accurate measurement of very low exposures is difficult.[17] This leads to imprecise results, especially when the matrix lines are used as internal standard. To assess this effect 5 photoplates were taken, each containing 15 identical exposures varying from 3×10^{-9} to 10^{-12} C. A number of lines of roughly equal transmission were measured and the integrated intensities were averaged. The results are indicated in Table 7, column 3. As the precision of the optical density measurement can be assumed to remain constant, the monitor readings become much more unreliable for low exposure values. Care was taken to measure matrix or major element lines at the lowest exposures to eliminate effects due to inhomogeneity.

Sample. Apart from the instrumental parameters considered above, the sample itself may be a source of errors due to inhomogeneities, inaccurate certification and spectral interferences. The reference standard materials NBS 661–665 are often used for the evaluation of the precision of spark-source mass-spectrometric procedures because of their homogeneity. Nevertheless very little material is consumed for a single exposure and the influence of possible inhomogeneities on our results cannot be excluded. The standards exhibit widely different errors in their certified concentrations. For example, NBS-661 is specified to within 0·5% relative for Ni and 45% relative for Sn. Table 8 summarizes these data for the different reference materials.

One of the major problems in spark-source mass-spectrometry is spectral interference. A number of interferences were identified and the corresponding isotopes were omitted. The agreement between the results obtained by mass spectrometry and neutron activation for the iron sample is an indication that interferences are virtually absent from the data in Tables 2 and 3. Special attention was given to the occurrence of unusual isotopic ratios and to widely scattered S_R values as indicators for possible spectral interferences.

Influence of instrumental parameters

A number of instrumental conditions which might have an effect on the analysis have been studied, with NBS-SRM 661 steel standard as sample.

Duty cycle. The effect of changes in pulse length was investigated by taking 3 identical exposures and varying the pulse length (20, 40 and 80 μsec). In order to cover the concentration range from ppm to matrix, this was done for 5 different exposures. All these mass spectra were recorded on the same photoplate. The intensities of the mass-lines were measured and the reproducibility was calculated (Table 7, column 4). Comparison with the standard deviation at fixed pulse length (Table 7, column 3) by using the statistical F-test shows that there is no significant contribution from the changes in pulse length to the precision. The effect of changes in pulse repetition frequency (30, 100, 300, 1000, 3000 and 10,000/sec), was studied in the same way. Again, no systematic trends could be observed and the precision decreased by an insignificant amount. The experiments above indicate that changes in duty cycle do not cause considerable changes in the analytical results, supporting the findings of Short and Keene[13] and Owens and Giardino.[18]

Radiofrequency spark voltage. The effect of changes in the radiofrequency spark voltage was determined in a similar way. Some of the results are plotted in Fig. 3. It was found that changes in radiofrequency voltage did not degrade the precision. This is consistent with the results found by Wong,[19] who indicated that "analytical results are not significantly affected by changes in applied r.f. voltage".

Accelerating voltage. The influence of changing the accelerating voltage seems to be more important (about 10% r.s.d.). This effect however could not be studied with sufficient accuracy; indeed, variation of the accelerating voltage changes the ion-energy and hence necessitates adjustments in the applied electrostatic field. In addition, the trajectory of a given kind

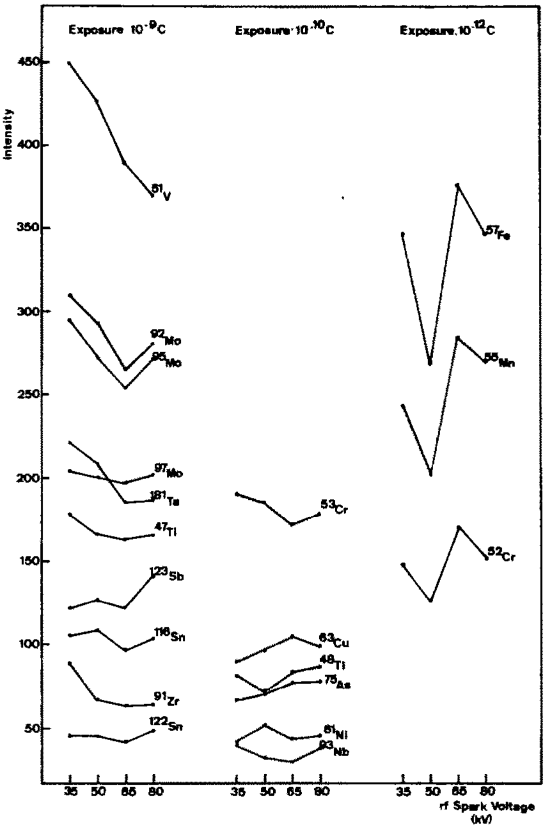

Fig. 3. Variation of photographically measured intensities with the radiofrequency spark voltage.

of ion through the magnetic field changes and so affects the transmission. Further study is needed to elucidate the relative contribution of these effects to the recorded line intensity.

CONCLUSIONS

Significant differences were found to exist between relative sensitivity coefficients for different elements in the same standard, but relative sensitivity coefficients of an individual element did not change significantly from standard to standard in spite of the widely differing concentration levels. A precision of about 15% was obtained. Comparison with neutron-activation analysis showed that the accuracy of spark-source analyses of steel and iron samples, using the experimentally determined sensitivity coefficients, was of the same order. The random variation of the spark plasma, the densitometer error and the heterogeneous distribution of the trace elements may be regarded as the prime precision-limiting factors in the overall analytical error. Better precision may be obtained when the internal standard (isotope) has about the same concentration as the impurities so that long exposures are used and the influence of monitor measurement errors is decreased. For the precise determination of relative sensitivity coefficients, it is imperative to use reliable, well-characterized standards; unfortunately, the NBS steel standards used in this work have an average uncertainty of about 7% for the elements determined here. Relative sensitivity coefficients cannot be determined if spectral interferences occur. Variations in pulse length, pulse repetition frequency and spark voltage do not have a large influence on the precision.

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A RAPID FIRE-ASSAY/ATOMIC-ABSORPTION METHOD FOR THE DETERMINATION OF PLATINUM, PALLADIUM AND GOLD IN ORES AND CONCENTRATES: A MODIFICATION OF THE TIN-COLLECTION SCHEME*

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Summary—The tin-collection scheme of fire-assaying has been simplified to permit the rapid and accurate determination of platinum, palladium and gold in ores and related materials. The presence of tellurium in the charge ensures that the precious metals remain insoluble during the parting of the tin button with hydrochloric acid. The residue is easily collected and dissolved and the resultant solution analysed for the precious metals by AAS. The accuracy of the method has been established by application to five diverse certified reference materials.

The tin-collection scheme[1–4] for the determination of the precious metals in ores and concentrates has been used in our laboratories for approximately 10 years. Its accuracy, reliability and versatility have been well proved in interlaboratory studies.[5–7]

When this scheme is applied to the determination of gold, silver, and the platinum-group metals, solutions derived from tin assay buttons are treated by rather tedious ion-exchange and extraction processes and the analysis is finished either spectrophotometrically or by atomic-absorption spectrophotometry (AAS).[3] However, it is often necessary to determine only platinum, palladium and possibly gold, and a simplified procedure would be desirable.

The basis for such a method was recognized several years ago when it was established that the intermetallic compounds formed by platinum, palladium, and gold with tin are essentially insoluble in the hydrochloric acid used to part the tin-assay button.[1–2] However, it was also observed that copper and nickel tend to increase the solubility of the precious metals during the parting operation.

Tellurium has been used to precipitate platinum, palladium, rhodium and iridium by reduction[8] and it is known to form intermetallic compounds such as $PtTe_2$, $PdTe_2$.[9] Tellurium was therefore added to the fire-assay charge to assess it as a "carrier" or "fixing agent" for platinum, palladium and gold. The results showed that an easily collected insoluble residue containing the three precious metals is formed quantitatively during the decomposition of the tin-assay button in hydrochloric acid. This forms the basis of the proposed method, which is rapid, accurate, and widely applicable.

EXPERIMENTAL

Apparatus

Furnaces. A 15-kW Globar type with suitable thermocouple and temperature controller, capable of accommodating 6 40-g assay crucibles and maintaining their temperature at 1250°. A Jelrus "Handy-Melt" portable electric furnace. (Jelrus Technical Products Corp. New Hyde Park, N.Y.) or similar. The Jelrus is a small vertical furnace equipped with removable graphite crucibles, used in this work for melting tin-base assay buttons before their granulation in water. It is recommended that after 4–6 months of relatively constant use the bottom of the crucibles be examined for small holes.

Reagents

Tin (IV) oxide. B.D.H. reagent-grade is preferred because it has consistently given a gold blank value of 150–200 ng/g.

Tellurium powder. Reagent grade.

Standard solutions of platinum, palladium and gold. Prepared by dissolving accurately weighed quantities of Johnson Matthey "Specpure" sponge in *aqua regia*. Each solution is evaporated to dryness, then the residues are dissolved in concentrated hydrochloric acid and the solution evaporated to dryness again, this being repeated several times. Finally, the salts are dissolved in, and diluted to volume with, $1M$ hydrochloric acid. The gold solution is standardized gravimetrically by the classical fire-assay procedure with lead, and the platinum and palladium solutions are standardized spectrophotometrically.

Mixed cadmium–copper sulphate solution.[10] Prepared by dissolving 98 g of $CuSO_4.5H_2O$ and 57 g of $3CdSO_4.8H_2O$ in 500 ml of $12M$ hydrochloric acid and 300 ml of water, followed by dilution to 1 litre with water

Flux for fire-assay. SnO_2 40 g, Na_2CO_3 50 g, $Na_2B_4O_7$ 10 g, flour 35 g, Te 25 mg, silica 10–20 g according to the amount of silica in the sample, make enough flux for a sample up to 1 assay-ton (29·17 g) in size.

Procedures

Although aspects of certain of the following procedures have been described previously,[3] they are repeated here for completeness and for the convenience of the reader.

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Pretreatment of samples

Roasting. Before the crucible fusion procedure, all samples except those of copper-nickel matte are roasted at 750–800° for approximately 1 hr to decompose sulphides and volatilize arsenic and antimony. The sample is placed on a shallow fire-clay dish and stirred intermittently during the roasting process. In cases where only a few grams of material (particularly sulphides) are to be roasted, the sample is placed on a bed of silica to prevent possible loss of the resultant calcine to the surface of the dish (the silica is included as part of that required in the flux above).

Leaching of copper-nickel matte. Leaching is performed to remove the bulk of the copper and nickel from the residue of precious metals. The sample, weighing up to 2 assay-tons, is placed in a 1500-ml beaker and treated with 25 g of ammonium chloride and 100–200 ml of 12*M* hydrochloric acid. The sample is heated until the amount of insoluble matter appears not to exceed 2–3 g. With large samples, it may be necessary to treat the residue once or twice more with fresh acid after intervening filtrations. The combined sample solution (approximately 100 ml) is diluted with an equal volume of water and the solution containing most of the nickel and copper is filtered through a moderately fast paper. The solids are completely washed onto the paper with dilute (~5%) hydrochloric acid. The washed residue and paper are dried at ~110° for about 1 hr and then mixed with the recommended assay flux for fusion.

Chromite. Chromite is not completely decomposed during the fusion process, and samples containing an appreciable proportion of it must be subjected to a pretreatment that will decompose it. This can be done by sintering with sodium peroxide. The sample is mixed with 1·5 times its weight of sodium peroxide, then placed on a 10-g bed of silica in a roasting dish and roasted at 700° for about 1 hr. The sinter cake and underlying silica are ground together in a mortar and mixed with the flux for the crucible fusion process. The weights of sodium peroxide and silica are subtracted from the weights of sodium carbonate and silica, respectively, in the flux described above.

Procedure for preparation of buttons

Powdered samples. For powdered samples, the standard assay practice of blending the samples with the flux on glazed paper and transferring the charge to a "40-gram" crucible is followed.

Solutions (synthetic samples for method development). When solutions are to be mixed with the flux, approximately one-third of the flux is placed in the crucible and a 30-cm square of thin, commercial wrapping-film is pressed into the crucible to form an envelope, and then the remainder of the flux is transferred into this envelope. With a spatula, a cavity is formed in the bed of flux and the sample solution is transferred slowly into the depression so as to avoid wetting the film or crucible walls. The crucible is then heated in a drying oven at 110° for at least 2 hr. After drying, the material in the wrapping film is ground in a mortar, mixed well, and placed back in the film in the crucible. It is to be noted that, after drying, the salted portion of the charge is lumpy and difficult to pulverize and mix with the rest of the charge. This could lead to occasional spurious results (Table 2).

Fusion. The crucible is placed in the assay furnace at 1250° for about 90 min to fuse the charge. At the completion of the fusion period, the melt should not be viscous or lumpy nor should there be extensive crust formation at the top of the melt.

The melt is poured into a conical steel mould and, when it is cool, the tin button is separated from adhering slag by tapping with a small hammer.

Granulation of buttons. The button is placed in the crucible of the Jelrus furnace, from which air is purged by nitrogen delivered through a ceramic tube placed directly over the button. The temperature is increased until the button melts (600–1000° depending upon composition), then the melt is poured into a pail of water to granulate the alloy. Any large pieces are easily reduced in size with metal shears.

Analysis of granulated tin buttons. Each sample of granulated tin alloy is treated with 150 ml of 12*M* hydrochloric acid in a covered 600-ml beaker and heated until the excess of tin has dissolved and vigorous evolution of bubbles from the residue has ceased. A further 15–25-ml portion of acid is added and the sample is boiled for approximately 10 min. Water is added to give a volume of approximately 400 ml and the residue is allowed to settle The supernatant solution is decanted through a filter pad The residue in the beaker is washed several times, by decantation, with 15% v/v hydrochloric acid, the washings being passed through the filter pad.

The residue in the beaker is treated with a mixture of 15 ml of 12*M* hydrochloric acid and 5 ml of 30% hydrogen peroxide, and the beaker is heated gently for a few minutes to ensure complete dissolution of the residue. The residue on the filter pad is eluted with 20 ml of a 3:1 mixture of 8*M* hydrochloric acid and 30% hydrogen peroxide, and added to the beaker.

Approximately 50 mg of sodium chloride are added, and the sample solution is evaporated to dryness. When the evolution of fumes has nearly ceased, the beaker is removed from the evaporator and the sides are washed with ~10 ml of a 7:2 mixture of hydrochloric and hydrobromic acids. The sample is again evaporated to dryness to volatilize the remaining tin. The beaker is cooled, 10–15 ml of 12*M* hydrochloric acid are added and, while the beaker is being swirled, 30% hydrogen peroxide is cautiously added until it is evident that an excess is present. The beaker is heated for a few minutes, then, after cooling, the sides are washed with water. After filtration of the solution through a fast paper into a 400-ml beaker and washing of the paper several times with 15% hydrochloric acid, approximately 5 ml of *aqua regia* are added and the solution is evaporated to approximately 1 ml.

To the cooled sample solution, 5 ml of cadmium–copper sulphate solution is added and the mixture is transferred to a 25-ml volumetric flask and diluted to volume with water. The platinum, palladium and gold content of the sample is then determined by AAS. Any silver, rhodium, ruthenium or iridium remaining in the solution will not interfere.

NOTE. For milligram amounts of the precious metals, the solution obtained after the volatilization of tin is filtered into a 100–500-ml flask and diluted to volume with 15% hydrochloric acid to prevent hydrolysis. An aliquot is taken and treated by the procedure given above.

Calibration for AAS. Calibration curves for gold and palladium are linear in the ranges 0·2–3 ppm and 0·4–3 ppm respectively. However, for the determination of platinum it is necessary to use the interpolative method with standard solutions

Correction for gold in stannic oxide. Because all batches of stannic oxide tested in this laboratory were found to contain gold, it is deemed necessary to carry a blank through the analytical scheme.

RESULTS AND DISCUSSION

Effect of tellurium on precious metals during the determination by AAS

To determine the magnitude of possible interference by tellurium in the AAS determination of the three precious metals, synthetic solutions were prepared in which the Te:precious metal ratio was varied over an appreciable range. Each solution was evaporated

Table 1. Effect of tellurium on AAS determination of platinum, palladium and gold

Tellurium added, *mg*	Platinum, *μg*		Palladium, *μg*		Gold, *μg*	
	Added	Found	Added	Found	Added	Found
3	28	28	16	16	10	10
	42	40	31	31	20	20
	71	73	62	61	30	30
6	28	29	62	62	10	10
	42	43	31	31	20	20
	71	73	16	17	30	30
12	28	28	62	62	10	10
	42	44	16	16	20	20
	71	72	31	32	30	29
100	28	28	62	57	30	28
	42	40	16	15	10	9
	71	66	31	29	20	19

to approximately 1 ml and then conditioned for atomization by the procedures described above. The results, given in Table 1, show that tellurium has a moderate depressant effect on the determination of the precious metals when the Te:precious metal ratio is approximately 1000:1. However, in subsequent tests (Table 2) it was established that the amount of tellurium required (*i.e.*, ~ 15 mg) to act as an effective carrier during the fusion of the charge would ultimately result in a lower ratio in the final solution for atomization and, consequently, not interfere. The results in Table 1 also confirm that cadmium–copper sulphate buffer solution prevents interelement interference among the three precious metals,[10] at least in the ranges investigated.

Efficiency of tellurium as carrier during fusion and parting of tin button

To establish the efficiency of tellurium as a "carrier" during fusion and button-parting steps, a number of fire-assay charges were salted with tellurium, platinum, palladium and gold, and 0·5 g each of copper and nickel oxides to simulate ore samples. These samples were fused to produce tin buttons which were each analysed for the precious metals according to the procedures given above. The results of these tests, given in Table 2, show that when tellurium is not present, the recovery of the precious metals from the tin button is incomplete in most cases. Because it is known that collection of the precious metals by tin is quantitative, the losses no doubt occurred during the parting operation.

In earlier work, the hydrochloric acid–stannous chloride solution obtained on dissolution of the tin button was not boiled with additional fresh acid to reduce the amount of undissolved copper. Under those conditions, quantitative recoveries of platinum, palladium and gold were often achieved. In the present method, the parting step is protracted to ensure that there is less than approximately 0·1 g of copper in the residue. This amount, when diluted to 25 ml will not interfere subsequently in the AAS determination of the precious metals. (For example, by the procedure given above, less than 0·05 g of copper remained in the residue obtained on the parting of a granulated tin button that originally contained 0·75 g of copper.)

The results in Table 2 indicate that when 15–20 mg of tellurium are added to the charge, sufficient tellurium enters the button to act as a carrier for at least 7 mg of combined platinum, palladium and gold during the hydrochloric acid parting step. Of course, in practice, most samples would contain substantially less than milligram amounts of the precious metals (*e.g.*, Table 3).

In certain experiments with blank charges containing 50–200 mg of tellurium, it was found that a significant proportion of finely divided tellurium remained at the surface of the melt during fusion and subsequently stained the crucible wall at the top of the

Table 2. Effect of tellurium on recovery of precious metals from synthetic samples

Tellurium added, *mg*	Platinum, *μg*		Palladium, *μg*		Gold, *μg*	
	Added	Found	Added	Found	Added	Found
—	71	71	62	54	40	29
—	71	67	62	56	40	35
—	1540	1200	2180	1500	3000	2800
6	28	28	16	15	30	30
12	71	71	62	62	10	12
18	42	48	31	31	20	19
100	42	40	31	31	20	19
18	1540	1520	2180	2120	3000	2800
100	1540	1550	2180	2100	3000	3000

Table 3. Application of proposed method to certified reference materials

Sample	Sample wt., *g*	Element	Results, *ppm*	Mean, *ppm*	Std. devn., *ppm*	Relative std. devn., %	Certified value, *ppm*	Average of within lab rel. std. devn. of certifying labs., %
Magnetite conc. PTA-1[5]	14·58	Pt	3·02, 3·26, 3·05, 3·05, 3·26	3·12	0·10	3·2	3·05	15·7
Flotation conc. PTC-1[6]	14·58	Pt	2, 81, 3·16, 2·98, 3·26, 2·98	3·05	0·17	5·6	2·98	11·3
		Pd	12·8, 13·4, 12·2, 12·2, 12·8	12·7	0·48	3·8	12·7	7·2
		Au	0·65, 0·82, 0·58, 0·65, 0·58	0·65	0·10	15·0	0·65	20·2
Cu-Ni matte PTM-1[13]	14·58	Pt	5·66, 5·66, 5·87, 5·87, 5·73	5·76	0·10	1·7	5·83	5·2
		Pd	8·64, 8·40, 8·58, 8·58, 8·23	8·47	0·17	2·0	8·23	7·9
		Au	1·96, 1·99, 1·92, 1·99, 1·96	1·96	0·03	1·5	1·78	9·7
Gold ore MA-1[14]	14·58	Au	17·5, 17·5, 16·8, 18·5, 16·8	17·4	0·70	4·0	17·8	3·0
South African ore[7]	14·58	Pt	3·77, 3·84, 3·67, 3·77, 3·74	3·74	0·06	1·6	3·74	5·5*
		Pd	1·58, 1·58, 1·51, 1·51, 1·58	1·54	0·03	1·9	1·53	9·4*
		Au	0·31, 0·31, 0·27, 0·31, 0·27	0·31	0·02	6·5	0·31	18·0*

* Estimated from Table 15 of Ref. 7.

melt. In these tests the solubility of tellurium in tin may have been exceeded. In any case, using the recommended quantity of 25 mg ensures that sufficient tellurium ultimately appears in the button to act as an effective carrier for the precious metals.

The finely divided, amorphous, tellurium–precious metals residues from several synthetic samples were examined by microscopical methods and analysed by electron-microprobe techniques, and no discrete tellurium compounds could be identified.

A substantial fraction of the silver and rhodium that may be in the tin button will dissolve during parting, even when tellurium is present. Results from previous work,[11, 12] suggest that the same would be true for iridium and ruthenium. In any case, none of these metals, in the concentrations expected in the parting residue, will interfere ultimately with the AAS determination of platinum, palladium or gold.[3, 10]

Application to certified reference materials

The proposed method was applied to four certified reference materials prepared by the Canadian Certified Reference Materials Project, and also to a certified ore recently prepared by the National Institute for Metallurgy of South Africa. The analyses were performed in quintuplicate by the appropriate procedures described above, and the results are given in Table 3.

With the possible exception of the gold value for matte sample PTM-1, all results are in excellent agreement with the certified or recommended values for the five reference materials. Moreover, except for gold in MA-1, the coefficient of variation of the results by the proposed method is lower than the average of the coefficients of variation for the laboratories which participated in the certification of the reference materials.

CONCLUSION

The proposed modification of the tin-collection method, in which tellurium acts to prevent dissolution of platinum, palladium and gold during parting of the button in hydrochloric acid, offers several advantages over alternative fire-assay methods. It is simple and rapid; a set of samples can easily be carried from the fusion step through to completion within a working day. It is widely applicable and uses a flux of essentially fixed composition for all type of sample. No major separation steps are required to isolate and separate the precious metals after the fusion, *e.g.*, scorifications, ion-exchange or solvent extraction procedures, therefore potential losses are minimized. Its accuracy has been well established by analysis of a number of diverse certified reference materials.

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SPECTROFLUOROMETRIC DETERMINATION OF THIOPURINES—I
6-THIOGUANINE

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Summary—6-Thioguanine is oxidized to the corresponding *S*-oxide by reaction with hydrogen peroxide in 50% acetic acid at 50° for 5 min. The *S*-oxide is highly fluorescent and a rapid and sensitive fluorometric method of determination of thioguanine at the ng/ml level in water and μg/ml level in blood serum and urine has been developed on the basis of this reaction. The method has been used for the determination of thioguanine in blood and urine samples.

6-Thioguanine (2-amino-1,6-dihydro-6-thiopurine, I Fig. 1) is a chemotherapeutic drug used as an immunosuppressive agent and for treatment in the advanced stages of leukemia.[1,2] Very few methods have been reported for its determination although a spectrophotometric procedure has been used.[3] Spectrofluorometric methods of analysis generally have lower limits of detection than spectrophotometric methods. Although thioguanine is only weakly fluorescent it is often possible to modify non-fluorescent compounds chemically and so produce a fluorescent product (fluorophors).[4a,5] This can sometimes be done by oxidation.[6] Oxidation of thioguanine with 30% hydrogen peroxide in 50% acetic acid has been found to give a fluorescent product and a rapid and sensitive spectrofluorometric method of analysis for thioguanine has been developed which utilizes this reaction. The product of the oxidation appears to be the *S*-oxide of thioguanine (II in Fig. 1).

EXPERIMENTAL

Reagents

Thioguanine. The Koch-Light product was recrystallized before use.

Hydrogen peroxide. 30% (100-volume).

Acetic acid 50%. Analytical reagent grade glacial acetic acid diluted 1:1 (v/v) with distilled water.

Serum. Whole human blood (40–50 ml) was collected, allowed to coagulate in test-tubes and then centrifuged for 25 min. The serum collected (20–30 ml) was kept refrigerated (5°) until needed. No deterioration was observed after storage for 3 weeks.

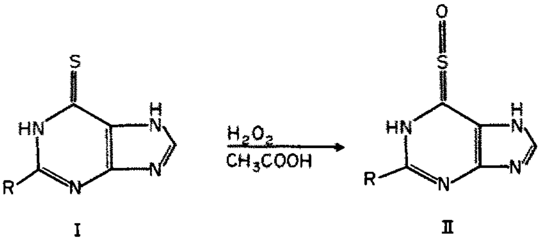

Fig. 1. Oxidation of 6-thioguanine (I, R = NH_2) to the *S*-oxide (II, R = NH_2) or of 6-mercaptopurine (I, R = H) to the *S*-oxide (II, R = H).

Sodium tungstate dihydrate solution, 10% *w/v.* $Na_2WO_4 \cdot 2H_2O$ (10 g) was dissolved in distilled water and the solution diluted to 100 ml.

Fluorescent reference standard. An approximately $10^{-5}M$ solution of ovalene in a solid polymer, manufactured by Perkin-Elmer, was used (excitation/emission wavelengths 340/480 nm).

Procedure

A stock solution of thioguanine in 50% acetic acid (300–400 μg/ml) is prepared by dissolving the thiopurine, with heating, in the acid. This solution is stable for at least 1 month at room temperature. A suitable aliquot of the stock solution is then oxidized by reaction with hydrogen peroxide at 50° for 5 min. The ratio of thioguanine solution to hydrogen peroxide is normally 10:1, *e.g.*, 1 ml of thioguanine solution to 0.1 ml of hydrogen peroxide.[6]

Calibration curve. After oxidation the solution is made up to standard volume (25 or 50 ml) with distilled water. This solution serves as a dilute oxidized stock solution of thioguanine (hereafter called the oxidized stock solution) and is stable for at least 24 hr. A calibration curve can then be constructed by taking appropriate aliquots of the oxidized stock solution, adjusting the pH to 6–7 with dilute sodium hydroxide solution (disodium hydrogen phosphate/potassium dihydrogen phosphate buffer, pH 6.9, can be added if desired), diluting to standard volume and measuring the fluorescence at 330/415 nm (excitation/emission).

Analysis of blood and urine samples. Blood serum (0.5 ml) is diluted with distilled water (2.0 ml) and 0.6*N* sulphuric acid (0.25 ml), mixed, and the protein precipitated by addition of sodium tungstate solution (0.25 ml).[4b] After centrifuging, 1.0 ml of the clear, protein-free serum is transferred into a standard flask, 3.0 ml of acetic acid (50%) are added, followed by 0.3 ml of hydrogen peroxide and the solution is oxidized by heating at 50° for 5 min. The solution is then diluted to volume (25 ml) with distilled water, a 1-ml aliquot is transferred into a 10-ml standard flask, the pH is adjusted to 6–7 and finally the solution is made up to volume and analysed. Care should be taken when transferring the deproteinated serum that no precipitated protein is carried over, otherwise high and variable blanks will result. A calibration curve is prepared by adding various volumes of standard aqueous thioguanine solution to 0.5-ml portions of serum, diluting with exactly enough water to give a volume of 2.0 ml, then deproteinating with sulphuric acid and sodium tungstate, and analysing as for serum samples.

For analysis of urine samples, 3 ml of acetic acid and 0.3 ml of hydrogen peroxide are added to 1 ml of urine in a 10-ml standard flask, then the mixture is heated at 50° for 5 min, and diluted as for the blood-serum samples. A calibration curve is prepared by adding various amounts of a thioguanine solution in 50% v/v acetic acid to the urine contained in the standard flask (25 ml), before the oxidation.

Apparatus

Fluorescence measurements were made with a Farrand spectrofluorimeter with 10-nm band-pass, fitted with a 150-W xenon arc lamp, RCA IP 28 photomultiplier, Honeywell Electronic 15 chart-recorder, and 10 × 10 × 45 mm quartz cells. All fluorescence spectra were uncorrected for instrumental artefacts.

Absorption spectra were obtained with a Unicam SP 800B recording ultraviolet spectrophotometer.

All glassware was cleaned by soaking overnight in dilute nitric acid, rinsing thoroughly with distilled water and then acetone, and allowing to dry.

RESULTS AND DISCUSSION

Acetic acid (50%) is a useful solvent for oxidations with hydrogen peroxide and has been recommended for the oxidation of phenothiazines.[6] Under these conditions, namely a 10:1 ratio of thioguanine solution in 50% acetic acid (*ca.* 350 μg/ml) to hydrogen peroxide, oxidation of thioguanine is complete after 20 min at room temperature (*ca.* 18°). It is, however, more convenient to carry out the reaction at 50°, oxidation then being complete after 5 min, and these reaction conditions were used throughout this study. A dilute solution of oxidized thioguanine (0.6 μg/ml) was stable for at least 24 hr.

Figure 2 shows the effect of pH on the fluorescence intensity of the oxidized thioguanine. On completion of oxidation the acetic acid is neutralized with sodium hydroxide to pH 6–7. A phosphate buffer can also be added, although experience has shown it is not essential, because of the wide pH-range for optimum fluorescence intensity.

Fluorescence characteristics

The absorption and fluorescence spectra of the oxidized product are shown in Figs. 3 and 4. The absorption spectrum of the unoxidized thioguanine in dilute acetic acid is also shown in Fig. 3. The excitation/emission wavelengths used for fluorescence analysis were 330 and 415 nm respectively, and the limits of detection and determination were 2 and 4 ng/ml respectively. The limit of detection is defined as that concentration of solution which gives a net signal equal to 4 times the standard deviation of the blank signal, and the limit of determination as the lowest concentration on the linear portion of the calibration curve (4–400 ng/ml). The standard deviation was 2 ng/ml for a thioguanine level of 110 ng/ml (15 replicates).

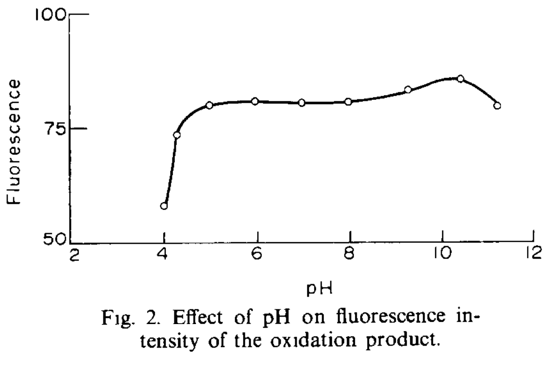

Fig. 2. Effect of pH on fluorescence intensity of the oxidation product.

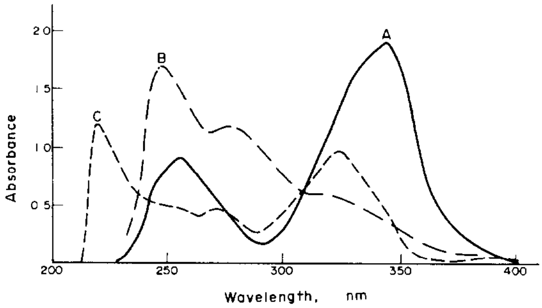

Fig. 3. Absorption spectra. (A)——Thioguanine in dilute acetic acid. (B) —·—Thioguanine oxidized with H_2O_2/CH_3COOH (C) – – – Thioguanine oxidized with alkaline permanganate.

Analysis of blood and urine samples

A blood sample was collected from a patient undergoing thioguanine chemotherapy, but it was not possible to detect the presence of the drug in the sample. This may be due to a number of factors. Moore and Le Page[3] found that thioguanine was absorbed very rapidly from the blood stream of mice, and converted into either thiouric acid or various nucleotides. It was also rapidly eliminated in the urine. Further, the amount of thioguanine in the blood at any one time did not exceed 3% of the dose given. The blood used for analysis here was taken approximately 3 hr after the patient had received a 40-mg dose of thioguanine. It is possible therefore, that the concentration of thio-

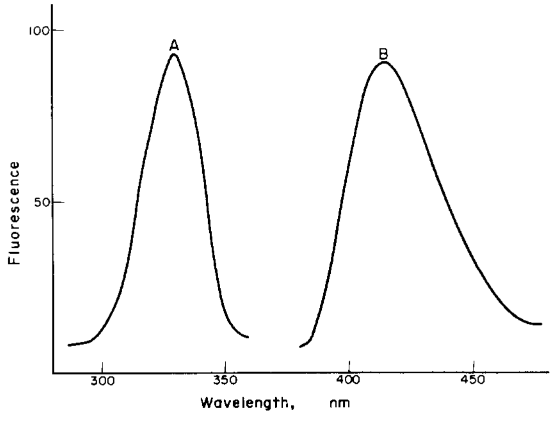

Fig. 4. Uncorrected excitation (A) and emission (B) spectra of thioguanine *S*-oxide in acetic acid.

Table 1. Determination of thioguanine in serum and urine

	Limit of detection µg/ml*	Linear calibration range, µg/ml*	Standard deviation, µg/ml
Urine	2.0	4–145	0.03 (1.34)†
Serum	2.0	4–174	0.01 (0.35)†

* Of sample.

† Concentration of the solution (µg/ml) analysed to determine the standard deviation; 15 solutions were analysed for the urine samples and 6 for the blood samples.

guanine in the blood stream would already have been below the detection limit at the time of sampling.

When different amounts of thioguanine were added to the control blood serum, before deproteination, and the sample was analysed as outlined above, an excellent linear calibration curve was obtained. Comparison of this curve with one obtained by adding thioguanine to the serum after deproteination, but before oxidation, showed that a large (but reproducible) amount of thioguanine (45%) is lost with the precipitated protein. This loss was confirmed by adding 10.35 µg of thioguanine to each of six samples of serum before the deproteination, and an equivalent amount (3.45 µg) to six samples of deproteinated serum, these being the amounts needed to give a final concentration of 0.35 µg/ml. Oxidation and analysis were then carried out and the fluorescence intensities for the two sets of solutions compared. They were 0.97 for the serum and 1.57 for the deproteinated serum (standard deviation 0.01 for both), indicating 45% loss during the deproteination.

The limit of detection for thioguanine in blood serum (Table 1) was obtained by addition of thioguanine to the serum before deproteination and subsequent oxidation. The loss of thioguanine from the serum during deproteination is compensated by a 95% enhancement of the fluorescence signal caused by the presence of the tungstate ion. The limiting detectable concentration of thioguanine in blood serum, allowing for deproteination, oxidation and dilution, is 2 µg/ml.

No urine samples were collected from the patient, so specimens from a healthy person were collected and various amounts of thioguanine were added. The limit of detection in urine samples is shown in Table 1, and is the same as for blood serum, despite the absence of any deproteination procedure, because of the high blank values obtained with urine. The conditions used for oxidation of thioguanine in blood and urine samples were chosen because they were found to give the highest signal-to-blank ratio and hence the lowest limit of detection. The limit of detection will probably vary from sample to sample because of differences in blank values and fluorescence backgrounds.

Comparison with other methods

Thioguanine has been determined by biological assay,[7] radio-tracer[8] and spectrophotometric[3] methods. In each case the limit of detection for the particular method has not been quoted, although the spectrophotometric method appears to be capable of determining blood levels of thioguanine in the 2–5 µg/ml range. It is not clear whether this value is the lower limit of detection for the method or has been obtained by extrapolation from more concentrated solutions. Although the limit of detection for thioguanine blood levels by the spectrofluorometric method is also 2 µg/ml, the analytical procedure would appear to be more rapid than any of the three methods mentioned above. Finkel,[9] in an independent study, has also reported a fluorometric method of determination of thioguanine, based on the fluorescence of the sulphonic acid of thioguanine, formed by oxidation with alkaline permanganate; the method has a comparable limit of detection for thioguanine (3 µg/ml). The analytical procedure however, requires more operations than the present method. The application of Finkel's method to the analysis of biological samples has not as yet been reported.

Oxidation product

Oxidation of thiopurines to the disulphide, or the sulphinic or sulphonic acid is well documented.[10,11] Oxidation to a thiopurine-*S*-oxide is rather less common and only one *S*-oxide, that of theophylline, has been isolated.[11,12] Other *S*-oxides have been prepared and their presence in solution has been demonstrated by a blue colour obtained when a ferric chloride solution is added to the suspected *S*-oxide. Oxidation to the *S*-oxide has generally been achieved with 30% hydrogen peroxide in either dimethylformamide (DMF) or dimethylsulphoxide (DMSO).[11,12] Oxidation of thioethers to the *S*-oxide by 30% hydrogen peroxide in acetic acid in the presence of traces of sulphuric acid has also been reported.[13] Walter *et al.*[12] have oxidized 6-mercaptopurine (**I**, Fig. 1) to the *S*-oxide with hydrogen peroxide in DMSO. This was repeated and the presence of the *S*-oxide indicated by addition of ferric chloride solution. Oxidation of thioguanine under the same conditions gave a similar result with the ferric chloride solution. The absorption spectrum

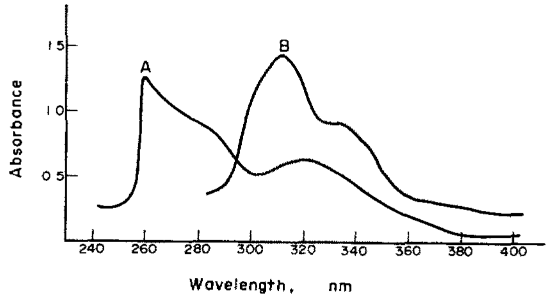

Fig. 5. Absorption spectra. **A**, Thioguanine oxidized with H_2O_2/DMSO. **B**, 6-mercaptopurine oxidized with H_2O_2/DMSO.

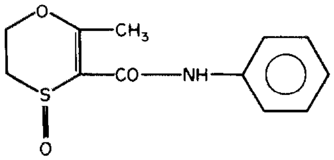

Fig. 6. "Vitavax" (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide) *S*-oxide.

of the *S*-oxide of thioguanine in DMSO was similar to that of the oxidation product of thioguanine in acetic acid (Figs. 3 and 5). The *S*-oxide of thioguanine in DMSO was also fluorescent with excitation/emission wavelengths at 330/395 nm. Oxidation of thioguanine with alkaline permanganate, which is known to form the sulphonic acid of thioguanine, resulted in a different absorption spectrum from that of the product of hydrogen peroxide oxidation (Fig. 3). It would appear then, that the product of oxidation of thioguanine by hydrogen peroxide is the *S*-oxide of thioguanine (**II**, Fig. 1). The *S*-oxide of mercaptopurine mentioned above fluoresced in DMSO solvent at 360/420 nm; its absorption spectrum had the same general shape as that of the oxidation product of thioguanine [Figs. 3 and 5].

CONCLUSION

Besides the *S*-oxides of thioguanine and 6-mercaptopurine the *S*-oxide of vitavax [5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide, Fig. 6] formed by oxidation with Ce(IV) is reported to be fluorescent.[14] The procedure outlined here may, therefore, have some potential as a method for spectrofluorimetric determination of thiopurines and sulphur-containing compounds such as thiouracil and 2,4-dithiouracil.

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SHORT COMMUNICATIONS

AN IMPROVED ION-SELECTIVE ELECTRODE FOR PERCHLORATE

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Currently, the Orion Model 92–81 perchlorate-selective electrode, as characterized by Rechnitz,[1] has a broad spectrum of uses such as the determination of solubilities of perchlorate salts,[1] the determination of vicinal glycols[2] and the determination of perchlorate levels in solution. However, it is possible that problems have arisen owing to its poor selectivity with respect to hydroxide ion. For this reason the preparation and preliminary investigation of a better perchlorate-selective electrode was initiated. The electrode, a liquid-membrane type, is based on the perchlorate salt of tetrakistriphenylphosphinesilver(I). The range and selectivity of the electrode have been studied and the results indicate an improvement over the Orion model, most markedly in the selectivity with respect to hydroxide.

EXPERIMENTAL

Reagents

The salt was prepared as described by Cotton and Goodgame:[3] 1·55 g of silver perchlorate were dissolved in 4 ml of hot abslute ethanol and added to a solution of 7·87 g of triphenylphosphine in 30 ml of hot ethanol. The solid which precipitated immediately was filtered off, and recrystallized from acetonitrile (3 g in 125 ml), and the crystals were washed with methanol and dried *in vacuo*. The triphenylphosphine was obtained from the J. T. Baker Chemical Co. and the silver perchlorate from the G. F. Smith Chemical Co. All other chemicals used were reagent grade. Elemental analysis gave the following results: C, 69·1%; 4·9%; calculated for $C_{72}H_{60}AgClO_4P_4$, C, 68·82%; H, 4·82%. An approximately 2 mM solution of the salt in nitrobenzene was used as the exchanger.

Apparatus

The electrode was assembled in the versatile liquid-membrane body developed by Hildebrandt.[4] The porous membrane was a 0·45-μm "Millipore" filter. For most experiments, the internal reference electrode was an aqueous agar gel 2M in sodium chloride and 1M in sodium perchlorate, in contact with a Ag/AgCl element. The external reference electrode was a Corning 4·0M sodium chloride–calomel reference electrode. The electrodes were placed in a jacketed cell, kept at a constant temperature of 25·0°, containing about 50 ml of sample solution which was stirred continuously. Potentials were measured with the apparatus described in reference 5 and the pH was measured with a Beckman Research pH-meter.

RESULTS AND DISCUSSION

Electrode response

The potential measured as a function of perchlorate-ion activity and concentration is shown in Fig. 1. At $>10^{-5}M$, the response is $-58{\cdot}65 \pm 0{\cdot}20$ (95% confidence limit) mV per decade of activity. From 10^{-5} to $10^{-6}M$, the response is smaller, yet still shows enough change in potential from that of the base electrolyte for semiquantitative determinations to be made in this region. Single-ion activities were estimated from the extended Debye–Hückel equation:

$$-\log f_i = \frac{0{\cdot}5 Z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

The range was measured in the presence of 0·002M acetate buffer ($\mu = 0{\cdot}002$, pH = 5·07). It was found that when no background electrolyte was used, the slope was non-Nernstian. Acetate was employed because of its favourable selectivity constant. In 10^{-3}–10^{-1} M solutions of perchlorate, stable readings (drift < 0·05 mV/min) were obtained within 1 min. With more dilute solutions, up to 5 min were necessary. At concentrations of $<10^{-6}M$, as long as 15–20 min were needed to obtain a stable reading. Stability of readings was not a function of speed of stirring.

Effect of other anions

Selectivity coefficients ($K_{ClO_4^-/X}$) were determined by the separate-solution method and checked with the more accurate mixed-solution method. In the separate-solution method, the potentials of the electrode were measured first in 0·0091M sodium perchlorate and then in 0·0091M solutions of the sodium salts of various potentially interfering anions. (For bivalent anions, 0·0027M solutions of the disodium salts were used to keep the ionic strengths nearly equal). The selectivity coefficients were then calculated from the equation:[6]

$$\log_{10} K_{ClO_4^-/X} = \frac{E_{ClO_4^-} - E_X}{59{\cdot}1} + \log_{10} a_{ClO_4^-} - \frac{1}{z_X}\log_{10} a_X$$

The mixed-solution method was employed for Cl^-, OH^-,

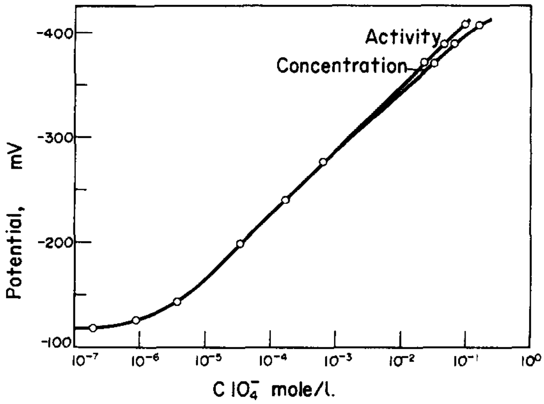

Fig. 1. Response of perchlorate-selective electrode in acetate buffer ($\mu = 0{\cdot}002$, pH = 5·07) as a function of activity and of concentration.

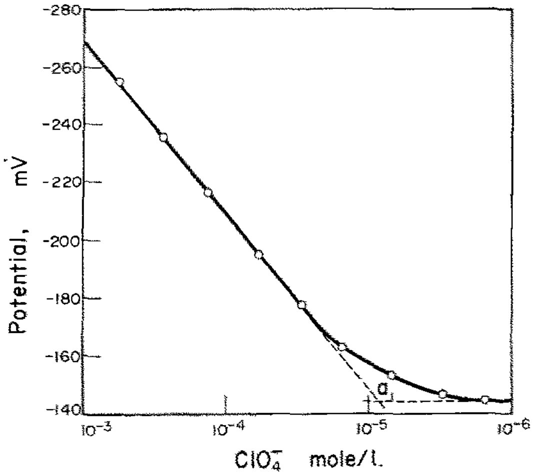

Fig. 2. Typical curve obtained by mixed-solution method for the perchlorate-selective electrode. Interfering electrolyte is $10^{-1}M$ sodium hydroxide.

NO_3^-, acetate and SO_4^{2-}. The interfering anions were used at a nearly constant concentration of 0·0091*M* (0·0027*M* for SO_4^{2-}). Known volumes of perchlorate were then added to this solution of interfering anion and the potential was recorded after each addition. A plot such as that in Fig. 2 was obtained. The selectivity coefficients were calculated from the equation:[6]

$$K_{ClO_4^-/X} = \frac{a_{ClO_4^-}}{a_X^{1/z_X}}$$

where z_X is the charge on the interfering anion, a_X the single-ion activity and $a_{ClO_4^-}$ is the activity of perchlorate at which the first observable potential change is noticed. This activity is obtained from the graph in Fig. 2. The selectivity coefficients obtained this way agreed acceptably with those from the separate-solution method.

Fluctuations of less than 0·5 mV were observed for the stable readings in the separate-solution method, with little or no drift. Response time in the mixed-solution method was similar to that mentioned previously.

Table 1. Selectivity coefficients for the perchlorate-selective electrode

		$K_{ClO_4^-/X}$	
Anion (X)	*E, mV**	Separate solution	Mixed solution
ClO_4^-	−168·9	—	–
NO_3^-	−13·8	$2{\cdot}4 \times 10^{-3}$	$2{\cdot}8 \times 10^{-3}$
OAc^-	+27·7	$4{\cdot}7 \times 10^{-4}$	$1{\cdot}6 \times 10^{-4}$
OH^-	+25·0	$4{\cdot}3 \times 10^{-4}$	$8{\cdot}3 \times 10^{-5}$
Cl^-	−16·0	$2{\cdot}6 \times 10^{-3}$	$2{\cdot}4 \times 10^{-4}$
HCO_3^-	+35·8	$3{\cdot}4 \times 10^{-4}$	–
$H_2PO_4^-$	+39·6	$2{\cdot}9 \times 10^{-4}$	–
SO_4^{-2}	+35·0	$2{\cdot}2 \times 10^{-5}$	$3{\cdot}4 \times 10^{-5}$
HPO_4^{-2}	+22·0	$3{\cdot}9 \times 10^{-5}$	–

* These potential values refer to pure solutions of sodium salts of the anions listed and were used to calculate the separate-solution selectivity constants given in column 3.

For these tests the phosphate concentration was $2{\cdot}7 \times 10^{-3}M$ ($\mu = 0{\cdot}0082$) and all other anion concentrations were $9{\cdot}1 \times 10^{-3}M$ ($\mu = 0{\cdot}0091$).

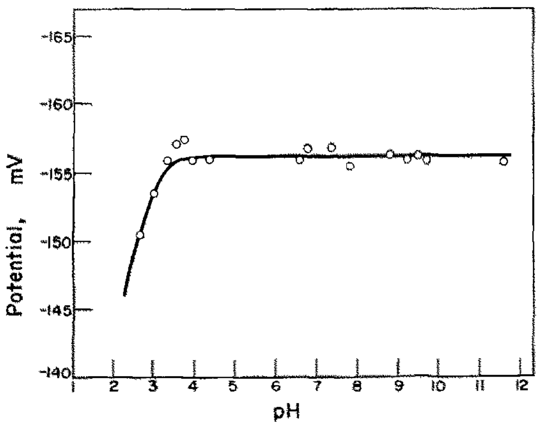

Fig. 3. Effect of pH on the response of the perchlorate-selective electrode. Perchlorate concentration was 0·002*M*.

Selectivity coefficients are given in Table 1. All interferences measured are well within acceptable ranges and are comparable to those given by Orion[7] and those reported by Rechnitz,[1] with the exception of that of hydroxide. At least a 10^4-fold improvement in selectivity is found here.

The effect of pH on the electrode response was determined by the addition of 0·1*M* perchlorate or sodium hydroxide to adjust the pH of a solution of 0·002*M* perchlorate. In Fig. 3 the change in potential is given as a function of the measured pH. Potentials plotted in Fig. 3 have been corrected for dilution in the case of sodium hydroxide additions and for the added perchlorate in the case of perchloric acid additions. Note that the potential scale of Fig. 3 is offset by approximately 120 mV from that of Figs. 1 and 2. This is due to the fact that a different external reference electrode was used for this experiment and the aqueous agar internal reference gel contained a higher concentration of sodium chloride than was used in the other experiments. The useful pH range for the electrode is from 3 to 12. Over this range the potential varies less than 5 mV

Conclusion

The new perchlorate-selective electrode described in this paper has been shown to be superior to the Orion electrode as regards its selectivity with respect to hydroxide ion. Other common anions show very similar selectivities to those reported for the Orion product. Low perchlorate concentrations in basic solutions can now be estimated without the difficult corrections based on the large selectivity coefficient ($K_{ClO_4^-/OH^-}$) characteristic of the Orion model 92–81 electrode

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Summary—A new liquid-membrane ion-selective electrode for perchlorate ion based on tetrakistriphenylphosphine silver(I) perchlorate in nitrobenzene is described. Its dynamic range and selectivities relative to most common anions are comparable to those of the Orion model 92–81 perchlorate sensor However, it suffers much less hydroxide-ion interference than the Orion product.

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DETERMINATION OF TRACE AMOUNTS OF BARIUM IN SILICATE ROCKS AND MINERALS BY ION-EXCHANGE CHROMATOGRAPHY AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY*

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In geochemical analyses it is often necessary to determine alkali and alkaline earth metals. Most of these determinations are easily carried out by conventional analytical techniques such as atomic-absorption spectrophotometry (for Ca, Li, Mg and Sr) and flame emission photometry (for Na, K and Rb).[1]

To complete the range of determinations we have tried to determine trace amounts of barium in rocks and minerals by atomic-absorption spectrophotometry (AAS) because of the absence of data obtained with this technique for standard silicate rocks. The physical methods employed in barium determination are direct reading spectrography, optical spectrography, X-ray fluorescence spectrometry and neutron-activation analysis,[2,3,4] but these are expensive and not readily available. The difficulty with determining trace amounts of barium by AAS is the existence of strong matrix effects.[5,6] The present work overcomes this difficulty by a prior ion-exchange separation.

EXPERIMENTAL

Interferences

The determination of barium by AAS suffers from two kinds of interference from the very high calcium concentration found in most rock and mineral samples. The CaOH formed in the flame has an emission band with a maximum at 554 nm, overlapping the analytical line (553·4 nm) for barium. Source modulation improves the situation but when the calcium concentration is very high the emission saturates the detector, giving a background too high to permit reliable analysis. Further the radiation at 553·5 nm may be absorbed by the CaOH molecules.[7,8] These interferences have been shown to be due to the presence of alkaline earths.[9,10] In addition, lanthanum also interferes in the determination of barium[8] owing to the presence of LaO which has an absorption band with a maximum at 553·6 nm.[11]

Aluminium has also been shown to interfere in the determination[12] of alkaline earth metals and this effect is removed by the addition of a lanthanum solution[13] when strontium is determined. Koirtyohann and Pickett[14] reported a study of the interference of aluminium in the determination of barium and showed that this was less than 1% for an Al:Ba ratio of 1000:1. These authors eliminate the aluminium interference by adding lanthanum solution (for Ca and Sr determination) and take account of the interference caused by the LaO band. Maruta *et al.*[15] observed that aluminium forms refractory compounds which are not easily dissociated and may be responsible for the depressant effect of aluminium on the barium absorption. They suggested suppressing aluminium interferences by the addition of oxine and ammonium chloride. Magnesium oxide also gives an interfering band at a wavelength of 553·5 nm.[14] Silicon interferes when in the form of sodium silicate but this interference is due to sodium. Alkali metals reduce the ionization of barium atoms, with consequent enhancement of the atomic absorption.[14] All these interferences give rise to poor reproducibility in the atomic-absorption and flame emission determination of barium when performed directly on the original sample.

Further, the interference is sufficiently strong to invalidate results obtained by the method of standard additions. Therefore we have recognized the necessity of separating barium from other elements in the matrix. The separation of barium is carried out by ion-exchange chromatography. This technique gives quantitative separations of a large number of ions[16,17] and it may be applied to rock analysis.[18–23] Ba^{2+} may be separated from other cations on ion-exchange resins, employing aqueous alcoholic solution of hydrochloric acid as eluents. Strelow[24] and other workers[25] have shown that ethanol is the most satisfactory alcohol for this purpose. A synthetic sample, containing major and some trace elements, was prepared in order to test the separation. Weighed amounts of pure salts of the most important interfering elements were mixed in the ratio appropriate to common rock samples. Silica is absent from this mixture because in the pretreatment of a rock sample with a hydrofluoric–perchloric acid mixture, silica is removed by volatilization of the fluoride. In any case, after passage through a cation-exchange resin, silicate anions are separated from the other ions. Table 1 shows the composition of the synthetic sample and that of the basalt BR (C.R.P.G.–A.N.R.T.). Major elements are expressed as oxides—trace elements are expressed as metals.

The separation is carried out on the strong acid sulphonated resin. Dowex 50 × 8, 200–400 mesh, H^+-form. The resin column is 18 cm long and 2·2 cm in diameter. All elements (except Ba) are eluted with 3*M* hydrochloric acid in 20% aqueous ethanol. Barium is eluted with 3*M* hydrochloric acid; the elution curve is plotted from results on 10-ml aliquots of eluate, in Fig. 1. The elements are determined in each fraction by AAS (Al, Fe, Mg, Ca, Ba and Sr) and flame emission photometry (Na, K).

In this separation heavy rare earth elements are eluted together with strontium, and light rare earth elements are retained (and successively eluted) with barium.[23,24] Nevertheless we did not think it necessary to separate light rare earth elements (lanthanum in particular) because of the

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* This work is financially supported by C.N.R., Italy.

Table 1. Matrix element/barium ratios of synthetic sample and basalt BR

Ratio	Synthetic sample	Basalt BR
Al_2O_3/Ba	103	97
Fe_2O_3/Ba	110	123
MgO/Ba	139	127
CaO/Ba	141	131
Na_2/OBa	34	29
K_2/OBa	13	13
Sr/Ba	1·3	1·3

very small amounts of these elements present in common rock and mineral samples.

To confirm the reproducibility of the method, the separation was performed on aliquots of the synthetic solution. In six aliquots, each containing 12·0 mg of barium, 11·7, 11·7, 11·4, 11·5, 11·5 and 11·8 mg were found. The quantitative determination of the separated barium is carried out by AAS, employing a nitrous oxide–acetylene flame, with potassium as ionization suppressor.[5,14] The sensitivity of the method (1% absorption) is about 0·2 ppm barium.

Reagents

Hydrochloric acid (*3M*) *in 20% ethanol.*

Potassium solution, 10^5 *ppm* (19% solution of potassium chloride).

Standard solution of barium, 100 *ppm.*

Apparatus

A Metrohm Multi-dosimat E-415 automatic sampler–microburette and an atomic-absorption spectrophotometer Jarrell-Ash "Atomsorb" Model 82·271 equipped with a B-5 Kipp and Zonen recorder were used; the source was a Westinghouse hollow-cathode lamp.

Column packing and calibration

Fill a borosilicate glass tube with dry Dowex 50 × 8 resin (200–400 mesh) to give a column height of 18 cm and wash it with 300 ml of 3*M* hydrochloric acid. Wash with water until free from any acid reaction.

Weigh 1·4369 g of barium carbonate into a large beaker. Add 10 ml of 1:1 v/v hydrochloric acid and 100 ml of water. Pour into a 1 litre graduated flask and make up to the mark with water. Dilute this solution 1:10 with water to provide a 100-ppm barium solution and store in polythene bottles. Pipette 1, 3, 5, 7 and 11 ml portions of this solution into separate 100-ml graduated flasks. Add 10 ml of 10^5-ppm potassium solution to each flask and dilute to 100 ml. Pour 10 ml of the 10^5-ppm potassium solution into a further 100 ml flask and dilute to 100 ml to provide the calibration curve blank. Aspirate the solution into a 5-cm laminar-flow burner employing a nitrous oxide–acetylene flame, setting the monochromator to a wavelength of 553·5 nm. Measure the recorded signals, subtracting the blank. Plot the curve of measured absorbance against concentration.[26]

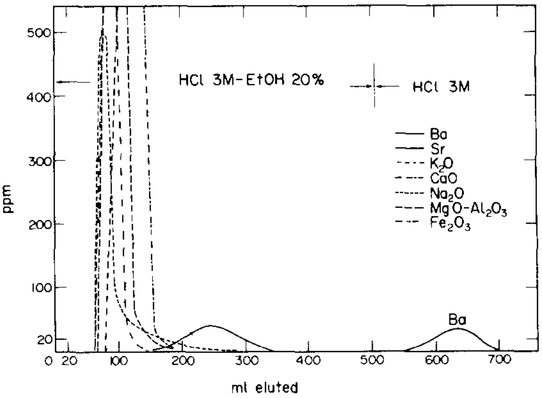

Fig. 1 Synthetic sample elution curve.

Analytical procedure

Weigh out 1 ± 0·0001 g of finely powdered (120-mesh) sample, in a PTFE dish. Moisten the powder with water to avoid spattering. Add 10 ml of 40% hydrofluoric acid and 10 ml of 70% perchloric acid, mixing with a platinum or PTFE rod. Allow to stand overnight in the fume-cupboard and then heat to dryness. Add 10 ml of hydrofluoric acid and 10 ml of perchloric acid and heat to dryness. Add 5 ml of perchloric acid and heat to dryness. Add 20 ml of water and 5 ml of hydrochloric acid. Repeat this procedure but without a sample, to obtain a blank solution.

Transfer the solution to a 100-ml graduated flask and dilute to 100 ml. Pass the sample solution through the ion-exchange column at a flow-rate of 2·5 ± 0·3 ml/min. Elute with 500 ml of 3*M* hydrochloric acid in 20% ethanol (all major elements which can be determined with the commonly used methods are present in this portion). Elute with a further 500 ml of 3*M* hydrochloric acid and evaporate the barium solution to about 50 ml. Transfer to a 100-ml graduated flask with rinsing, add 10 ml of 10^5-ppm potassium solution and dilute to 100 ml with water. This treatment is also performed on the blank solution. Aspirate

Table 2. Barium content of rock and mineral standard samples, *ppm*

Sample		Found	Recommended or median value	Range	Methods*	Remarks
Diabase	W–1	170	160	—	—	Flanagan (1973)
Andesite	AGV–1	1121	1208	1047–2700	OS, XRF,INAA	Flanagan (1969, 1973)
Basalt	BCR–1	700	675	480–1230	OS, XRF,INAA	,,
Dunite	DTS–1	4	2·4	—	OS, XRF	,,
Peridotite	PCC–1	5	1·2	—	OS, XRF	,,
Granodiorite	GSP–1	1225	1300	855–2000	OS, XRF, INAA	,,
Granite	G–2	2188	1870	1500–3000	OS, XRF, INAA	,,
Basalt	BR	1037	1050	—	—	Flanagan (1973)
Granite	GA	787	850	—	—	,,
Granite	GH	23	22	—	—	,,
Granite	GR	1095	1050	—	—	,,
Serpentine	UB–N	60	40	10–65	OS, XRF, DS	De la Roche, Govindaraju (1973b)
Diorite	DR–N	376	380	345–860	OS, XRF, DS	,,
Bauxite	BX–N	40	30	-	DS	,,
Disthene	DT–N	45	40	—	DS	,,
Synthetic glass	VS–N	973	896	842–1500	OS, XRF, DS	De la Roche, Govindaraju (1973a)
Feldspar	FK–N	510	—	—	—	—
Granite	GS–N	1270	—	—	—	—

* OS = Optical spectrography, DS = Direct reading spectrometry, XRF = X-ray fluorescence, INAA = Instrumental neutron-activation analysis.

the sample and blank solutions into the burner as described previously. Correct the sample absorption by subtracting the blank. Calculate the barium concentration by reference to the calibration curve.

BX-N (bauxite) and DT-N (disthene) samples are not easily solubilized by the acid attack and a fusion procedure is adopted for these samples, as follows.

Weigh out 1 ± 0·0001 g of finely powdered sample, in a platinum crucible. Add 2·5 of 5:1 sodium carbonate–boric oxide mixture and mix. Heat on a bunsen burner to expel carbon dioxide and transfer to a muffle at 1000° for about 20 min. Cool and dissolve the melt in 5 ml of hydrochloric acid and 200 ml of water. Evaporate the solution to about 70 ml, transfer to a 100-ml graduated flask and dilute to volume. This procedure requires a blank from 2·5 g of fusion mixture and 5% hydrochloric acid. The solutions are passed through ion-exchange columns and analysed as described above.

RESULTS AND CONCLUSION

Barium contents of the standards are shown in Table 2. Recommended or median values are those indicated by Flanagan[27] for U.S.G.S. samples (W-1, AGV-1, BCR-1, DTS-1, PCC-1, GSP-1, G-2), and for C.R.P.G.-A.N.R.T. samples (BR, GA, GH, GR). Range values are indicated by Flanagan[2] for the samples cited and by De la Roche and Govindaraju[3,4] for the other samples. These authors report one value only for the BX-N and DT-N samples. Feldspar FK-N and granite GS-N are new C.R.P.G.-A.N.R.T. standards. All values found are in good agreement with the recommended or median values and the ranges reported.

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Summary—Trace amounts of barium are determined in the standard silicate rocks and minerals, W-1, AGV-1, BCR-1, DTS-1, GSP-1, G-2 of the U.S. Geological Survey and BR, GA, GH, GR, UB-N, DR-N, BX-N, DT-N, VS-N, FK-N, GS-N of the Centre de Recherche Petrographique et Geochimique de Nancy and the Association Nationale de la Recherche Technique. After an ion-exchange separation, the analyses are carried out by atomic-absorption spectrophotometry. The separation is performed to eliminate interferences due to matrix effects.

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MICRO AND SUBMICRO IODOMETRIC DETERMINATION OF ARSENITE AND SULPHITE IONS BY AMPLIFICATION REACTIONS

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Both chemical and physicochemical methods are available for the determination of arsenite and sulphite. Arsenite, after treatment with various oxidants, can be determined gravimetrically as magnesium ammonium arsenite[1] or as quinoline molybdoarsenate.[2] Cyanotungstates or molybdates,[3] ceric sulphate,[4] *N*-bromosuccinimide,[5] sodium peroxymolybdate[6] or potassium permanganate[7,8] have been utilized as redox reagents for the volumetric determination of arsenite. Potentiometric,[9] biamperometric,[10] and spectrophotometric[11] methods have also been described.

Methods for sulphite include oxidation by iodine[12,13] or by permanganate and iodine monochloride,[14] complexometry,[15] spectrophotometry,[16] potentiometry,[17] and polarography [18]

Because amplification reactions increase the sensitivity of determination of some ions,[19,20] the present work was aimed at extending their use to determination of arsenite and sulphite.

The arsenite method is based upon oxidation with periodate, masking of the excess with molybdate, and subsequent iodometric titration of the liberated iodate. The method for sulphite depends upon oxidation with iodine in a bicarbonate medium, extraction of the excess with chloroform, oxidation of the resulting iodide with bromine-water, and finally iodometric titration of the iodate produced. In this way, the degree of amplification involved in the two iodometric methods is 3- and 6-fold, respectively.

EXPERIMENTAL

Reagents

The reagents used were of analytical grade and doubly distilled boiled-out water was always used.

Ammonium molybdate tetrahydrate, 10% *aqueous solution.*

Arsenite ($NaAsO_2$) *solutions*, 0·05 *and* 0·5 *g/l.*

Buffer solution, *pH* 2·5–3. Prepared by adding *ca.* 110 ml of glacial acetic acid to 40 ml of 0·2*M* sodium acetate.

Potassium iodide. Aqueous solutions, 1 and 10%, prepared daily.

Potassium periodate solutions. Prepared fresh by dissolving (*A*) 1 g or (*B*) 2 g of the recrystallized salt in 600 ml of water, and kept in amber bottles.

Sodium thiosulphate, 0·002 *and* 0·01*M solutions.* Standardized against potassium iodate solutions.

Iodine solution, 0·13%, *in chloroform.*

Sodium sulphite solution The anhydrous salt (0·2 g) dissolved in water (1 litre).

Arsenite procedure

Introduce a portion (1–4 ml) of the sodium arsenite solution containing 0·05–0·20 mg into a 100-ml conical flask, add 5 ml of periodate solution *A* followed by 5 ml of the buffer solution, and immerse the flask in a water-bath at *ca.* 70° for 6 min. Cool, add 5 ml of each of the molybdate and the 1% potassium iodide solutions, stopper the flask, and leave aside for 2 min in a dark place. Then, titrate the liberated iodine with 0·002*M* thiosulphate, using starch as indicator as usual. Carry out a blank experiment and calculate the arsenite content.

1 ml of 0·002*M* thiosulphate = 0·0433 mg of $NaAsO_2$

For amounts of sodium arsenite between 0·20 and 2·0 mg, use 10 ml of periodate solution *B* and heat in the water-bath for 25 min at 60–70°. After cooling, add 10 ml of the molybdate solution and 5 ml of the 10% iodide solution and complete the determination as before, including a blank, using 0·01*M* thiosulphate solution for the titration.

1 ml of 0·01*M* thiosulphate ≡ 0·2165 mg of $NaAsO_2$

Sulphite procedure

Transfer a 1–10 ml portion of the test solution containing 0·2–2·0 mg of sodium sulphite into a 100-ml separating funnel, add 20 ml of 5% potassium bicarbonate solution followed by 5 ml of iodine solution and shake for 5 min. Add 10 ml of water, mix thoroughly and then leave till the layers have completely separated. Discard the chloroform layer and remove traces of iodine from the aqueous layer by extraction with three 10-ml portions of chloroform. Transfer the aqueous layer quantitatively into a 250-ml conical flask, add 3 ml of 2*M* sodium acetate solution and 5 ml of saturated bromine-water and stir the solution for 15 min on a magnetic stirrer. Destroy the excess of bromide by dropwise addition of formic acid (*ca.* 0·4 ml), add 20 ml of the acetate–acetic acid buffer, 2 ml of 10% potassium iodide solution, and titrate the liberated iodine with 0·01*M* sodium thiosulphate, adding starch as indicator just before the end-point. Run a blank and calculate the amount of sodium sulphite.

1 ml of 0·01*M* thiosulphate ≡ 0·1050 mg of Na_2SO_3

RESULTS AND DISCUSSION

The arsenite method

Potassium periodate in slightly acidic medium has been reported[21] to be a suitable reagent for the direct oxidimetric titration of arsenic(III), with diphenylamine as indicator. The reaction, which is catalysed by iron(II), proceeds according to the equation.

$$As^{3+} + IO_4^- + 2H^+ \rightarrow As^{5+} + IO_3^- + H_2O \qquad (i)$$

This reaction formed the basis of the amplification method developed in the present work:

$$AsO_2^- + IO_4^- \rightarrow AsO_3^- + IO_3^- \qquad (ii)$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (iii)$$

During the development of the method from reaction (*ii*), the following factors were studied to optimize the conditions.

Reaction time and temperature. At room temperature the oxidation of microgram amounts (50–200 μg) of sodium arsenite was found to proceed slowly, so recovery was quantitative only after 35-min reaction time. Raising the reaction temperature to *ca.* 70° enabled complete oxidation to occur after 6 min. For larger amounts (0·5–2·0 mg), however, heating at 70° for 25 min was necessary.

Effect of pH. The optimum pH value for the periodate oxidation was found to be 3. Higher pH renders the reaction rather sluggish, as might be expected from equation (*i*). On the other hand, pH values lower than 3 gave rise to inconsistently high (*ca.* 3–5%) recoveries of arsenite. This may be ascribed to partial oxidation of the iodide added, by the arsenate ion produced, and to incomplete masking[22] of the unreacted periodate with molybdate.

The function of the molybdate. As in previous work,[22] complete masking of the unreacted periodate was achieved by addition of a large excess of ammonium molybdate (5 ml of a 10% solution) at pH 3, which is stated to be the optimum value for masking. The excess of molybdate also proved to play another role, namely preventing oxidation of added iodide by the arsenate ion resulting from the reaction, probably by formation of arsenomolybdate complexes.

The procedure finally developed was applied to determination of amounts of sodium arsenite ranging between 50 μg and 2·0 mg. Highly satisfactory results (Table 1) were obtained. The maximum and minimum recoveries are 101·2 and 99·0% and the average recovery is 99·9%. All the values in Table 1 were calculated on the basis of a 3-fold amplification, which proves that the molybdate-catalysed 4-fold amplification reaction,[19] involving the additional reaction

$$AsO_3^- + 2I + 2H^+ \rightarrow AsO_2^- + I_2 + H_2O \qquad (iv)$$

does not take place.

The blank values found were reasonable; periodate solution *A* gave a negligible value, solution *B* gave a maximum value of 0·24 ml of 0·01*M* thiosulphate. The latter blank value is probably due to the 25-min heating period as compared with the 6-min period employed in case of solution *A*.

The sulphite method

The usual iodimetric determination[12,23] of sulphite is based on the reaction:

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2HI \qquad (v)$$

Much controversy exists in the literature[12,23] regarding the iodimetric titration of sulphite. The main errors are loss of SO_2 by volatilization, air-oxidation of sulphite and the precipitation of sulphur as represented in the following equations:

$$H_2SO_3 + 4HI \rightarrow 2I_2 + S + 3H_2O \qquad (vi)$$

$$3H_2SO_3 \rightarrow 2H_2SO_4 + S + H_2O \qquad (vii)$$

Table 1. Micro and submicro determination of sodium arsenite by oxidation with periodate

Sodium arsenite, *mg*		
Taken	Found	Recovery*,%
2·000	1·980	99·0
	1·996	99·8
1·500	1·498	99·9
	1·492	99·5
0·500	0·499	99·8
	0·498	99·6
0·200	0·1990	99·5
	0·1999	100·0
0·150	0·1500	100·0
	0·1497	99·8
0·100	0·1004	100·4
	0·0995	99·5
0·050	0·0503	100·6
	0·0506	101·2

* The average recovery is 99·9%.

The latter reaction (*vii*) is said to be catalysed[23] by hydriodic acid. Certainly, on subjection of the method to a drastic check, persistently low (3–4%) sulphite recoveries were obtained. Despite the sources of inaccuracy inherent in this method, it is still the one in use for the assay of sulphite, probably because of the popular iodimetric finish. The apparent inaccuracies motivated our search for an accurate method preferably retaining the simple and rapid iodometric finish.

The method developed is based on the reactions:

$$Na_2SO_3 + I_2 + 2HCO_3^- \rightarrow Na_2SO_4 + 2I^- + 2CO_2 + H_2O \qquad (viii)$$

$$2I^- + 6Br_2 + 6H_2O \rightarrow 2IO_3^- + 12HBr \qquad (xi)$$

$$2IO_3^- + 10I^- + 12H^+ \rightarrow 6I_2 + 6H_2O \qquad (x)$$

As clear from equations (*viii*)–(*x*), each mole of sulphite is ultimately equivalent to 12 iodine atoms. Thus, this method gives a 6-fold amplification as compared with the original direct iodimetric method shown in equation (*v*).

During the working out of the procedure, it was realized that the potassium bicarbonate plays a significant role, not only shifting the reaction towards complete oxidation of sulphite, but also eliminating reactions (*vi*) and (*vii*). A further advantage is that no volatilization of SO_2 occurs, in contrast to the direct iodimetric method[23] in acidic medium.

However, experiments with increasing amounts of sulphite (0·2–2·0 mg) revealed that the concentration of bicarbonate should be increased proportionally (2·0–20·0 ml of 5% solution) indicating that its role is definitely not simply an effect of pH, which remains almost constant at *ca.* 8·3 throughout the whole range of bicarbonate added. If the weight ratio of potassium bicarbonate to sodium sulphite was lower than 500, the sulphite recoveries were always low. Fortunately, however, although a deficiency of bicarbonate must be avoided, a larger excess does not affect the accuracy. A representative series of results, showing the effect of bicarbonate concentration on the sulphite recovery, is given in Table 2.

It was interesting to test whether the reaction would also proceed quantitatively at a higher pH value. For this purpose, 5% potassium carbonate solution (pH 10·5) was used. Very high and inconsistent values were obtained, amounting to about double the expected sulphite recoveries. This may be due to formation of hypoiodite in such an alkaline medium. Hypoiodite can easily oxidize the iodide added for the iodate titration, giving rise to an additional amount of iodine and erroneously high recoveries.

Regarding the use of iodine as oxidant for the sulphite, an aqueous solution is not suitable in the present work owing to the necessity of dissolving the iodine in potassium iodide which interferes seriously throughout the procedure

Table 2. Effect of concentration of bicarbonate and iodine on the oxidation of sodium sulphite

Sodium sulphite, *mg*		Volume of $KHCO_3$ solution, *ml*	Volume of iodine solution, *ml*	Recovery, %
Taken	Found			
0·200	0·0652	1	0·2	32·6
	0·1249	1	0·5	62·5
	0·1978	2	0·5	98·8
	0·1991	10	0·5	99·6
	0·1996	20	0·5	99·8
	0·1980	20	5·0	99·0
2·000	0·0994	20	0·5	5·0
	1·9964	20	5·0	99·8

Table 3. Micro and submicro determination of sodium sulphite by oxidation with iodine

Sodium sulphite, *mg* Taken	Found	Recovery* %
2·000	1·991	99·6
	2·012	100·6
1·200	1·184	98·7
	1·182	98·5
0·800	0·789	98·6
	0·790	98·8
0·400	0·404	101·0
	0·395	98·8
0·200	0·199	99·5
	0·198	99·0

* The average recovery is 99·3%.

except in the last step of the iodate–iodide reaction. A chloroform solution of iodine, however, proved not only suitable for quantitative oxidation but also made the susceptibility of sulphite to air-oxidation negligible This may be due to chloroform vapour over the organic–aqueous suspension almost preventing access of air to the solution during the oxidation step.

The amount of iodine required for oxidation depends, of course, on the sulphite concentration under test, and 0·5 ml of the iodine solution (about 50% excess) was found sufficient for complete oxidation of 0·2 mg of sodium sulphite (*cf*. Table 2). For larger amounts of sulphite more iodine is required, and the 5·0 ml required for oxidation of the largest amount of sulphite to be determined (2·0 mg) was found not to affect the results for the smallest (0·2 mg) and was therefore chosen for the general procedure

The procedure gave satisfactory results (Table 3). The minimum and maximum recoveries are 98·5 and 101·0% and the average recovery is 99·3%. The blank value found for the sulphite method did not exceed 0·22 ml of 0·01*M* thiosulphate

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Summary—Two methods are described for the micro and submicro iodometric determination of arsenite and sulphite ions involving 3- and 6-fold amplification reactions, respectively. The arsenite method is based on oxidation with an excess of periodate, masking of the unreacted periodate with molybdate, and final iodometric titration of the iodate released. The sulphite method depends upon oxidation with iodine and removal of its excess by extraction with chloroform, and oxidation of the iodide formed to iodate, which is determined iodometrically as usual. The two methods are simple, rapid, and accurate. The average recoveries obtained are 99·9 and 99·3% for arsenite and sulphite, respectively.

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DETERMINATION OF THE ELEMENTAL SULPHUR CONTENT OF MINERALS AND ORES

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Elemental sulphur can be formed at the surfaces either during the comminution or flotation of a sulphide mineral or ore.[1–3] Indeed, it has been suggested tentatively[4] that it is elemental sulphur which renders sulphide-mineral surfaces hydrophobic during flotation. A method to determine accurately the elemental sulphur content of minerals or ores would, therefore, be useful in a study of both the effect of comminution on sulphide minerals and the mechanism of flotation.

In all existing methods, the elemental sulphur is extracted from the mineral or ore with acetone,[5] benzene,[6] carbon disulphide[6,7] or chloroform.[8] A direct ultraviolet spectrophotometric determination of sulphur is often possible[6,8] but the presence of other sulphur compounds such as sulphates, thiosulphates and xanthates or of extraneous organic matter which also absorb in the ultraviolet will interfere.[9] (The presence of S^{2-}, SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$ was shown not to interfere, however, if monohydric alcohols were used as solvent.[10]) Moreover, traces of oxidizing impurities in the solvent could lead to high results for materials having a very low elemental sulphur content. The preparation of high-purity solvents can be laborious.

This paper describes a method in which elemental sulphur is separated from the sample by vaporization in a closed tube. The sulphur then undergoes continuous sublimation in a section of tube heated by a furnace, with movement, in a flow of nitrogen, towards a cold-finger condenser. The sulphur is ultimately determined by spectrophotometry in ethanol.

EXPERIMENTAL

Materials

Sublimed sulphur (Fisher Scientific Co.) was washed with hot distilled water until free from acid and any iodine-consuming substances, twice recrystallized from pyridine–ethanol,[9] heated at 110° for 2 hr to convert any amorphous sulphur into the rhombic form[11] and then crushed to pass a 100-mesh sieve.

A sulphur–sodium chloride mixture was prepared as test material to evaluate the variables that affect the efficiency of the apparatus (described below) for the determination of elemental sulphur by sublimation. The sodium chloride served only to facilitate the weighing of small amounts of sulphur. Approximately 250 mg of sulphur and 6 g of sodium chloride were ground together in an automated mortar grinder for 1 hr to achieve thorough mixing. The sulphur content was found by ethanol extraction to be 4·89 ± 0·07% (6 determinations)

The procedure developed was applied to two certified reference ores, MP-1[12] and KC-1,[13] and galena. A massive sample of galena was crushed, and the 65–100 mesh fraction was collected and purified from siliceous matter by heavy-liquid separation. A small portion of this prepared galena was then ground to finer than 400-mesh. A sample of KC-1, hereafter denoted by KC-1 (T), which had been kept at 67° and 62% relative humidity for 7 weeks was also analysed for elemental sulphur. The KC-1 gained 2·57% in weight because of oxidation.

Apparatus

The easily constructed apparatus (Fig. 1) consisted of a 20-cm and a 35-cm section of Pyrex tube (22 mm outside diameter) connected with a ₮ 19/38 glass joint, the female joint being attached to the 20-cm tube, hereafter called the "collector tube". The open end of the 35-cm tube, the "reactor tube", contained a removable plug with a gas-dispersion tube to pass nitrogen through the system. The open end of the collector tube was also equipped with a female ₮ 19/38 joint to accommodate a cold-finger condenser. A small outlet tube near this latter joint allowed the nitrogen to escape. The Pyrex tubes were inserted into the ports of a 23-cm horizontal-tube furnace (30 mm inside diameter) so that the tip of the condenser was at the port of the furnace. The connected tubes were not in contact with the furnace tube. The temperature was controlled with a variable transformer and monitored with a Pt, Rh/Pt thermocouple.

Procedure

The absorption spectrum of sulphur in ethanol was essentially the same as that found by Heatley and Page.[9] Beer's law was obeyed at 274 nm for sulphur concentrations from 0 to 49 μg/ml. A second calibration curve for 0–8 μg/ml, applicable to samples of very low sulphur content, was prepared by scale expansion of the range 0–0·2 absorbance units. The temperature of all solutions used in the preparation of the calibration curves was kept at 20·0 ± 0·1°. A Unicam SP 1800 Spectrophotometer and AR 25 Linear Recorder were employed for all measurements.

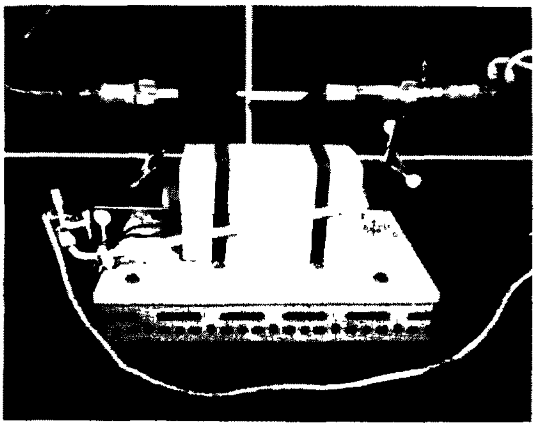

Fig. 1. Apparatus for the determination of the elemental sulphur content in minerals and ores by sublimation.

Sublimation method. The sample was weighed into a glazed porcelain boat (60 × 10 × 8 mm, Coors) and inserted into the reactor tube to rest approximately in the centre of the furnace. The plug with gas inlet tube was repositioned and the sulphur allowed to vaporize under the selected temperature and time conditions. The nitrogen flow-rate was 30 ml/min. At the conclusion of the reaction period, the collector tube was removed from the furnace and connected to either a 50- or 100-ml round-bottom flask (Ŧ 24/40) containing 12 or 25 ml of 95% ethanol, respectively, by means of a short connector constructed from Ŧ 24/40 and Ŧ 19/38 male joints. (Teflon sleeves were used with all Ŧ connections.) The ethanol was heated under reflux for 15 min to dissolve the sulphur that had sublimed onto the cold-finger condenser and wall of the collector tube. After cooling, the ethanolic sulphur solution was transferred to a 25- or 50-ml volumetric flask, brought to 20° in a thermostat and diluted to the mark. The absorbance at 274 nm was measured and the sulphur concentration determined from the calibration curve. For the evaluation of the variables affecting the determination of elemental sulphur, 20·1 ± 0·1 mg samples of sulphur–sodium chloride mixture were used. For the determination of elemental sulphur in MP-1, KC-1 or galena, 0·5-g samples were used.

Extraction method. The elemental sulphur in MP-1, KC-1 and galena was also determined by extraction into ethanol. About 0·5 g of sample and 25·00 ml of ethanol were heated under reflux for 4 hr, allowed to cool and centrifuged at 1800 rpm for 30 min to ensure complete separation of solid matter. The absorbance at 274 nm was measured and the spectrum in the range 250–350 nm was recorded for comparison with that of elemental sulphur.

RESULTS AND DISCUSSION

The effect of the temperature of the furnace on the fraction of sulphur recovered is illustrated in Fig. 2. The heating period was 3 hr and a sample weight of ~ 20 mg of sulphur–sodium chloride mixture was chosen to yield ~ 1 mg sulphur. It was decided semi-arbitrarily that all further developmental work on this method would be performed at 123° It was considered that the rate of recovery was acceptable and that significant decomposition of the mineral or ore sample would probably not occur at this temperature. It should be pointed out that there is, of course, no reason why any other furnace temperature in the 115–140° range (with an appropriate heating period) should not be equally successful.

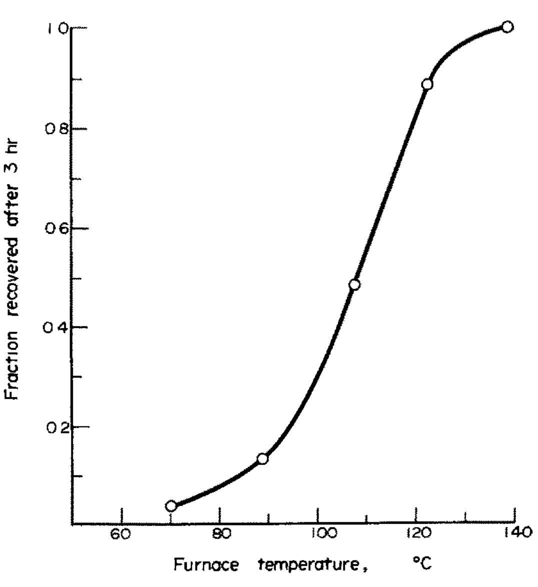

Fig. 2. Fraction of elemental sulphur recovered during a 3-hr heating period, as a function of the furnace temperature.

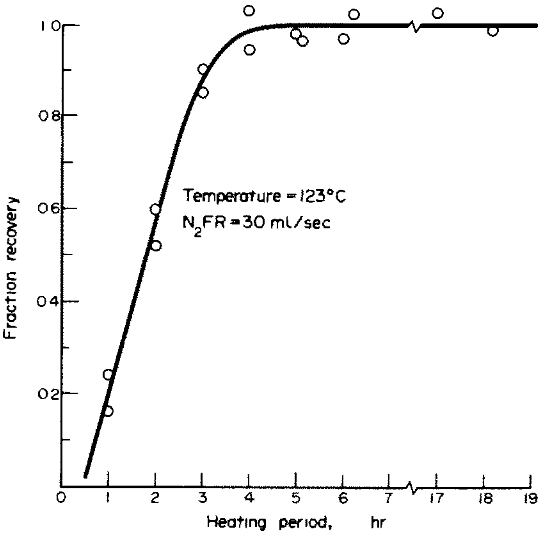

Fig. 3. Fraction of elemental sulphur recovered as a function of the heating period.

The effect of the duration of heating on the fraction of sulphur recovered at a furnace temperature of 123° is shown in Fig. 3. With short heating times, the fraction of sulphur recovered showed a slight dependence on the way the sample was packed in the boat. This is, of course, because the sulphur volatilizes more readily if the sample is more loosely packed. The packing, however, is immaterial if the heating period is long enough for complete sulphur recovery. With heating times of 4 hr or longer, 1 mg sulphur can be recovered (and subsequently determined) by the sublimation technique with a precision of ~ 3%. The same precision was also obtained for the recovery of 0·5 and 0·25 mg of sulphur (4 trials each; results not shown) with heating for 6 hr.

Because the samples for the determination of elemental sulphur in minerals or ore will be appreciably larger than those of the sulphur–sodium chloride mixture, heating time of 6 hr was chosen for subsequent work, to ensure sufficient margin for the complete recovery of sulphur. Subsequent tests indicated that the recovery of sulphur was complete in a 6-hr heating period at nitrogen flow-rates of 5–85 ml/min.

In order to test possible interferences in this sublimation method, trial runs with samples of ~ 10 mg of sodium sulphate, sulphite and thiosulphate (all analytical grade); potassium ethyl xanthate (Eastman Kodak twice recrystallized from ethanol–petroleum ether) and ethyl dixanthogen[14] were performed. In all cases, no elemental sulphur was detected. Ethyl dixanthogen distilled, but without apparent decomposition; this is discussed further below.

The results for the determination of elemental sulphur in MP-1, KC-1 and galena are summarized in Table 1. One very long heating period was used in one run for each of MP-1 and KC-1 to illustrate that 6 hr was indeed sufficient for complete sulphur recovery. The results by ethanol extraction and by sublimation are in good agreement with the exception of those for KC-1 (T) and the 400-mesh galena. The spectrum (in the region 250–330 nm) of the ethanol extract of KC-1 (T) is depicted in Fig. 4. Also shown is the theoretical elemental sulphur spectrum having the same absorbance at 274 nm; this spectrum was calculated from predetermined values of the molar absorptivity of elemental sulphur in ethanol. It is apparent that in the region 250–265 nm the determination of elemental sulphur

Table 1. Elemental sulphur in minerals or ores

Sample	EtOH extn., %	Sublimation %	Heating time, *hr*
MP-1	0·010	0·009	6
	0·010	0·009	6
		0·009	72
KC-1	0·130	0·125	6
	0·127	0·121	6
		0·123	16
KC-1 (T)	0·034*	0·006	6
Galena; 65–100 mesh	0·007	0·006	6
	0·006	0·006	6
Galena; 400-mesh	0·010*	0·002	6
		0·002	6

* Non-typical sulphur spectrum.

in KC-1 (T) by ethanol extraction is subject to interference. If it is assumed that the sublimation technique gives an accurate determination of elemental sulphur in KC-1 (T), the theoretical contribution of sulphur to the spectrum of the ethanol extract can be calculated. The contribution due to non-elemental sulphur components can, therefore, be calculated and is illustrated in Fig. 4. Similarly, the ethanol extract of 400-mesh galena did not give a typical elemental sulphur spectrum. The superiority of the sublimation technique, at least for these two examples, is clearly apparent.

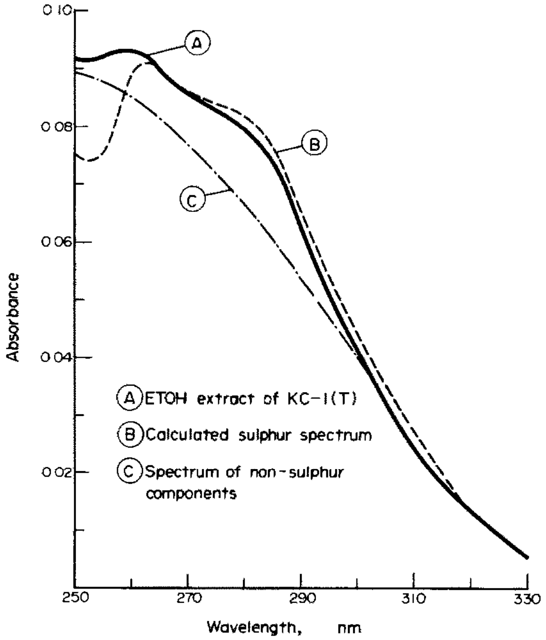

Fig. 4. Spectra pertaining to the ethanol extract of KC-1 (T).

Possible interference due to ethyl dixanthogen adsorbed by minerals or ores was tested as follows. A sample of KC-1 was equilibrated with an ethanolic solution of ethyl dixanthogen. Although ethyl dixanthogen was indeed adsorbed by KC-1, it could not be detected by either the ethanol extraction or sublimation determination of elemental sulphur. These two methods, however, gave widely different results for elemental sulphur, neither of which agreed with that of untreated KC-1. The same observation but to a lesser extent was noted for KC-1 equilibrated with potassium ethyl xanthate in ethanol. It is thought that this observation may give some insight into the interaction between xanthate or dixanthogen and the mineral or ore, and a study is now under way to elucidate the mechanism of this interaction.

Sensitivity

Because of instrument noise in the expanded scale, the limit of instrument response to sulphur in ethanol was 0·16 μg/ml when 1-cm cells were used. The sensitivity can, therefore, be calculated to be 0·2 μg/ml.[15] For analytical purposes, however, it is doubtful whether results for sulphur less than 0·5 μg/ml are truly significant.[10]

The sensitivity can be improved as follows. First, the sample size may be increased. Here, however, a prolongation in heating period may become necessary. Second, the sulphur may be dissolved in less than 25 ml of ethanol or longer path-lengths can be used, or both. Another possibility might be to extract a large sample (*e.g.*, 50 g) with ethanol, concentrate the extract by evaporation *e.g.*, on NaCl, then sublime.

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Summary—A new technique has been developed to determine trace quantities of elemental sulphur in minerals and ores. After separation from the sample by sublimation, the sulphur is determined spectrophotometrically in ethanol. Sulphide, sulphite, sulphate and thiosulphate do not interfere. The effect of the presence of xanthate or dixanthogen is discussed briefly.

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RAMAN SPECTRA OF PHENOTHIAZINE AND SOME PHARMACEUTICAL DERIVATIVES

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Phenothiazines are widely used as antipsychotic drugs and for this reason there has been much effort devoted to the spectroscopic characterization of these compounds. Although the infrared spectra of phenothiazines have been well characterized,[1] there have been no reports of the Raman spectra. Raman spectrometry appears useful in the identification of phenothiazines because of the presence of carbon–sulphur bonds and because the technique is well suited to the examination of solids, the physical form of most pharmaceutical preparations. In the present communication we report the spectra of several solid phenothiazines in the 600–1600-cm^{-1} region and present preliminary assignments of the major bands.

EXPERIMENTAL

The formulae of the substituted phenothiazines studied are presented in Table 1. Compounds **I** (trifluoropromazine hydrochloride) and **II** were obtained from the Squibb Institute. Compounds **III** and **IV** were obtained from Searle Laboratories. These compounds were used without further purification. Unsubstituted phenothiazine (Aldrich Chemical Co.) was recrystallized from benzene.

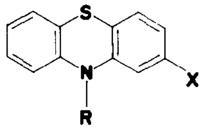
Raman spectra were recorded on a Spex 1401 double monochromator equipped with a cooled RCA C31034 photomultiplier and both photon-counting and d.c. detection systems. He–Ne 632·8-nm excitation (25–35 mW at the sample) was employed. Samples were irradiated for about 30 min in the laser beam to remove residual fluorescence. Samples were introduced into the laser beam as powders contained in standard glass melting-point capillaries. All spectra were recorded with 10 cm^{-1} resolution.

RESULTS AND DISCUSSION

The Raman spectra of the phenothiazines examined are presented in Table 2. Because the samples were examined as polycrystalline solids, depolarization ratios were not taken.

The phenothiazine spectra can be interpreted as derived from the spectra of diphenylamine, diphenyl sulphide and the various saturated compounds which make up the side-chains. Such an approach is valid, since the phenothiazine is known to be folded about the S–N axis, with a dihedral angle between the phenylene rings of about 140–154°, depending on the substitution pattern.[2,3] Thus, the two phenylene rings are more or less independent and the spectra will be closely related to those of simpler substituted benzenes. The ring mode dominated by symmetric phenylene–sulphur stretching appears at 670–680 cm^{-1} for the phenothiazines investigated. In diphenyl sulphide (liquid) this vibration occurs at 668 cm^{-1}.[4] The differences may be attributed to both the difference in the phase and to the presence of an *ortho*-substituent in phenothiazine and possibly to the difference in the C–S–C bond angle. This band is in the same region as the C–C out-of-plane deformation, which is responsible for the infrared absorption

Table 1 Formulae of substituted phenothiazines



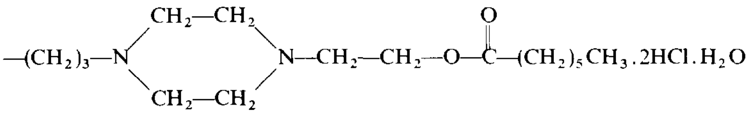
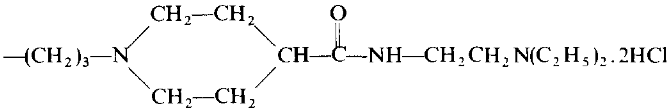
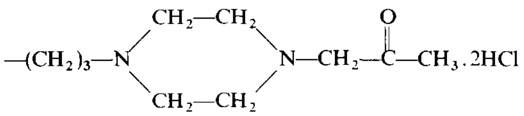
Compound	X	R
I	CF_3	$-(CH_2)_3N(CH_3)_2.2HCl$
II	CF_3	
III	Cl	
IV	Cl	

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Table 2. Raman spectra of phenothiazines

Phenothiazine	I	II	III	IV	Assignment
				605w	
	610w	610w		610w	
			620m	620w	
			645m		
	660w		670w		
685w	680s	680s	685s	675vs	Symmetric Ph–S–Ph
	700w	705w		700m	stretch
720w	720w	725w		720w	
		735w	735w		
750w	740w		745w		
	760w			760w	
	775w	770m	795m	780w	
	850w	800w			
		810w	815m		Symmetric
		825w		820m	C–N–C
	840w		840w	835w	stretch, tert.
			855w	850w	aliphatic amines
		870w		865w	
	880w		880w		
890w			890w		
			905w	900w	
		925w	930m	925w	
	940w	940m	945w		
			955w	960w	
		970w			
			980s		
				995w	
			1010m	1015w	
1040vs	1040s	1040vs	1040s	1045vs	CH ring deformation
	1060m	1055m	1060m		
1085w	1088w	1080w	1070w	1075w	Asymmetric Ph–S–Ph stretch
	1110vs	1110s	1110vs	1100vs	Asymmetric C–N–C stretch
1130w		1125m	1130w	1125w	
	1145w	1150w	1145w	1145m	
1165w	1165w	1160w	1170m	1175w	CH ring deformation
		1180w			
		1185w			
			1195m	1200w	
			1210m		
		1220w		1220w	
			1235m		
1250m	1245w	1240w	1250w	1250s	symmetric
	1260w	1260w			Ph–N–Ph stretch
			1270m	1280w	
	1290w		1290w	1295m	
			1300m		
	1310m	1315s	1325w	1320w	methylene twisting
		1340m	1335m	1335w	
	1365m				
			1370m		
				1380w	
			1410w	1405w	
			1420w	1425m	
	1435w	1430m			
		1445m	1440m		
	1465w		1460w	1465w	
			1475m	1475w	
		1500w			
			1525m	1520w	
1570m	1570s	1580s	1570s	1570s	ring stretching
	1590m	1595m	1590w	1590w	ring stretching
1605m	1605m	1605m	1605sh	1605sh	ring stretching

in the 690-cm^{-1} region.[4,5] Overlap with this mode, which is active in *ortho*-disubstituted benzenes,[6] cannot be ruled out.

The asymmetric phenylene-sulphur stretches occur in the 1070-1090-cm^{-1} region. In diphenyl sulphide this band occurs at around 1080 cm^{-1}.[4,5]

The medium intensity symmetric phenylene-nitrogen stretch is found at 1240-1250 cm^{-1}. In solid diphenylamine, this vibration is observed in the infrared at 1250 cm^{-1}.

The intense 1040-cm^{-1} band we assign to a C-H ring deformation. This is a strong band at 1040 cm^{-1} for diphenylamine and at 1026 cm^{-1} for diphenyl sulphide.[4] A weaker C-H deformation occurs at 1165-1175 cm^{-1} and is observed at 1153 cm^{-1} for diphenyl sulphide.[4]

In the spectrum of unsubstituted phenothiazine a pair of ring modes occurs at 1570 and 1605 cm^{-1}. These are the two components of a ring-stretching mode (l and k in Whiffen's notation). In the spectra of the ring-substituted phenothiazines, three bands occur in this region, owing to the non-equivalence of the two phenylene rings. We have not attempted detailed assignments of the bands due to vibrations of the alkyl side chains. We present only a few general assignments, but do not attribute bands to individual amines or alkyl groups.

The pharmaceutical derivatives have a group of bands between 800 and 900 cm^{-1}, due to symmetric C-N-C stretches of the tertiary amino groups.[8] The asymmetric C-N-C stretches appear as strong bands at 1100-1110 cm^{-1}. Similarly, the band at 1310-1325 cm^{-1} is assignable to a methylene twisting mode of the alkyl chains common to all of the substituted phenothiazines.[9]

Further refinement of these spectra and their extensions to higher and lower frequencies are in progress and will be reported at a later date.

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THE DETERMINATION OF METALLIC IRON IN THE PRESENCE OF FAYALITE

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(*Received* 20 *August* 1975. *Accepted* 7 *October* 1975)

A current investigation in these laboratories, into the treatment of low-grade tin ores, involved the reduction of tin calcines under various conditions. During the analysis of these reduced calcines difficulty was encountered in determining metallic iron. The reduced samples contained metallic iron, tin and tin-iron alloys, tin and iron oxides, aluminium-iron oxides (hercynite), and iron silicate (fayalite, $2FeO.SiO_2$).

It was confirmed that metallic iron can be determined satisfactorily in the presence of iron oxides (both ferrous, ferric and complex oxides such as hercynite) by methods such as those of Kraft and Fischer[1] or Blum and Searl[2] whereby the sample is treated with bromine in methanol under reflux conditions. The oxide residue is subsequently filtered off, washed with methanol, and, following the evaporation of alcohol from the filtrate, the iron equivalent to the metallic iron content is determined in dilute hydrochloric acid solution.

The method above, however, does not give accurate results for metallic iron when iron silicates such as fayalite are present in the sample to be analysed. The errors arise because fayalite is attacked by hydrogen bromide which apparently forms in the alcoholic solution of bromine even when moisture is rigorously excluded.[3] In Fig. 1, (*a*) and (*b*), are shown portions of the X-ray diffraction patterns of a synthetic sample containing iron (II) oxide, silica, and approximately 6% fayalite before and after treatment with bromine in methanol. It is clear that most of the fayalite has been dissolved during this treatment.

Several variations of the method of Kraft and Fischer[1] were studied in order to overcome this problem. It was found that whereas iodine in methanol did not attack the fayalite, the metallics—tin, iron, and iron-tin alloys—were halogenated only slowly. A more satisfactory variation was to treat the sample with bromine alone under reflux, then evaporate all excess of bromine before extracting the iron in the 690-cm^{-1} region.[4,5] Overlap with this mode, which is active in *ortho*-disubstituted benzenes,[6] cannot be ruled out.

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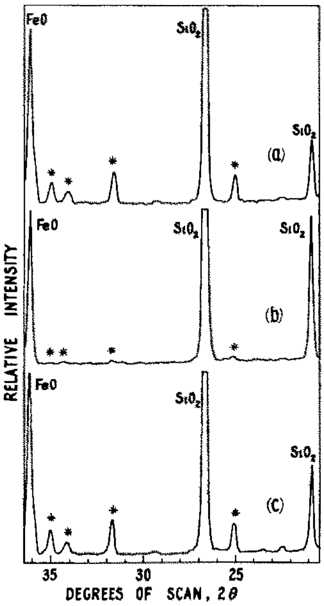

Fig. 1. X-Ray diffraction patterns, using Cu*K*α radiation, of (*a*) reference sample containing FeO, SiO_2, and about 6% fayalite; (*b*) as for (*a*) after treatment with bromine in methanol; (*c*) as for (*a*) after treatment with bromine alone and subsequent washing with methanol. Asterisks = fayalite peaks.

bromide with methanol (Fig. 1). This has been developed, and constitutes the proposed method described here.

EXPERIMENTAL

Sample materials

In order to test the accuracy of the proposed method a synthetic fayalite free from metallic iron was required. Fayalite is difficult to prepare, however, in pure form. When it is made by reducing mixtures of iron oxides and silica the reaction is incomplete at low temperatures (below 1000°),[4] although it is known that fayalite will form more readily at such temperatures when aluminium is present.[5] A synthetic fayalite was therefore prepared by reducing a mixture of analytical grade iron(III) oxide (Merck) and kaolin (Suprex clay) with 10% carbon (Colcarb Grade I, activated carbon) at 870° for 60 min in an enclosed vibrated silica reactor. The initial mixture contained a small excess of iron(III) oxide (about 6%) over the stoichiometric requirement to form fayalite from the silica in the kaolin. X-Ray diffraction revealed no free silica or metallic iron in the product, and apart from a trace of magnetite, iron was present either as iron(II) oxide or orthosilicate. No crystalline aluminium phase other than hercynite could be detected. The total iron content of the sample was determined by chemical analysis to be 41·0%. From the X-ray diffraction pattern and chemical analysis a fayalite content of 60–70% was indicated.

An iron–tin alloy was used as a source of metallic iron, since the metallic iron was in this form in the reduced tin calcines for which the method was developed. This alloy was prepared by melting iron and tin metal in an alumina crucible in an induction furnace. The iron content was found to be 74·6% and the tin content 25·4%.

Reagents

All chemicals should be of analytical reagent quality. The methanol used should contain no more than 0·1% water.

Procedure

Transfer an accurately weighed sample, containing up to 100 mg of metallic iron, into a 100-ml conical flask (ground-glass joint). Add 10 ml of bromine (cooled to 5°), fit a reflux condenser, and reflux at 58° for 1 hr to ensure complete dissolution of the metallic iron and tin. After cooling, remove the condenser, and pass dry air through the flask to remove excess of bromine. Do not heat the sample too strongly (above 60°), or loss of iron bromide may result Trap the excess of bromine (if necessary) by bubbling the effluent gases through 5*M* sodium hydroxide. To prevent formation of hydrogen bromide, which will react with the fayalite, exclude water from the reagents and glassware during the bromination process and during and immediately after removal of excess of bromine. Store the samples, if required, in a desiccator over phosphorus pentoxide.

When the bromine has been completely removed, add 70 ml of methanol to the flask and stir magnetically at 60° for 30 min to dissolve the iron bromides. After cooling, filter this solution through a filter of pore-size < 0·5 μm (Millipore BDWP or equivalent) and wash the residue well with methanol.

Transfer the filtrate to a 300–400 ml beaker and evaporate it to 20 ml. Add 50 ml of hydrochloric acid and again evaporate to 20 ml to remove the methanol. Transfer this solution into a 100-ml volumetric flask and make up to volume with distilled water—solution A.

Carefully transfer the filter pad containing the residue to a zirconium or nickel crucible and ignite at about 600° to remove organic matter. When cool, add to the residue 4 g of sodium peroxide, mix, and fuse at about 600° until a homogeneous liquid flux is obtained. Cool, then add distilled water (about 20–30 ml) slowly to the fusion mixture, with a watch-glass covering as much as possible of the crucible. When the reaction has ceased, transfer the reaction mixture into a 150-ml beaker and wash the crucible with 20 ml of concentrated hydrochloric acid, followed by distilled water, transferring these washings to the beaker Heat to boiling to dissolve the solids and remove any dissolved hydrogen peroxide. Cool, transfer the solution into a 100-ml volumetric flask, and make up to volume with distilled water—solution B.

Take suitable aliquots of solutions A and B, make them 4*N* in hydrochloric acid, heat, reduce the iron to iron(II) with 10% stannous chloride solution, adding 2 or 3 drops in excess, cool, add 10 ml of 4·5% mercuric chloride solution, 90 ml of 0·5*N* sulphuric acid and 10 ml of orthophosphoric acid (1 + 1) and let stand for 5–10 min. Titrate with 0·01*N* potassium dichromate, using barium diphenylaminesulphonate as indicator.

The titration of solution A gives the amount of metallic iron and that of solution B the iron present as oxide or fayalite.

If a titration volume greater than 5 ml cannot be obtained it is preferable to determine the iron by atomic-absorption spectrometry, using iron standards containing the same matrix as the samples.

RESULTS AND DISCUSSION

To test the effectiveness of the separation technique a series of synthetic fayalite and metallic iron mixtures was prepared from the metallic tin–iron alloy and synthetic fayalite mentioned earlier. The mixtures prepared, and the results of their analysis by the proposed method, are listed in Table 1.

The method has been successfully applied to the analysis of reduced tin calcines containing a wide concentration range of metallic iron. Four reduced tin calcine samples were prepared under different conditions to give:

(A) high metallic iron (as iron–tin alloy) and negligible fayalite content; (B) moderate metallic iron and high faya-

Table 1. Results for the determination of metallic iron in the presence of fayalite

Fe°/fayalite in sample (approx.)	Metallic Fe added,* *mg*	Metallic Fe found, *mg*	Differences, *mg*	Fe as oxide added†, *mg*	Fe as oxide found, *mg*	Difference, *mg*
0·00	nil	0·25	+0·25	85·3	85·2	−0·1
0·02	1·94	2·70	+0·76	83·2	81·8	−1·4
0·10	11·6	12·6	+1·0	76·3	77·7	+1·4
0·40	38·8	41·4	+2·6	61·7	61·0	−0·7
1·06	72·8	73·5	+0·7	43·5	43·9	+0·4
1·14	76·2	77·2	+1·0	41·5	41·4	−0·1
1·14	76·8	78·2	+1·4	42·5	42·8	+0·3

* Metallic iron added as 74·6% Fe–Sn alloy.
† Iron added as synthetic fayalite containing 60–70% $2FeO.SiO_2$.

Table 2. Determination of metallic iron and iron oxide in reduced tin calcines

	Extraction using bromine in methanol*			Extraction using proposed method (bromine alone)		
Sample	Fe as oxide,† %	Fe as metal, %	Total Fe, %	Fe as oxide,† %	Fe as metal, %	Total Fe, %
A§	8·3	26·0	34·3	8·3	26·2	34·5
B	2·8	28·9	31·7	20·6	12·0	32·6
C	12·9	17·1	30·0	29·2	1·70	30·9
D	22·5	3·4	25·9	25·2	0·19	25·4

* See Refs. 1, 2.
† Including fayalite.
§ Negligible fayalite content.

lite content; (C) low metallic iron and high fayalite content; (D) very low metallic iron and high fayalite content.

The nature of these samples was confirmed by X-ray diffraction. Table 2 compares the results obtained by using the proposed method (bromine alone) for all four samples and the bromine–methanol method of Kraft and Fischer for samples A, C and D and that of Blum and Searl for sample B. The bromine-in-methanol results for metallic iron in samples B, C, and D (high fayalite content) were much too high to correlate with the X-ray diffraction data. X-Ray data for the residues from these samples after treatment with bromine in methanol showed also that for samples B, C, and D some fayalite was dissolving with the metallic iron. In sample A (negligible fayalite) the two methods gave the same result.

The use of bromine in methanol to separate metallic tin from tin(IV) oxide (cassiterite) has been demonstrated by Tsukahara, Yamamato and Tonomura.[6] The present authors' proposed method (bromine alone) has resulted in metallic tin being separated from tin(IV) oxide simultaneously with the separation of metallic iron from fayalite. However, as in the bromine-in-methanol method, complete recovery of the tin in the filtrate was not achieved, because of the loss of tin(IV) bromide as the methanol evaporated. Addition of sulphuric acid did not reduce the loss of tin(IV) bromide, as it does for tin(IV) chloride,[7] and so far the concentration of metallic tin in the samples has been determined by difference.

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Summary—In a proposed new procedure the sample is treated with bromine, the excess of bromine removed, and the residue extracted with methanol. After filtration the filtrate is evaporated to remove methanol and the bromides are dissolved in hydrochloric acid for determination of metallic iron. The oxide residue from the filtration is fused in sodium peroxide and then dissolved in hydrochloric acid for the determination of iron present either as oxide or silicate. Iron in the hydrochloric acid solutions from the residue and filtrate is determined either by titration with standard potassium dichromate solution or by atomic-absorption spectrometry.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH 1,1,1-TRIFLUORO-3-(2-THENOYL)ACETONE

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(*Received* 18 *September* 1975. *Accepted* 1 *November* 1975)

The spectrophotometric determination of copper(II) with 1,1,1-trifluoro-3-(2-thenoyl)acetone (HTTA) has been reported[1,2] to have the drawback that the maximum absorption of the extracted species, $Cu(TTA)_2$, at around 340 nm cannot be used because of the interference caused by the residual HTTA which shows a strong absorption band near 340 nm. Similar interference occurs in the method using 1,1,1-trifluoro-3-(2-thiothenoyl)acetone.[3] An improved method uses adduct formation of $Cu(TTA)_2$ with pyridine.[4] It is now shown that the excess of HTTA can be removed by scrubbing with sodium hydroxide solution without any decomposition of $Cu(TTA)_2$ if chloroform is used as a diluent, and a highly sensitive method results.

EXPERIMENTAL

Reagents

A standard solution of copper(II) (100 μg/ml) was prepared by dissolving copper(II) sulphate pentahydrate in distilled water. Acetate buffer, pH *ca* 5.4, prepared by mixing 0.2*M* sodium acetate and 0.2*M* acetic acid was purified by shaking with 0.001*M* HTTA in chloroform; the aqueous phase was washed with chloroform three times and filtered.

General procedure

Transfer the sample solution containing not more than 10 μg of copper(II) to a separatory-funnel. Add, if necessary, 5 ml of 4% potassium fluoride solution for masking. Adjust the pH to *ca*. 5.4 by addition of acetate buffer, then shake the aqueous phase vigorously for 3 min with 10 ml of 0.001*M* HTTA in chloroform. Allow the phases to separate and draw off the extract into another separatory-funnel. Add 10 ml of 0.005*M* sodium hydroxide and shake the mixture for 4 min. Measure the absorbance of the organic phase at 344 nm against a reagent blank.

RESULTS AND DISCUSSION

Effect of organic solvent

Table 1 lists the absorbances obtained with use of different organic solvents. Values of the partition coefficients of $Cu(TTA)_2$, P_{MA}, calculated from the literature data,[5–7] are also shown. The resistance of the extracted $Cu(TTA)_2$ to attack by hydroxide is explained in terms of the differences in P_{MA} for the five solvents. Since the decomposition of $Cu(TTA)_2$ is considered to occur in the aqueous phase, a high P_{MA} value will lead to increased resistance to the alkali treatment. In particularly, the hydrogen-bonding of chloroform to copper(II) β-diketonates[8] may result in a higher value of P_{MA} than with the other solvents.

Table 1. Effect of organic solvent on the absorbance

Solvent	Absorbance	log P_{MA}
Cyclohexane	0.123	-2.52
Xylene	0.496	—
Benzene	0.541	1.12
Carbon tetrachloride	0.549	0.72
Chloroform	0.621	1.41

Absorption spectra

Figure 1 shows the absorption spectra of the $Cu(TTA)_2$ complex in chloroform and of the reagent blank, obtained by the procedure described, showing almost complete removal of the residual HTTA in the organic phase. The complex has maximum absorbance at 344 nm, molar absorptivity 4.9 × 10^4 l. $mole^{-1}.cm^{-1}$ in good agreement with that measured for a chloroform solution of crystalline $Cu(TTA)_2$. Therefore, the decomposition of $Cu(TTA)_2$ during the alkali treatment was confirmed to be negligible.

Effect of pH

Copper(II) is efficiently extracted over the pH range 5–6.2, but extraction is incomplete outside this pH range, hence a pH of 5.4 was adopted.

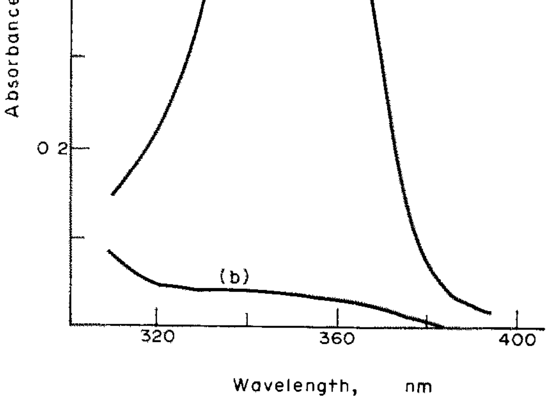

Fig 1. Absorption spectra of (a) $Cu(TTA)_2$ chelate and (b) reagent blank in chloroform. Cu(II): 8 μg.

Calibration curve

The calibration curve obtained at pH 5.4 is linear over the range 0–10 μg of copper(II). In 9 determinations of 5 μg of copper(II), the absorbance was 0.399 ± 0.003, the relative standard deviation being 1.0%. The Sandell sensitivity

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*Present address, National Institute for Researches in Inorganic Materials, Sakura, Niihari, Ibaraki 300-31 is 0.0013 μg/cm^2, is considerably higher than that for the dithizone method (0.0022 μg/cm^2) or the HTTA–pyridine method (0.0023 μg/cm^2).

Interferences

No interference in determination of 5 μg of copper(II) was observed for 1 mg of Mg, Ca, Sr, 100 μg of Mn(II), Zn, Ag(I), Cd, Hg(II), Pb, and 20 μg of Co(II), Ni. Forty times as much as Al, Fe(III), and Cr(III) as copper(II) taken will interfere seriously because of formation of hydrolysis products, but these metals can be masked by adding 5 ml of 4% potassium fluoride solution before adjusting the pH.

Determination of copper(II) in natural water

The present method was applied to the determination of copper(II) in a natural water sample taken from the Watarase river. The analytical value (five determinations) was 0.060 ± 0.001 μg/ml. The average recovery, tested by doing four determinations with 5 μg of copper(II) added to the sample solutions, was 101%

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Summary—Copper(II)-trifluorothenoylacetone complex in chloroform does not undergo decomposition when scrubbed with sodium hydroxide solution. This allows the complete removal of the residual reagent, and a highly sensitive method for the extraction and spectrophotometric determination of copper(II) results.

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ANALYTICAL DATA

A POTENTIOMETRIC STUDY OF THE COMPLEXES FORMED BETWEEN Ni(II) AND Zn(II) AND 3-MERCAPTOPROPIONIC ACID

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(*Received* 11 *March* 1975. *Revised* 28 *August* 1975. *Accepted* 3 *September* 1975)

In earlier investigations[1–4] the complexation of the metal ions Ni^{2+} and Zn^{2+} with the following thiols as ligands was studied: 2-mercaptoethanol (MEL), 3-mercapto-1,2-propanediol (MPD), thioglycollic acid (TGA) and thiolactic acid (TLA).

Not much work has been done on the complexation of 3-mercaptopropionic acid (3-MPA). Saxena and Gupta[5,6] studied the Ni^{2+} and Cd^{2+} complexes of this ligand and found only mononuclear complexes. This is not surprising, taking into account that the range of total metal ion concentration used was rather restricted. In the present work the complexation of Ni^{2+} and Zn^{2+} with 3-mercaptopropionic acid is studied over a large concentration range. This ligand is interesting for comparison of the results with those obtained for TGA and TLA, since the carboxyl group is substituted in the β-position relative to the $-SH$ group.

EXPERIMENTAL

Apparatus

A digital pH-meter "Radiometer pHM52" was used, equipped with a G 202 C glass electrode and a saturated calomel electrode as reference. The glass electrode was standardized with an NBS standard 0·01*M* borax buffer, pH 9·18 at 25°.[7] All solutions were kept at 25°.

Reagents

Stock solutions (0·2*M*) of nickel and zinc nitrate were prepared and standardized as before.[1,2] 3-Mercaptopropionic acid (3-MPA) was obtained from Fluka and redistilled just before use. Aqueous solutions of 3-MPA are stable for a long period if they are prepared with oxygen-free water and regularly flushed with pure nitrogen.[9] All solutions were made up to an ionic strength of 0·5 with potassium nitrate (Merck *p.a.*) to keep the activity coefficients as constant as possible.

Procedure

The titration procedure for zinc was as described before.[1] The total metal ion concentration was varied from 0·001 to 0·016*M*. The initial ligand concentration was five times the total metal ion concentration. The reaction of nickel(II) with 3-MPA was too slow for direct titration. Therefore a series of 50-ml volumetric flasks was prepared, containing solutions with constant total metal ion and ligand concentrations but increasing amounts of base. A 25-ml aliquot of each solution was diluted to 50-ml with 0·5*M* potassium nitrate, giving a second series with half the original total metal ion concentration. A constant pH-value was obtained after 1 hour.

Calculations

The calculations were performed with a number of computer programs written in FORTRAN IV. All programs were executed on a Siemens 4004/150 computer.

RESULTS AND MATHEMATICAL TREATMENT

The symbols used are those listed earlier,[3] except that B represents Ni^{2+} or Zn^{2+} (and B the total metal ion concentration), A represents 3-MPA (and A the total ligand concentration).

The protonation constants $\log K_{H_i}$ of the carboxylate and mercapto group of 3-mercaptopropionic acid (3-MPA) were calculated by a method described by Thiers, Van Poucke and Herman[9] and found to be 4·16 and 10·10 respectively.

With a general computer program ZPAF the formation functions $Z(pa)_B$ were calculated as before.[3] A proportionality factor described before[10] was used to calculate $[H^+]$ from the activity of the hydrogen ion.

The formation curves for the Zn^{2+}/3-MPA complex all crossed at a value $Z = \pm 1{\cdot}45$, forming a real or pseudo cross-over point. From graphical analysis of the formation curves[11,12] it appeared that a mixture of mononuclear complexes BA, BA_2 and a "core + links" series $B(A_6B)_n$ with $n_{max} = 3$ was very probable. To find out which complexes were really present the computer program PNUC was used.[4]

This program is based on minimization of the function U related to the difference between calculated and experimental Z-values:

$$U = \Sigma(Z_{cal} - Z_{exp})^2 \tag{1}$$

The standard deviation of Z is given by

$$\sigma^2(Z) = U_{min}/(n_{exp} - n_{par}) \tag{2}$$

where n_{exp} is the number of experimental points and n_{par} is the number of complexes. This calculation is repeated for different complex compositions, and the set of complexes that is really present will give the lowest values of U_{min} and $\sigma(Z)$.

The calculation is started with guessed stability constants. Bad guesses can ruin the calculation. If the guess for a certain stability constant is too low, its contribution to U is negligible and the constant remains unchanged during the calculation. The best guesses are 3–5 log β units higher than the finally obtained results.

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Input values for a complex B_QA_P can be calculated[13] from

$$\log \beta_{Q,P}(\text{guessed}) = 2{\cdot}1\,(Q-1) + P.pa \qquad (3)$$

where pa is the value of $-\log a$ for $B = 0{\cdot}016$ and $Z = 0{\cdot}5$.

The distribution of complexes ($\alpha_{q,p}$) was calculated from

$$\alpha_{q,p} = \frac{100\,q\beta_{q,p}b^q a^p}{B} \qquad (4)$$

The results for the zinc system are given in Table 1. The possible complexes are BA, BA_2, B_2A_2, B_3A_4 and B_4A_6. The complexes BA and B_2A_2 are rejected and the system Zn^{2+}/3-MPA can be represented by the formation of the complexes BA_2, B_3A_4 and B_4A_6.

The formation curves for the Ni/3-MPA system are shown in Fig. 1. The "core + links" theory could not be applied. As there is no "cross-over" point a mixture of poly- and mononuclear complexes is not very probable. Below $Z = 0{\cdot}7$ the spacing of the curves points to a "core + links" series $(A_2B)_n$, also found for other Ni^{2+} thiol complexes.[2-4] For $Z > 0{\cdot}7$ the spacing changes and all formation curves tend to a value of $Z_{max} = 2$, so complexes with a ligand/metal ratio of 2 are very probable. This system was also treated with the program PNUC, starting with two complexes B_3A_4 and B_3A_6, and adding sequentially all complexes with less than seven metal ions and a ligand/metal ratio < 2. The mononuclear complexes BA, BA_2, BA_3 and the polymeric complexes $(BA_2)_n$ with $n = 1$–9 were also tested The complexes were accepted or rejected as described elsewhere.[4] The lowest value for U_{min} and $\sigma^2(Z)$ was found for a mixture of complexes B_5A_{10}, B_6A_{12}, B_6A_9 and B_6A_{11}. As can be seen from Table 2 the predominant species are B_6A_{12} and B_6A_9

Table 1. Stability constants for 3-MPA/Zn^{2+} complexes from treatment with PNUC

System	$\log \beta_{q,p}$	$\alpha_{q,p_{max}}$	present	U_{min}	$\sigma^2(z)$
BA	3·44	<0·1	–	0·02553	$0{\cdot}61 \times 10^{-3}$
BA_2	12·18	97	+		
B_2A_2	11·95	<0·1	–		
B_3A_4	30·40	32	+		
B_4A_6	45·59	40	+		
BA_2	12·18	97	+	0·02718	$0{\cdot}63 \times 10^{-3}$
B_2A_2	11·95	<0·1	–		
B_3A_4	30·47	32	+		
B_4A_6	45·45	40	+		
BA	3·44	<0·1	–	0·02555	$0{\cdot}59 \times 10^{-3}$
BA_2	12·18	97	+		
B_3A_4	30·40	32	+		
B_4A_6	45·59	40	+		
BA_2	12·18	97	+	0·02539	$0{\cdot}58 \times 10^{-3}$
B_3A_4	30·40	32	+		
B_4A_6	45·59	40	+		

DISCUSSION

The complexes formed between Ni^{2+} and 3-MPA are totally different from the Zn^{2+} complexes of 3-MPA, which are analogous with those formed with TLA and TGA.

This different behaviour is not yet understood. From earlier measurements it was found that ligands such as MEL and MPD, containing the –SH group as the only complexing group, form polymeric complexes $B(A_2B)_n$ with high values of n. The implant of a second complexing group on the molecule can block the growth of the polymeric chain. The second group competes with the –SH and after formation of some links it can be energetically favourable to fill up the empty co-ordination places around Ni^{2+} with the second group instead of the –SH group. This may be the reason why complexes higher than B_3A_4 are lacking in the system Ni^{2+}/cysteamine.[1] By analogy with polymer chemistry we could call this a termination reaction, or the second group a "stop" group.

The second group can also confer an extra charge on the complex This is the case for TGA, TLA and 3-MPA. While the complexes of MEL, MPD and 2-MEA have two positive charges, the complexes of Ni^{2+} with TGA, TLA and 3-MPA receive two negative charges per BA_2 link. High charge on a complex will not be favourable for the stability of that complex.

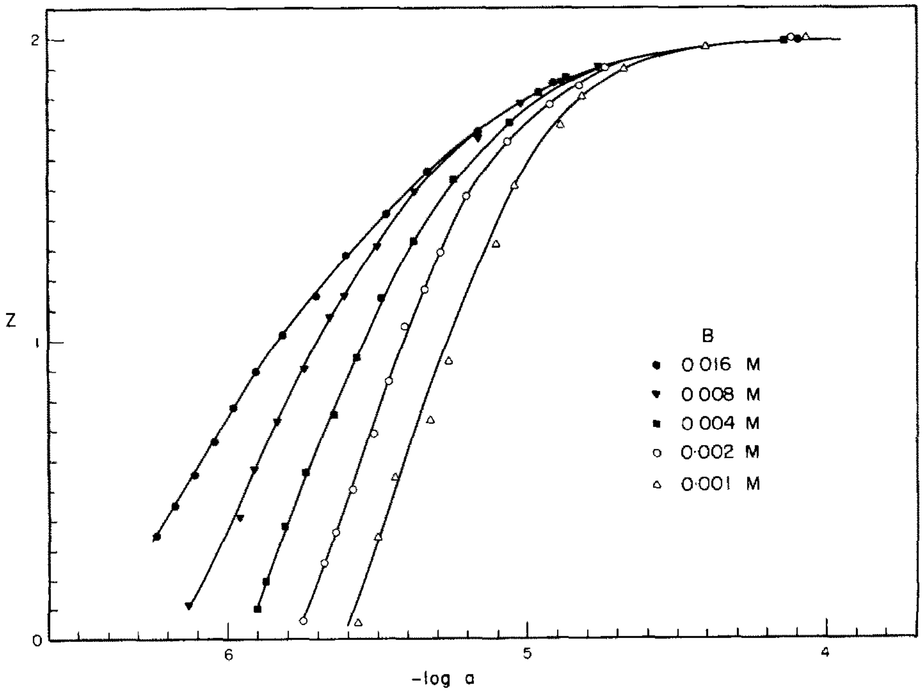

Fig. 1. The formation curves of the system nickel(II)-3MPA.

Table 2. Stability constants for Ni^{2+}/3-MPA complexes from treatment with PNUC

System	$\log \beta_{q,p}$	$x_{q,p_{max}}$	present	U_{min}	$\sigma^2(z)$
B_5A_{10}	64·54	16	+	0·2166	$0·31 \times 10^{-2}$
B_6A_{12}	78·94	86	+		
B_6A_9	63·58	68	+		
B_6A_{10}	67·80	<4	(±)−		
B_6A_{11}	73·31	12	+		
B_5A_{10}	64·49	16	+	0·2122	$0·30 \times 10^{-2}$
B_6A_{12}	78·89	83	+		
B_6A_9	63·58	69	+		
B_6A_{11}	73·60	23	+		
B_6A_{12}	79·03	83	+	0·2135	$0·29 \times 10^{-2}$
B_6A_9	63·61	73	+		
B_6A_{11}	73·36	13	+		
B_6A_{12}	79·10	99	+	0·2284	$0·31 \times 10^{-2}$
B_6A_9	63·63	82	+		

This could explain the complex formation between Ni^{2+} and 3-MPA. If, in the case of Ni^{2+}, a six-membered chelate, less stable than a five-membered chelate, is not able to stop the growing of the polymeric chain, the formation of higher complexes will be inhibited by the higher charge on the complexes.

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Summary—The composition and stability constants of the complexes formed between Ni^{2+} and Zn^{2+} and 3-mercaptopropionic acid (3-MPA) were studied by a potentiometric method at 25° and in 0·5*M* KNO_3. For the system Zn^{2+}/3-MPA a mixture of the mononuclear complex BA_2 and the polynuclear complexes B_3A_4 and B_4A_6 was found (B means the metal ion and A the ligand). The system Ni^{2+}/3-MPA can be represented by the complexes B_5A_{10}, B_6A_{11}, B_6A_9 and B_6A_{12}. In this series the last two complexes are predominant.

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PRELIMINARY COMMUNICATION

THE DETERMINATION OF GLYCEROL IN WATER BY FLOW-INJECTION ANALYSIS - A NOVEL WAY OF MEASURING VISCOSITY

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In a typical determination by flow-injection analysis a measured amount of sample is injected into a flowing stream of colour-forming reagent and the absorbance of the solution is continuously recorded at some suitable distance down-line.[1-4] The reaction between reagent and sample gives rise to a peak in absorbance, having a height proportional to the amount of sample injected.

The parameters such as flow-rate, sample size and length of tubing between the sample-injection point and the detector, are selected so that a linear relationship exists between peak height and concentration of sample. However there is necessarily some mixing of sample plug and the flowing stream of reagent. The extent of mixing will be reflected in the shape of the observed peak, and most obviously in the peak height. The degree of mixing will be a function of the viscosity of the sample solution. We have tested this hypothesis by injecting solutions of glycerol in water, which are widely used as standards for viscometry, into a flowing stream of water. The flowing stream had some colouring matter added so that the sample plug was identified by a reduction in absorbance.

EXPERIMENTAL

Apparatus

The flow-injection analyser has been described elsewhere.[1-4] Samples of 100 µl or greater were introduced by hypodermic syringe into a sample-injection block, whilst those of 50 µl were admitted through a newly designed sample inlet. A flow-rate of 4 ml/min was maintained. The absorbance was measured at 620 nm in a flow-cell with optical path of 10 mm. Occasionally there was some sample contamination from the previous sample, if it contained a high proportion of glycerol. It was rapidly washed away by water or the next sample. Substitution of Teflon or polyethylene tubing made no difference. The length of the tube was 1.4 m, bore 1.0 mm, for the set of experiments shown in Fig. 1.

Solutions

Mixtures of glycerol and water were made up by weighing each component. The flow-solution was 0.001% Bromothymol Blue in water, buffered at pH 9.2 with a borate buffer.

RESULTS

The results shown in Table 1 and Fig. 1 show that with pure glycerol there is virtually no dye in the sample plug, but the dye occurs increasingly as the concentration of glycerol is lowered. The method can be used to determine extremely rapidly the composition of a wide range of glycerol-water mixtures. The results obtained during trial runs in which tube lengths, flow-rates and sample size were varied suggest that it would be easy to obtain

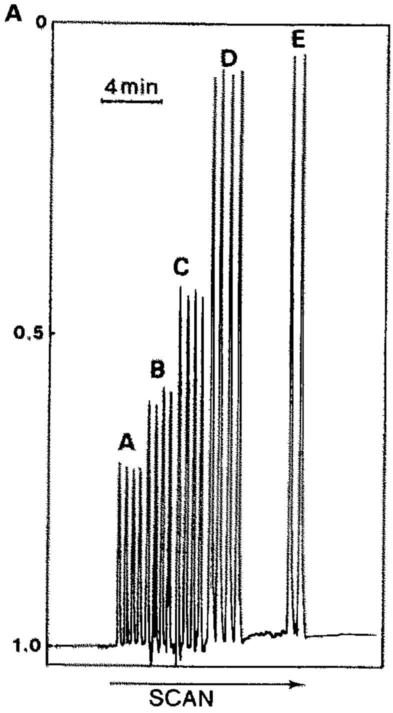

Fig. 1. Chart response from flow-injection of 100-µl samples of glycerol-water mixtures into a flowing stream of water (for details see Table 1)

Table 1. Chart response for flow-injection of 100-µl samples of glycerol-water mixtures of different viscosity

Sample	Glycerol, % w/w	Chart reading*	Log viscosity†
A	16.6	24.8	0.188
B	32.8	35.6	0.438
C	47.3	50.2	0.699
D	76.9	82.5	1.595
E	100	beyond range of spectrophotometer	3.097

* Mean of 4 readings, range = mean ± 1

† Interpolated for 21.8° from values (cP) in ref. 5

precise results for the composition over a narrow range. The method should be generally applicable to the determination of the composition of mixtures of miscible liquids.

The viscosity of the sample is an important factor in the extent of mixing and these results suggest that there is the possibility of measuring viscosity simply and rapidly by injection-flow analysis.

Many more experiments will be required to assess the validity of this hypothesis, but the present results have far-reaching implications for the scope of flow-injection analysis and could not have been obtained with "Auto-Analyzers" which depend on air-bubbles to separate samples. They also point to the need to ensure that the viscosities of sample and standard solutions are equal, or at least maintained constant throughout a run on the flow-injection analyser. This may present a special problem in clinical analysis, where serum samples have considerably higher viscosity than aqueous standards.

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CHLOROFORM EXTRACTION OF METAL ETHYL XANTHATES FROM HYDROCHLORIC ACID MEDIA

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Summary—The chloroform extraction of 32 elements (Fe, Co, Ni, Zn, Cd, Ge, Sn, Pb, V, As, Sb, Bi, Cu, Ag, Au, Mn, Re, Ga, In, Tl, Ce, Se, Te, Cr, Mo, U, Pt, Pd, Rh, Ir, Ru and Os) from 0.1–10*M* hydrochloric acid media in the presence of potassium ethyl xanthate has been studied. The oxidation states in which some elements react, and potential analytical separations, are discussed. Pd(II), As(III) and Se(IV) are completely extracted as ethyl xanthate complexes, Te(IV) is almost completely extracted, and Au(III) is largely extracted over the range of acid concentration investigated. Mn(II), Zn, Rh(III), Ir(IV), Ru(III), Os(IV), Cr(III), Cr(VI), Ce(III) and Ce(IV) are not extracted. Ge is partly extracted from 6–10*M* media as the chloro-complex. Depending on the acid concentration, the remaining elements are all partially extracted as xanthate complexes.

In a recent review[1] on the solvent extraction of metal xanthates, particularly those formed by ethyl xanthate, the characteristics and analytical uses of these complexes were described. Much of the information in this and previous reviews[2–5] appears in obscure Soviet journals and other papers not readily accessible to Western readers, or for which English translations are not available. In many cases, the abstracts of these papers do not provide information on the optimum range of pH or acid concentration required for the extraction of the elements under consideration, or the extent to which some are extracted from relatively strongly acidic media.

Published data,[6] and information obtained by the author in previous work, involving the separation of molybdenum from tungsten[7] and bismuth from lead[8] by chloroform extraction of their ethyl xanthate complexes, suggested the possibility of the simultaneous group extraction of xanthates of elements such as arsenic, antimony, bismuth, selenium and tellurium from hydrochloric acid media. For this reason, it was considered worthwhile to investigate the extraction of the ethyl xanthate complexes of these and other elements into chloroform from 0.1–10*M* hydrochloric acid media. It is expected that such separations will be useful in the atomic-absorption analysis of metalliferous materials for many of these elements at levels ranging from minor to trace.

EXPERIMENTAL

Reagents

Solutions of selenium(IV), cobalt(II), chromium(III) and (VI), rhenium(VII), cerium(III) and (IV), uranium(VI) and thallium(I) were prepared from analytical-reagent grade salts by dissolving them in water.

Solutions of rhodium(III), ruthenium(III), iridium(IV), osmium(IV) and iron(II) were prepared by dissolving appropriate salts in water plus sufficient 10*M* hydrochloric acid for the final hydrochloric acid concentration to be 1*M*. Solutions of molybdenum(VI), arsenic(III), vanadium(V) and germanium were prepared by dissolving the oxides in dilute sodium hydroxide solution and adjusting the pH of the solutions to ~7 with dilute hydrochloric acid.

Nickel, zinc and manganese(II) solutions were prepared by dissolving the metals in hydrochloric acid. An iron(III) solution was prepared by dissolving the metal in hydrochloric acid and oxidizing with hydrogen peroxide. Solutions of bismuth, lead, indium(III) and copper(II) were prepared by dissolving the metals in nitric acid. A cadmium solution was prepared by dissolving cadmium carbonate in hydrochloric acid. Silver and gallium solutions were prepared by dissolving silver sulphate and gallium oxide in nitric acid. Aliquots of these solutions were evaporated to dryness to remove the acids before extraction.

Gold(III), platinum(IV) and palladium(II) solutions were prepared by dissolving the metals in *aqua regia*. Aliquots of the gold and platinum solutions were evaporated to dryness on a hot water-bath, 10 drops of *aqua regia* were added and the solutions were evaporated to dryness in a stream of air before extraction, to prevent thermal decomposition of the salts. Aliquots of the palladium solution were evaporated to dryness on a hot water-bath before extraction.

A stock solution of tin(IV) was prepared by dissolving the metal in 10*M* hydrochloric acid and diluting to volume with the same acid solution. A working solution, 1*M* in hydrochloric acid, was prepared by 10-fold dilution of this solution.

A solution of antimony(III) was prepared by dissolving antimony potassium tartrate in water containing sufficient tartaric acid for its final concentration to be 1%, and adjusting the pH of the solution to ~7 with dilute ammonia solution.

A solution of tellurium(IV) was prepared by dissolving tellurium dioxide in sufficient 10*M* hydrochloric acid for the final solution to be 0.5*M* in hydrochloric acid.

All these working solutions were prepared so as to have a 100 μg/ml concentration of the element concerned, and weighings based on formula weights were taken as correct. Analytical-reagent grade chloroform was used without further purification.

General procedure for extraction

Sufficient 10*M* or concentrated hydrochloric acid to provide the range 0.1–10*M* was added to 150-ml beakers, each

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Table 1. Analytical methods used for determination of the degree of extraction

Element	Method	
Fe	Spectrophotometry, as thiocyanate	(478 nm)
Co	Atomic-absorption spectrophotometry	(240 73 nm)
Ni	Spectrophotometry, with dimethylglyoxime	(530 nm)
Zn	Atomic-absorption spectrophotometry	(213 86 nm)
Cd	Atomic-absorption spectrophotometry	(228 80 nm)
Ge	Spectrophotometry with ammonium molybdate	(830 nm)
Sn	Spectrophotometry with gallein	(496 nm)
Pb	Atomic-absorption spectrophotometry	(217 0 nm)
V	Spectrophotometry as phosphotungstovanadate	(410 nm)
As	Spectrophotometry with ammonium molybdate	(845 nm)
Sb	Spectrophotometry as iodide	(425 nm)
Bi	Spectrophotometry as iodide	(460 nm)
Cu	Atomic-absorption spectrophotometry	(324 75 nm)
Ag	Atomic-absorption spectrophotometry	(328 2 nm)
Au	Atomic-absorption spectrophotometry	(242.8 nm)
Mn	Spectrophotometry as permanganate	(546 nm)
Re	Spectrophotometry as thiocyanate	(425 nm)
Ga	Atomic-absorption spectrophotometry	(294.36–294 42 nm doublet)
In	Polarography	
Tl	Polarography	
Ce	Spectrophotometry after oxidation to cerium(IV)	(350 nm)
Se	Spectrophotometry with 3,3'-diaminobenzidine hydrochloride	(420 nm)
Te	Spectrophotometry with thiourea	(330 nm)
Cr	Spectrophotometry as chromate	(366 nm)
Mo	Spectrophotometry as thiocyanate	(460 nm)
U	Spectrophotometry with sodium azide	(360 nm)
Pt	Spectrophotometry with stannous chloride	(405 nm)
Pd	Spectrophotometry as iodide	(408 nm)
Rh	Spectrophotometry with stannous chloride	(475 nm)
Ir	Spectrophotometry with *o*-dianisidine	(530 nm)
Ru	Spectrophotometry with thiourea	(620 nm)
Os	Spectrophotometry with thiourea	(480 nm)

containing 5-ml aliquots of a solution of the appropriate metal (i.e., 500 μg of the metal), or the residue obtained after evaporation of an aliquot to dryness (Note 1). Each solution was transferred to a 125-ml separatory funnel and diluted to 50 ml with water. Ten ml of chloroform were added, followed by 1 ml of freshly prepared 20% potassium ethyl xanthate solution, and the solution was extracted immediately (Note 2) by shaking for 1 min. The chloroform phase was drained into a 150-ml beaker. The aqueous phase was extracted twice more, in a similar manner, with 5-ml portions of chloroform and 1 and 0.5 ml of xanthate solution, then the aqueous phase was washed by shaking it for ~30 sec with 5 ml of chloroform. The combined extracts were treated with 10 ml of 50% v/v nitric acid (Note 3) and chloroform was removed by evaporation on a hot water-bath. Depending on the volatility and other properties of the element investigated, and the method used for its determination, the resulting solution was subsequently either evaporated to dryness, or treated with suitable acids or *aqua regia*, and evaporated to fumes or to dryness.

The amount of the metal in the chloroform extract was determined by the methods listed in Table 1. The percentage of metal extracted was then calculated from the initial known total amount of metal and that found in the organic phase after a triple extraction.

Notes

1. Tests with selenium, tellurium, arsenic, antimony and thallium in their highest oxidation states were carried out after oxidation of these elements with 0.5% potassium permanganate solution, in dilute (0.5*M* or less) hydrochloric acid media before the adjustment of the acid concentration of the solution with 10*M* or concentrated hydrochloric acid and subsequent dilution to 50 ml with water. In tests with platinum and gold, 5-ml aliquots of the solutions in 0.5 and 1*M* hydrochloric acid media, respectively, were also treated with permanganate solution to ensure that these elements were in their highest oxidation states before extraction.
2. Because of the instability of many metal xanthate complexes, the extraction was performed immediately after the addition of chloroform and xanthate solution.
3. Extracts obtained during tests with ruthenium(III) were evaporated to dryness with hydrochloric acid alone, to prevent loss of ruthenium as the volatile tetroxide.

RESULTS AND DISCUSSION

The degree of extraction of a number of elements into chloroform, as ethyl xanthate complexes, from 0.1–10*M* hydrochloric acid media is given in Table 2 and Figs. 1–4. The acid concentrations shown are the initial concentrations of the solutions before the addition, in three successive extraction stages, of a total volume of 2.5 ml of 20% potassium ethyl xanthate solution. The oxidation states of the elements shown are those in which they were initially added. Although arsenic, antimony, thallium and tellurium

Table 2. Extraction of metal ethyl xanthates into chloroform after a triple extraction

	Extraction from 0.1–10*M* hydrochloric acid media, %									
Species	0.1*M*	0.5*M*	1*M*	2*M*	3*M*	4*M*	5*M*	6*M*	8*M*	10*M*
Fe(II)	2.8	0.8	0.4	0	0	0	0	0	0	0
Fe(III)	13.6	19.2	16.6	14.0	9.6	11.4	4.6	2.0	0.4	0.2
Co(II)	97.6	29.6	7.8	2.8	0	0	0	0	0	0
Ni(II)	98.4	40.4	18.0	8.0	2.0	1.6	1.2	0.8	0	0
Cd(II)	84.4	0.3	0	0	0	0	0	0	0	0
Ga(III)	28.2	0	0	0	0	0	0	0	0	0
In(III)	99.6	82.4	37.6	0.6	0	0	0	0	0	0
Tl(I)	8.0	0.6	0.5	0.4	0.6	0.5	0	0	0	0
Tl(III)	51.0	20.2	17.8	18.0	22.2	40.8	36.4	42.0	2.8	0
Sn(IV)	74.4	54.8	28.0	14.0	5.6	2.2	1.0	0.4	0	0
Cu(II)	80.0	80.6	79.4	81.0	74.2	77.0	71.2	51.0	22.8	7.0
Ag(I)	48.8	74.0	84.8	90.0	92.0	0	0	0	0	0
Au(III)	88.6	81.0	89.0	88.0	86.0	91.0	88.6	79.8	85.0	86.0
Pt(IV)	60.8	35.0	28.5	26.8	25.2	19.8	18.0	13.4	12.0	12.4
Pd(II)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
V(V)	64.0	32.0	11.2	3.8	1.6	0.4	0	0	0	0
U(VI)	3.4	3.4	3.4	6.2	3.4	3.4	4 0	2.8	1.4	0.4

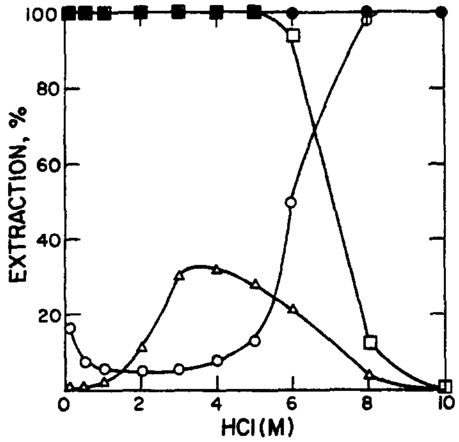

Fig. 1. Extraction of As(III) (●), As(V) (○), Sb(III) (□) and Sb(V) (△) as a function of HCl concentration.

are known to react with xanthate in their lower oxidation states, tests with these elements, and selenium, were also carried out in their highest oxidation states because of the known reducing action of xanthates.[1] Tests with other metal ions (not shown) showed that manganese(II), zinc, rhodium(III), iridium(IV), ruthenium(III), osmium(IV), chromium(III) and (VI) and cerium(III) and (IV) are not extracted from 0.1–10*M* hydrochloric acid. Germanium(IV) is partially extracted (~27–90%) from 6–10*M* media, not as a xanthate complex, but as the chloro-complex.

Iron, cobalt, nickel and cadmium

Table 2 shows that iron(III), cobalt(II) and nickel are partially extracted at low hydrochloric acid concentrations, particularly in the range 0.1–2*M*. The extraction of these ions is reasonably consistent with reported data.[1] The erratic results obtained for iron(III) can be attributed to its partial reduction by xanthate during or before the extraction.[9,10] The low extraction of iron(II) from 0.1–1*M* hydrochloric acid may be due to aerial oxidation before the extraction, because it has been reported that iron(II) does not react with xanthate.[9,10]

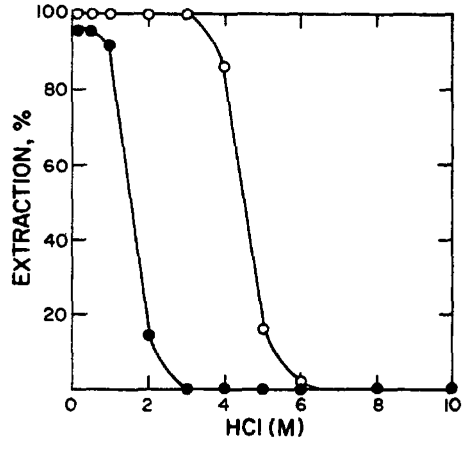

Fig. 2. Extraction of Pb(II) (●) and Bi(III) (○) as a function of HCl concentration.

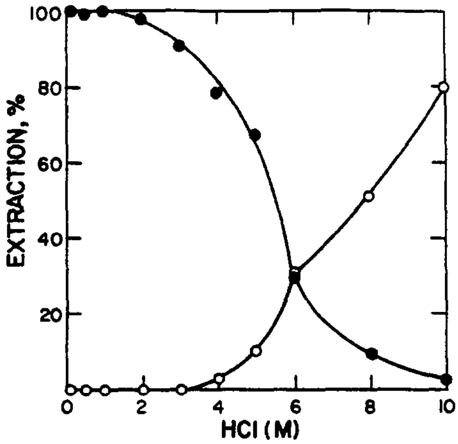

Fig. 3. Extraction of Mo(VI) (●) and Re(VII) (○) as a function of HCl concentration.

The high percentage of cadmium extracted from 0.1*M* hydrochloric acid is not consistent with earlier data, because cadmium ethyl xanthate has been reported as being insoluble in chloroform and other non-polar solvents (carbon tetrachloride, benzene, dichloroethane and petrol).[9]

Gallium, indium and thallium

Gallium(III) and indium(III) are partially and almost completely extracted, respectively, as colourless ethyl xanthate complexes from 0.1*M* hydrochloric acid. No references to the extraction of these complexes were found in the literature. However, solid complexes with the formulae $Ga(EX)_3$ and $In(EX)_3$, (EX = ethyl xanthate) have been reported.[11]

The low extraction of thallium(I) from 0.1*M* hydrochloric acid is consistent with earlier work[12,13] in which a number of colourless xanthate complexes of thallium(I) were found to be of limited solubility in non-polar solvents. A solid thallium(III) complex, $Tl(EX)_3$, has been prepared[11] but its solubility in organic solvents has not been reported. Table 2 shows that the thallium(III) complex (yellow) is moderately extracted into chloroform from 0.1*M* hydrochloric

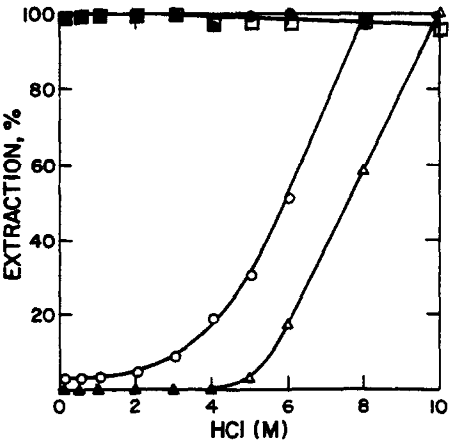

Fig. 4. Extraction of Se(IV) (●), Se(VI) (○), Te(IV) (□) and Te(VI) (△) as a function of HCl concentration

acid. The degree of extraction first decreases with increase in acid concentration, then increases somewhat over the range 4–6M acidity. The increase is probably due to the extraction of the thallium(III) chloro-complex. The ethyl xanthate complex is considerably more soluble in di-isopropyl ether than in chloroform.

Tin, copper and silver

Tin(IV) is partially extracted from 0.1–5M hydrochloric acid media. Previously, qualitative tests have shown that both tin(II) and (IV) can be extracted into carbon tetrachloride, chloroform and other non-polar solvents from weakly acidic media (pH ~4).[9] A solid tin(II) complex with the formula $Sn(EX)_2$ has been reported,[11] which suggests that tin(IV) is probably reduced during complex formation.

Table 2 shows that copper(II) is appreciably extracted over the whole range of acid concentration investigated. However, a yellow precipitate remained at the interface after the third extraction and the washing stage, and consequently erratic results were obtained in these tests. Presumably this was caused by the low solubility of copper(I) ethyl xanthate in chloroform. It has been reported that copper(II) is not directly reduced by xanthate ions but reacts to form copper(II) ethyl xanthate which rapidly decomposes to form copper(I) ethyl xanthate and dixanthogen. The copper(I) complex is reported to be insoluble in chloroform in the absence of pyridine.[14]

Silver(I) is only partially extracted as the ethyl xanthate complex from ~1M or less hydrochloric acid because of the partial formation of insoluble silver chloride. The degree of extraction at this or higher acidity (2–3M) is also influenced by the limited solubility of the yellow complex in chloroform. As with copper, some of the precipitate was not extracted and remained at the interface after the extraction and washing steps. Probably more complete extraction of up to ~500 μg of silver into chloroform from 2–3M hydrochloric acid can be obtained if larger volumes of solvent are used.

Gold, platinum and palladium

Table 2 shows that gold(III) is appreciably extracted over the whole range of acid concentration investigated. The extraction of a gold–ethyl xanthate complex has not been described previously, but the formation of a solid gold(I) complex has been reported.[11] In tests with gold(III), the extraction of the yellow complex appeared complete, and the dark yellow extract faded rapidly on standing, which suggests decomposition of the complex. It is considered that the reaction of gold(III) with ethyl xanthate is analogous to that of copper(II), *i.e.*, that gold reacts to form a gold(III) complex which rapidly decomposes to an insoluble gold(I) complex. A similar reaction has been observed for the gold(III) diethyldithiocarbamate complex.[11]

The extraction of platinum as a yellow ethyl xanthate complex has not been described previously, but Table 2 shows that it is partially extracted over the whole range of acid concentration investigated. A solid yellow compound with the formula $Pt(EX)_2$ has been reported,[15, 16] which indicates that xanthate reduces platinum(IV) to platinum(II) and that the latter reacts during complex formation.

Palladium(II) is completely extracted from 0.1–10M hydrochloric acid.

Vanadium and uranium

The extraction of both vanadium and uranium is consistent with reported data.[1] The orange–red uranium(VI) complex has been reported to be insoluble in chloroform and other non-polar solvents.[17] Presumably vanadium is reduced to vanadium(IV) by xanthate and reacts in the form of the VO^{2+} ion.[11]

Arsenic and antimony

Previous investigators[6] found that the optimum hydrochloric acid concentration for the quantitative extraction of arsenic(III) as the ethyl xanthate complex into carbon tetrachloride is 0.1–0.2M. Although Fig. 1 shows that it can be completely extracted into chloroform from 0.1–10M hydrochloric acid, tests showed that it is probably the chloro-complex that is extracted at high hydrochloric acid concentrations. In tests with arsenic(V), the increase in extraction from ~5–10M acid media is considered to be due to reduction of arsenic(V) by chloride[18] and subsequent extraction as either the arsenic(III) xanthate or chloro-complex. Arsenic(V) is not extracted as the chloro-complex from concentrated hydrochloric acid.[19] The degree of extraction from 0.1–4M acid media could be due to incomplete oxidation of arsenic (III) with potassium permanganate or partial reduction of arsenic(V) by xanthate before the extraction step.

The optimum hydrochloric acid concentration required for the quantitative extraction of antimony(III) as the ethyl xanthate complex into carbon tetrachloride has been reported as 1.8–2.5M.[6] Figure 1 shows that it can be completely extracted into chloroform from 0.1–5M hydrochloric acid. It is considered that antimony(V) probably extracts as the chloro-complex.[20]

Lead and bismuth

Previous investigators[6] found that the extraction of bismuth ethyl xanthate into carbon tetrachloride starts at pH 0.16 and becomes quantitative at pH 1–4. Figure 2 shows that bismuth is completely extracted into chloroform from 0.1–3M hydrochloric acid. The extraction of lead, also shown in Fig. 2, agrees reasonably well with earlier work.[1]

Molybdenum and rhenium

The acid conditions required for the extraction of molybdenum are shown in Fig. 3. Molybdenum(VI) is reduced by xanthate to molybdenum(V) and it is the latter that subsequently forms the xanthate complex.[21]

Although Fig. 3 shows that rhenium is partially extracted into chloroform from 4–10*M* hydrochloric acid, no references were found pertaining to the formation or extraction of a rhenium xanthate complex. Tests showed that rhenium, initially present in oxidation state (VII), is not extracted as a chloro-complex. It is known that rhenium(III) forms extractable complexes, with the general formula $ReCl_2(NR_2 \cdot CS_2)$, with dialkyldithiocarbamates,[22] which are analogous compounds to xanthates. Consequently, it may be possible that rhenium(VII) is reduced to rhenium(III) by xanthate and/or chloride ions in relatively concentrated hydrochloric acid media and that rhenium(III) subsequently reacts to form an analogous type of ethyl xanthate compound.

Selenium and tellurium

No previous study had been made of the conditions required for the extraction of selenium and tellurium as ethyl xanthate complexes, although it has been reported that these elements form extractable complexes in dilute acid media.[7,23,24] Figure 4 shows that selenium(IV) can be completely extracted into chloroform from 0.1–10*M* hydrochloric acid. It also shows that tellurium(IV) is completely, or almost completely, extracted (97–100%) under the same conditions. Tests showed that neither selenium(VI) nor tellurium(VI) is extracted as the chloro-complex into chloroform from concentrated hydrochloric acid media. It is considered that the extraction of these ions as xanthate complexes at high hydrochloric acid concentrations is due to their reduction by chloride ions,[25] xanthate ions, or both. Solid selenium and tellurium ethyl xanthate complexes, $Se(EX)_2$ and $Te(EX)_2$, in which the elements are present in the bivalent state, have been reported.[11] This indicates that selenium(IV) and tellurium(IV) are reduced by xanthate during complex formation.

ANALYTICAL APPLICATIONS

The results of the present work indicate that it is possible to separate arsenic, selenium, tellurium, palladium and possibly gold from all of the other elements investigated, except germanium, rhenium, platinum and copper, by chloroform extraction of their ethyl xanthate complexes from 10*M* or possibly concentrated hydrochloric acid. The group separation of arsenic, antimony, bismuth, selenium and tellurium from zinc, manganese, iron, copper and probably nickel and lead matrices should be possible by extracting from ~3*M* hydrochloric acid. Co-extraction of iron(III) can be avoided by reducing it to the bivalent state with ascorbic acid before extraction. Co-extraction of copper(II) can be eliminated by complexing it with thiourea. Complexation of other elements with tartrate and fluoride ions (*e.g.*, tungsten, titanium, niobium, tantalum and tin) is also possible.

Xanthate–chloroform extraction from acid media has been employed for the separation of molybdenum from rhenium[1] and of bismuth from lead.[8] Separation of rhenium from molybdenum may also be possible by extracting it from a concentrated hydrochloric acid medium. Separation of arsenic from antimony is possible by extracting it from 10*M* or concentrated hydrochloric acid. Depending on the hydrochloric acid concentration of the aqueous phase during extraction, group separations of numerous elements from elements such as aluminium, beryllium, manganese, zinc, chromium, calcium, magnesium, strontium, barium, rhenium and germanium can be accomplished by employing potassium ethyl xanthate in conjunction with cupferron[26] and/or ammonium pyrrolidinedithiocarbamate[27] as mixed chelating agents.

Care must be taken in applying the results shown in this paper to specific analytical problems because the extraction profiles of the elements, shown in Figs. 1–4 and Table 2, may change somewhat with factors such as the amount of the species to be extracted, the amount of matrix elements present, the presence of complexing agents (*e.g.*, tartrate or fluoride), and the amount of potassium ethyl xanthate and the volume of chloroform used for extraction.

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SOLVENT EXTRACTION OF METAL XANTHATES

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Summary—The solvent extraction of metal xanthates is reviewed with emphasis on the characteristics and analytical uses of ethyl xanthate complexes. Elements reviewed include As, Sb, Bi, Cd, Co, Cu, Cr, Ga, Au, In, Fe, Pb, Mn, Hg, Mo, Ni, Pd, Pt, Re, Ag, Se, Te, Tc, Tl, Sn, U, V and Zn.

Although it has been known for a long time that alkyl xanthates react with metal ions to form extractable chelates of the type, $M(RCOS_2)_n$, few reviews have been published in English dealing with the analytical applications of xanthates and/or the solvent extraction of their metal complexes. Reviews on analytical reagents containing thiol and thione groups, including xanthates,[1] the analytical uses of metal xanthates,[2] and methods for the determination of xanthate by means of reactions with metal ions[3] have appeared in obscure Soviet and other journals, but unfortunately they are not available as English translations. Some relatively recent reviews[4–7] have appeared in English but the emphasis in these is on co-ordination chemistry rather than on analytical applications or solvent extraction.

Within the last 18 years, some information on the solvent extraction of metal xanthates has appeared in several books[8–10] dealing with the extraction of metal chelates; also a short review has been published in English.[11] However, in these sources combined, the extraction behaviour of only 16 elements was reviewed briefly, and the literature pertaining to other elements previously known to be extractable was not reviewed. Because of the increasing analytical use and potential importance of the solvent extraction of metal xanthates, and because recent work by the author[12] has shown that many more metal ions (*e.g.*, gallium, indium, gold, platinum and rhenium) can be extracted as xanthates than has been hitherto reported, it was considered that a comprehensive "up-to-date" review of the extraction and characteristics of metal xanthate complexes would be of interest to analytical chemists.

This review is concerned mainly with ethyl xanthate complexes because this reagent has been most widely used in analytical work. In cases where the original papers or English translations were not readily available, references have been made both to the papers and abstracts. The solvent extraction of 28 elements, arranged in roughly alphabetical order, is reviewed up to approximately mid-1975.

EXTRACTION AND CHARACTERISTICS OF METAL XANTHATES

Arsenic

Chakrabarty and De[13] studied the extraction of arsenic(III) ethyl xanthate into carbon tetrachloride from acid media and found that extraction occurs from hydrochloric acid that is $>0.01M$ and is quantitative from the $0.1M$ acid if a double extraction is used. The optimum acidity is 0.1–$0.2M$ hydrochloric acid. From $0.05M$ sulphuric acid a double extraction is also quantitative. After removal of the solvent by evaporation, arsenic is determined by a conventional iodometric method. Moderate amounts (up to ~ 80 mg) of fluoride, citrate, tartrate and EDTA do not interfere in the extraction. Lead, copper(II), cobalt(II), iron(III), antimony(III), bismuth, tin(IV) and vanadium(V) interfere.

Arsenic has been determined in foods by the molybdenum blue method, after its reduction to the tervalent state with potassium iodide, removal of liberated iodine with sodium thiosulphate, and isolation by xanthate–carbon tetrachloride extraction from a sulphuric acid medium.[14] Interference from antimony and tin is eliminated by washing the extract with concentrated hydrochloric acid containing stannous chloride. The solvent is removed by evaporation and arsenic(III) is oxidized with bromine before the spectrophotometric determination. Similar methods have been used for the isolation and subsequent determination of arsenic in zinc- and lead-base materials[15] and pyrite and pyrite ashes[16] after xanthate–carbon tetrachloride extraction from dilute and $\sim 2M$ sulphuric acid, respectively, followed by back-extraction (and oxidation) of the arsenic with bromine water. Antimony interferes in both methods.

Xanthate–carbon tetrachloride extraction of arsenic(III) has also been used for its isolation and subsequent determination in natural water, silicates and biological materials after its separation by co-precipitation with hydrous ferric oxide.[17] The colourless complex is partly extracted into carbon tetrachloride and other solvents (chloroform, dichloroethane, benzene and gasoline) at ~pH 4.[18]

Recent studies by the author have shown that arsenic(III) can be quantitatively extracted into chloroform from 0.1–10*M* hydrochloric acid.[12] Thermal studies have shown that it forms a 1:3 ethyl xanthate complex[19] with the formula $As(EX)_3$,[6] where EX is the ethyl xanthate ion ($C_2H_5OCS_2$).

Antimony

Chakrabarty and De[13] found that the colourless antimony(III) complex is extracted into carbon tetrachloride from >0.1*M* hydrochloric acid, a double extraction from the 1.8M acid being quantitative. The optimum acidity is 1.8–2.5*M*. From sulphuric acid media, the extraction starts at a concentration of 0.25*M* and is quantitative from the 0.75*M* acid (double extraction). After removal of the solvent by evaporation, antimony is determined by iodometric titration. Moderate amounts (up to ~25 mg) of lead, cobalt(II), iron(III), bismuth, tin(IV), fluoride, citrate, tartrate and EDTA do not interfere, but copper(II), arsenic(III) and vanadium(V) interfere seriously. In most of the above-mentioned methods for arsenic, antimony is co-extracted and interferes. Similarly to that of arsenic(III), the complex is partly extracted into carbon tetrachloride and other non-polar solvents at ~pH 4.[18]

Recent studies have shown that antimony(III) can be quantitatively extracted from 0.1–5*M* hydrochloric acid.[12] Thermal studies have shown that it forms a 1:3 complex[19] with the formula $Sb(EX)_3$.[6]

Bismuth

Chakrabarty and De[13] found that bismuth(III) ethyl xanthate is extracted into carbon tetrachloride at pH > 0.16, quantitatively at pH 1–4. The yellow extract can be employed for the spectrophotometric determination of mg-amounts of bismuth. Beer's law is obeyed, at 400 nm, over the concentration range 5–50 μg/ml. The complex is stable for 48 hr and its molar absorptivity is $287\,l \cdot mole^{-1} \cdot mm^{-1}$ at 400 nm. At pH 1.24, moderate amounts (up to ~25 mg) of cadmium, chromium(III), aluminium, fluoride, sulphate and EDTA do not interfere. Lead, copper(II), mercury(II), iron(III), arsenic(III), antimony(III), vanadium(V), citrate, phosphate and tartrate interfere seriously. These investigators claim that bismuth can be separated from arsenic by selective extraction at pH 4.5; arsenic(III) can subsequently be extracted from the residual aqueous phase at pH 1.0. Bismuth can also be extracted, at ~pH 4, into chloroform, dichloroethane, benzene and gasoline.[18]

The complex has been extracted into a 1:4 mixture of pyridine and ethyl acetate from a sodium formate medium.[20] The extract can be used for the spectrophotometric determination of bismuth. Beer's law is followed, at 420 nm, over the concentration range 0.06–0.14 mg/ml. In the presence of 0.1% sodium cyanide and 0.1% EDTA, the method is reported to be selective for bismuth in the presence of copper, cobalt, nickel and various other ions, but thallium, high concentrations of ammonia, and citrate interfere. Extraction from the stated medium into pyridine–ethyl acetate has also been used for the column chromatographic separation of bismuth ethyl xanthate and mixtures of other metal xanthates (cobalt, nickel, copper, iron, cadmium and mercury).[21]

Xanthate–chloroform extraction has been employed by the author, in the determination of lead in ores by EDTA titration, for the separation of bismuth from lead in a 2*M* hydrochloric acid–tartaric acid medium.[22] Recently, the author has also shown that bismuth can be quantitatively extracted from 0.1–3*M* hydrochloric acid.[12] Analysis of the bismuth ethyl xanthate precipitate[13] and thermal studies[19] have shown that it is a 1:3 complex with the formula $Bi(EX)_3$.[6]

Cadmium

According to Pilipenko and Ulko,[18] cadmium forms a white ethyl xanthate complex, at ~pH 4–9, that is not extracted into carbon tetrachloride, chloroform or other non-polar solvents. However, recent studies on the extraction of metal ethyl xanthates into chloroform from hydrochloric acid media have shown that cadmium is appreciably extracted (~85% in a triple extraction) from 0.1*M* hydrochloric acid initially containing 500 μg.[12] Probably complete extraction into chloroform can be obtained at pH > 1.

Sheyanova *et al.*[23] found that the cadmium benzyl xanthate complex can be completely extracted into chloroform in the pH range 1.9–5.2 with a 3:1 volume ratio of aqueous to organic phase and a 100–500-fold excess of reagent. They found that cadmium can be separated from large amounts of zinc at pH > 10.

The ethyl xanthate complex can also be extracted into a 1:4 mixture of pyridine and ethyl acetate from a sodium formate medium.[21] Solubility studies have shown that cadmium forms a 1:2 complex[24] while spectrophotometric and kinetic studies by the same investigators[25,26] indicate a 1:1 complex. The formation of a 1:2 complex is more probable and is supported by the fact that a solid complex with the formula $Cd(EX)_2$ has been reported.[27]

Cobalt

Pilipenko and Ulko[18] found that the green cobalt complex can be extracted into carbon tetrachloride and other non-polar solvents from weakly acid media or at pH up to ~9. They state that only cobalt ethyl xanthate can be extracted from an alkaline medium (*cf.* cadmium, manganese and copper). They developed a spectrophotometric procedure for the determination of cobalt in nickel salts, nickel metal, iron–nickel ores and steels, based on extraction of the complex into carbon tetrachloride from dilute hydrochloric or sulphuric acid media. The absorbance of the extract is measured at 465 nm. Interference from co-extracted nickel alone is eliminated by shaking the extract with

50% v/v ammonia solution; that from iron(III) (and nickel) by shaking it with ammoniacal ammonium tartrate solution. The solution of cobalt ethyl xanthate in the organic solvent was found to be stable for 3 days if kept under water. Spectrophotometric studies showed that cobalt and ethyl xanthate react in 1:2 ratio. Beer's law is obeyed over the concentration range of ~5–50 μg/ml. Large amounts of copper, mercury and silver interfere. This procedure was later adapted to the determination of cobalt in manganese ores and manganese-containing slags.[28]

Extraction of cobalt ethyl xanthate into amyl acetate (or methyl isobutyl ketone) has been employed for the separation of cobalt from zinc solutions containing nickel.[29] After adjustment of the pH to 5.8, sufficient potassium ethyl xanthate is added to precipitate nickel (molar ratio xanthate:nickel = 6:1). After extraction of the nickel, fresh xanthate solution is added to precipitate the cobalt, then the solution is oxidized by air before the extraction and subsequent spectrophotometric determination of cobalt. Air-oxidation of cobalt is recommended because it was observed that cobalt(II) reacts considerably more slowly with xanthate ions than does cobalt(III). The complex formed under these conditions was found to be a 1:3 complex.

Hayashi *et al.*[30] studied the effects of pH, ionic strength and ethyl xanthate concentration on the extraction of cobalt(II) into carbon tetrachloride. They found that the optimum pH range for practically quantitative extraction is 6.5–9. Beer's law is obeyed, the complex formed is a 1:2 complex, and the molar absorptivity is 1.34×10^3 l·mole^{-1}·mm^{-1} at 356 nm, the wavelength of maximum absorption. No evidence was found for a complex containing cobalt and xanthate in a higher combining ratio.

Xanthate–ethyl acetate extraction has been used for the spectrophotometric determination of cobalt in ores and alloys.[31] Cobalt is extracted (almost completely), in two extractions, at pH 5–9 in the presence of potassium chloride or sodium formate as salting-out agents, followed by direct measurement of the absorbance of the extract at 420 nm. Interference from co-extracted nickel is eliminated by shaking the extract with 1 or 2 drops of concentrated perchloric acid. Beer's law is obeyed over the concentration range 12–40 μg/ml. Copper is also extracted but can be masked with thiourea. The same investigators used a mixture of pyridine and ethyl acetate (1:4) for the extraction and subsequent determination of cobalt under approximately the same conditions.[20] They found that the solution of the xanthate–pyridine adduct obeys Beer's law, at 420 nm, over the concentration range 10–55 μg/ml. Moderate amounts of nickel (up to 0.1 mg in 0.2 mg of cobalt) do not interfere, but thallium, high concentrations of ammonia, and citrate do interfere. The modified extraction procedure was also applied to the separation of cobalt ethyl xanthate and mixtures of other xanthates (see bismuth) by column chromatography.[21]

Cobalt benzyl xanthate can be completely extracted into chloroform, at pH 0.9–5.2, with a 3:1 volume ratio of aqueous to organic phase and a 100–500-fold excess of reagent.[23] Recent studies have shown that the ethyl xanthate complex can be almost completely extracted into chloroform from 0.1*M* hydrochloric acid.[12] It can also be extracted from ammoniacal media with ethers[32] and chlorinated and aromatic solvents, particularly dichloromethane and cyclohexanone.[33]

There are divergent views in the literature about the composition of the cobalt ethyl xanthate complex, *i.e.*, whether the complex contains cobalt in oxidation state (II)[18,34] or (III).[32,35] According to Allison,[36] cobalt reacts in alkaline or weakly acidic media (~pH 4–10) to form a 1:3 cobalt(III) complex, while in strong acid media a 1:2 cobalt(II) complex is formed. Similarly, Zagyanskii[37] found that cobalt(III) xanthate is precipitated at high pH values, while in sulphate solutions, at pH 2.5–3.5, cobalt is precipitated mainly in the cobalt(II) state. He explained the formation of cobalt(III) xanthate [$Co(EX)_3$] by the formation of dixanthogen, which facilitates the oxidation of cobalt(II) xanthate [$Co(EX)_2$] to the cobalt(III) compound; apparently dixanthogen cannot be formed at pH values less than ~4–5.

Copper

Pilipenko and Ulko[18] reported that the yellow copper ethyl xanthate complex is insoluble in carbon tetrachloride, chloroform and other non-polar solvents. However, copper has been found to be co-extracted to a certain extent into some of these solvents and to interfere in various methods based on extraction of metal xanthates (*e.g.*, see arsenic, antimony, lead and nickel). Recent studies have shown that it is appreciably extracted into chloroform (~70–80% in three extractions) from 0.1–5*M* hydrochloric acid initially containing 500 μg of the element.[12]

Extraction of the complex into pyridine–ethyl acetate (1:4) from a sodium formate medium has been used for the separation of copper and other metal xanthates by column chromatography.[21] The extract of the copper–pyridine adduct can be employed for the spectrophotometric determination of copper.[20] Beer's law is followed, at 420 nm, for copper up to 40 μg/ml. Interference from cobalt and nickel is avoided by extracting from a 0.1% EDTA medium. Thallium, high concentrations of ammonia, and citrate interfere. Extraction of the complex into diethyl ether from alkaline media (pH 7–8.5) has been used as a fractional flotation test for copper.[8,38]

Pohlandt *et al.*[39] developed a spectrophotometric method for the determination of xanthate, based on extraction of the copper(II) complex into chloroform from an alkaline cyanide medium. The absorbance of the extract is measured at 305 nm. Measurement must be made immediately after extraction because of the instability of the extracted complex. In these studies, and in later solubility[24] and spectrophotometric[40] studies, copper and ethyl xanthate were found to combine in a 1:2 ratio, indicating that it is copper(II) that reacts. In earlier work[41,42] it was assumed that copper(II) and xanthate ions react directly (by a reduction process) to form copper(I) xanthate and dixanthogen. According to Pohlandt *et al.*[39] they react in two stages, *i.e.*, the formation of copper(II) xanthate and the subsequent decomposition of this compound into copper(I) xanthate and dixanthogen. They reported that copper(I) xanthate is insoluble in chloroform in the absence of pyridine.

Chromium

The green chromium(VI) complex is partially extracted into carbon tetrachloride, chloroform and other non-polar solvents from weakly acidic media (pH ~ 4).[18] It is reported that the complex is intensely coloured but that its formation is slow and not quantitative. Xanthate is purported to react not only with chromium(VI) but also with chromium(II) and, on long standing, with chromium(III). The absorption spectra of the reaction products in carbon tetrachloride, in the presence of excess of xanthate, indicated that the end-product is the same in each case. The composition of the extracted compound was not established, but it has been reported subsequently[43] that chromium(III) forms a dark blue compound with the formula $Cr(EX)_3$.

Neither chromium(VI) nor chromium(III) is extracted into chloroform from ~0.1–10*M* hydrochloric acid.[12]

Gallium

References pertaining to the extraction of a gallium(III) ethyl xanthate complex have not been found in the literature, but a white complex with the formula $Ga(EX)_3$ has been reported.[6] Recent studies by the author have shown that a colourless gallium(III) complex is partially extracted into chloroform (~28% in three extractions) from 0.1*M* hydrochloric acid initially containing 500 μg of gallium.[12] Complete extraction can probably be obtained at pH values >1.

Gold

Although the extraction of gold as an ethyl xanthate complex has not been reported previously, the formation and stability of a gold(I) complex has been studied.[44,45] Recently, it was shown that a yellow complex is appreciably extracted into chloroform (~80–90% in three extractions) from 0.1–10*M* hydrochloric acid initially containing 500 μg of gold(III).[12] The dark yellow extract faded rapidly on standing, indicating the formation and extraction of an unstable complex. It is considered that gold reacts initially to form a gold(III) complex that rapidly decomposes to yield a gold(I) complex.

Indium

The extraction of indium has not been reported previously, but recent studies have shown that a colourless indium(III) ethyl xanthate complex can be quantitatively extracted into chloroform from 0.1*M* hydrochloric acid.[12] The formula of the complex is reported to be $In(EX)_3$.[6]

Iron

The extraction of a brown iron(III) complex into carbon tetrachloride, chloroform and other non-polar solvents from media of pH ~ 4–7 has been reported.[18] Iron(III) has also been extracted from a sodium formate medium into ethyl acetate or a mixture (4:1) of ethyl acetate and pyridine.[21] It is co-extracted and interferes in many methods based on extraction of metal xanthates from weakly acidic and alkaline media (*e.g.*, see arsenic, bismuth, molybdenum, lead, cobalt and nickel). It is partly extracted into chloroform from 0.1–5*M* hydrochloric acid.[12]

According to Pilipenko and Ulko,[18] iron(III) is partially reduced by xanthates to iron(II) (presumably in dilute acid media), which is reported not to react with xanthate.[40] However, Allison[36] found that a blood-red precipitate, presumed to be iron(II) ethyl xanthate, is formed in oxygen-free solutions. Studies of the iron(III) system have shown that a very stable 1:3 complex is formed in the pH range ~3.5–11 (optimum pH = 10).[11,46] Studies by Allison[36] of the decomposition of solutions of xanthates in the presence of iron(III) have confirmed this combining ratio. The formula of the complex is reported to be $Fe(EX)_3$.[6]

Lead

The partial extraction of a colourless or pale yellow lead(II) complex into carbon tetrachloride, chloroform and other non-polar solvents at pH ~ 4 has been reported.[18] Recently, xanthate–carbon tetrachloride extraction of the complex from media ranging from neutral to ~0.005*M* nitric or hydrochloric acid has been suggested for the separation of lead before its titrimetric determination with EDTA.[47] Copper(II), cobalt(II), iron(III), mercury(II), zinc, cadmium, vanadium(V), fluoride, sulphate and EDTA interfere with the extraction. Interference from arsenic (III) can be eliminated by preferential extraction of lead at pH 6; that from antimony(III) by its preferential extraction from a 2*M* acid medium. Xanthate–carbon tetrachloride extraction has also been used for the separation of lead from silver at pH ~ 5, before its subsequent titration with EDTA.[48] It is claimed that complete extraction of up to 6 mg of lead can be obtained, at pH 3.5–6.5, in a single extraction, in the presence of 20 mg of xanthate and at least 15 ml of carbon tetrachloride; above pH 7 the rate of extraction becomes slow and the separation of silver is difficult. Silver is completely retained as a precipitate in the aqueous phase in the pH range 2.0–6.5.

Micro-amounts of lead in human tissue have been determined by atomic-absorption spectrophotometry on the solvent phase after extraction of the ethyl xanthate complex into methyl isobutyl ketone at pH

3·5–9·5.[49] Copper(II) and phosphate interfere with the extraction, but copper can be masked with thiourea. It has been shown that lead is appreciably extracted into chloroform (~90–95% in three extractions) from ~0.1–1M hydrochloric acid initially containing 500 μg of lead.[12] Solubility[24] and spectrophotometric studies,[40] as well as studies of the decomposition of solutions of xanthates in the presence of lead,[36] show that lead and ethyl xanthate form a 1:2 complex with the formula $Pb(EX)_2$.[6]

Manganese

It has been reported that manganese does not react with xanthate.[18] However, a recent method for the determination of manganese in human tissue[50] is based on the extraction of manganese(II) ethyl xanthate into methyl isobutyl ketone, at pH 6.5–9.0, from a 10% ammonium acetate medium containing a large excess of xanthate (11%). Manganese is subsequently determined in the solvent phase by atomic-absorption spectrophotometry. Interference from nickel, copper(II), silver, cadmium, aluminium and zinc is eliminated by their preliminary extraction with 1% potassium ethyl xanthate solution and methyl isobutyl ketone. Manganese(II) is not extracted into chloroform in the presence of potassium ethyl xanthate from 0.1–10M hydrochloric acid.[12]

Mercury

A colourless or light yellow mercury(II) complex is reported to be partially extracted into carbon tetrachloride at ~pH 4.[18] Extraction of the complex into ethyl acetate or a mixture (4:1) of ethyl acetate and pyridine has been used for the separation of mercury xanthate from mixtures of other metal xanthates by column chromatography.[21] Studies of the decomposition of xanthate solutions in the presence of mercury show that the complex formed is a 1:2 complex.[36]

Molybdenum

Extraction of the red-violet molybdenum complex into a mixture (1:2) of petroleum ether and diethyl ether from a sulphuric acid medium, followed by spectrophotometric measurement of the absorbance of the extract, has been used for the determination of molybdenum in steel, iron,[51] tungstic acid and rhenium.[52] Extraction into chloroform from a 4% (or ~0.5M) hydrochloric acid medium has been used for the separation of molybdenum from rhenium in technical products before the spectrophotometric determination of rhenium.[53] Rhenium has also been determined spectrophotometrically in ores, minerals and industrial concentrates after separation of molybdenum by xanthate–chloroform extraction,[54] and in minerals (*e.g.*, molybdenite) after separation of molybdenum from a hydrochloric acid medium by successive extraction into a 1:1 mixture of carbon tetrachloride and benzene.[55]

Xanthate–chloroform extraction of the complex from a dilute sulphuric acid medium has been employed for the separation and gravimetric determination of molybdenum in tungsten.[56] Iron, nickel and vanadium are co-extracted and interfere in this method. Tungsten has been determined spectrophotometrically in steel by a thiocyanate method based on extraction of the tungsten thiocyanate complex into a mixture of isoamyl alcohol and chloroform.[57] The tungsten and co-extracted molybdenum thiocyanate complex are stripped from the extract with ammonia solution, followed by separation of the molybdenum by successive chloroform extraction of its xanthate complex from a weakly acidic medium. Recently, xanthate–chloroform extraction of molybdenum, from ~1.5M hydrochloric acid containing tartaric acid, has been employed for its separation from tungsten before the spectrophotometric determination of tungsten by chloroform extraction of its thiocyanate–diantipyrylmethane ion-association complex.[58] More recent work by the same author has shown that molybdenum can be completely extracted into chloroform, in three successive extractions, from 0.1–1.5M hydrochloric acid.[12]

Extraction of the molybdenum complex at pH 1.8–1.9 into chloroform, followed by spectrophotometric measurement of the absorbance of the extract, has been advocated for the microchemical determination of molybdenum (*i.e.*, 10 μg or less).[59] It is claimed that the chloroform solution of the complex is stable for a long time. Extraction into toluene at pH 1.11–1.56 (or from 0.02–0.08M acid) has also been advocated.[60] The stability of the complex after extraction into organic solvents is said to be highest in petroleum ether and toluene (3 days). It is stable for ~14, 10 and 6 min, respectively, in benzene, chloroform (*cf.* above) and carbon tetrachloride. It is unstable in diethyl ether, isoamyl alcohol, amyl acetate and methyl isobutyl ketone and the colour fades immediately. Chloroform extraction of the complex and direct spectrophotometric measurement of the extract, at 510 nm, has been used for the determination of molybdenum in steel after the removal of interfering elements (*e.g.*, iron and nickel) by electrolysis with a mercury cathode.[61]

Recently,[62] a method based on the separation of molybdenum by chloroform extraction of its ethyl xanthate complex from 1M hydrochloric acid, after reduction of molybdenum(VI) in 2M hydrochloric acid with hydrazine sulphate, has been proposed for the determination of molybdenum in ferromolybdenum and other complex materials. After decomposition of the complex with liquid bromine, molybdenum is stripped from the extract with a dilute alkaline hydrogen peroxide solution and subsequently determined by standard gravimetric, volumetric or spectrophotometric methods. Complete extraction of molybdenum is obtained from 0.2–1.5M hydrochloric acid. Tungsten(VI), iron(III), copper(II) and vanadium(V) are masked with tartaric acid, ascorbic acid, thiourea and potassium hydrogen fluoride, respectively, before extraction. Large amounts of copper, iron and vanadium then do not interfere. Antimony(III), bismuth (III), palladium(II) and tin(II) are completely, or almost completely, extracted under the proposed conditions. Nickel(II), lead(II) and cobalt(II) are partially extracted. Large amounts of EDTA, tartrate, oxalate, citrate, phosphate and fluoride suppress the extractions of molybdenum. More than 100 mg of molybdenum can be separated by extraction, depending on the concentration of xanthate and the volume of chloroform used. Chloroform, benzene, carbon tetrachloride and diethyl ether were found to be the best extractants.

A method based on extraction of a mixed molybdenum–ethyl xanthate–thiocyanate complex into acetophenone from 4–7*M* hydrochloric acid, followed by spectrophotometric measurement of the extract, at 380 or 470 nm, has been applied recently to the determination of molybdenum in steel.[63] The extract is stable for 48 hr. Iron is complexed with ascorbic acid, and chromium(VI) and vanadium(V) are reduced with ferrous ammonium sulphate before extraction. Beer's law is obeyed over the concentration range 1.2–13.8 ppm of molybdenum(VI). Tin(II), lead, arsenic(III), antimony(III), iron(II), oxalate, citrate, fluoride and phosphate, in 1000-fold amounts, and copper(II), cobalt(II) and nickel, in 15-fold amounts, do not interfere. Interference from rhenium is eliminated by prior separation of molybdenum by xanthate–acetophenone extraction from a hydrochloric acid medium.

Chloroform or carbon tetrachloride extraction of molybdenum isopropyl xanthate at pH ~ 5 has been employed recently for the direct spectrophotometric determination of molybdenum at 520 nm.[64]

Early investigators suggested various formulae, *i.e.*, $MoO_2(EX)_2$,[65] $Mo(EX)_2$[66] and $MoO(OH)_2(EX)_2$[59] for the molybdenum ethyl xanthate complex, in which molybdenum is presumed to be present as molybdenum(VI). Montequi and Gallego[67] first formulated these compounds as a binuclear 2:4 compound, $Mo_2O_3(EX)_4$, and established, by chemical means, that molybdenum is present in oxidation state(V). Later Malatesta[68] also established this stoichiometry but suggested that molybdenum is present in both oxidation states. According to spectrophotometric experiments by Pilipenko and Gridchina,[69] in which the complex was extracted into dichloroethane from a dilute acid medium, only molybdenum(V) takes part in the formation of the coloured complex because molybdenum(VI) is reduced to molybdenum(V) by the xanthate. The following equation illustrates this reaction:

$$2\,MoO_4^{2-} + 6\,C_2H_5OCS_2^- + 10H^+ \rightarrow [Mo_2O_3(C_2H_5OCS_2)_4] + (C_2H_5OCS_2)_2 + 5\,H_2O$$

Identical absorption spectra were obtained in tests with both molybdenum(V) and (VI). Molybdenum(III) and (IV) do not react with xanthate. The minimum acid concentration required for the reaction was found to be 0.03*M* and the complex remains stable at acid concentrations up to 4.8*M*. Further confirmation of the reducing character of xanthate ions during complex formation is evident from the fact that solid molybdenum(VI) xanthate complexes cannot be prepared.[70]

Nickel

The yellowish-brown nickel(II) ethyl xanthate complex can be extracted into carbon tetrachloride, chloroform and other non-polar solvents at ~ pH 4–7.[18] Nickel has been recovered from zinc solutions by extraction of the complex into amyl acetate or methyl isobutyl ketone at pH 5.8.[29] It has been determined in manganese ores and manganese-containing slags after xanthate–chloroform extraction of heavy metals, including nickel, from a hydrochloric acid medium.[28] Nickel as the ammine (and iron as the tartrate) is stripped from the extract with an ammoniacal tartrate solution and subsequently determined in the aqueous layer. Chloroform extraction of the xanthate complex has also been used for the determination of xanthate.[71] The xanthate in the extract is titrated with mercury(II) acetate solution in the presence of diphenylcarbazone as indicator.

Rao and Singh[72] found that nickel is almost completely extracted into ethyl acetate at pH 5–9 in the presence of potassium chloride or sodium formate as salting-out agents. The extract can be used for the spectrophotometric determination of 0.05–5 mg of nickel at 435–480 nm. Manganese, aluminium, zinc, cadmium, chromate, molybdate and tungstate do not interfere. Copper(II) can be masked with thiourea before extraction. Later Rao and Singh[31] used this procedure for the simultaneous extraction and spectrophotometric determination of nickel and cobalt in ores and alloys. A similar procedure[20] involving extraction of the nickel xanthate–pyridine adduct into a 4:1 mixture of ethyl acetate and pyridine was found to be less sensitive. This procedure was applied to the separation of nickel and mixtures of other xanthates by column chromatography.[21]

It has been shown that nickel ethyl xanthate is almost completely extracted into chloroform, in three extractions, from 0.1*M* hydrochloric acid initially containing 500 μg of nickel.[12] The complex is partially extracted from 0.5–6*M* hydrochloric acid. Solubility studies[24] and studies of the decomposition of xanthate solutions in the presence of nickel[36] show that it combines with ethyl xanthate in a 1:2 ratio. The formula of the complex is $Ni(EX)_2$.[6]

Palladium

Recently, a method for the extraction and spectrophotometric determination of mg-amounts of palladium with potassium benzyl xanthate has been reported.[73] The yellow palladium(II) complex is completely extracted into chloroform (in a single extraction) at pH 2, followed by spectrophotometric measurement of the absorbance of the extract at 460 nm. Extraction is complete in the pH range 1–7 and Beer's law is obeyed over the palladium(II) concentration range 0.95–4.73 mg/25 ml of chloroform. The chloroform solution of the complex is stable for several days. Interference from iron(III) and lead(II) can be eliminated by complexation with ammonium hydrogen fluoride and sodium acetate, respectively. Nickel, cobalt(II) and cerium(III) can be masked with EDTA. Mercury(II) and cadmium, in 25-fold amounts, interfere by forming insoluble white complexes which remain in the chloroform layer. Bismuth and copper(II) are co-extracted and interfere because of the yellow colour of their complexes. Rhodium(III), ruthenium(III) and platinum(IV), in 2-fold amounts, do not interfere. Interference from osmium(VIII) can be eliminated by its preliminary extraction into chloroform in the presence of hexamethylenetetramine and EDTA. Citrate, tartrate, fluoride, oxalate and EDTA, in 50-fold amounts, do not interfere. Vanadate and molybdate interfere by preventing formation of the palladium complex.

The same investigators also studied the chloroform extraction of palladium with potassium butyl xanthate.[74] Beer's law is obeyed, at 460 nm, over the palladium concentration range 8–50 mg/100 ml of chloroform. Extraction is quantitative over the same pH range but the optimum pH for rapid extraction is 2. All the interfering ions mentioned above also interfere in this method. Interference from iron(III), lead, cobalt(II), nickel, cerium(III) and osmium(VIII) can also be eliminated as described above.

In a recent method for molybdenum in ferromolybdenum and other complex materials,[62] based on its separation by xanthate–chloroform extraction, it was reported that palladium(II) is completely extracted as the ethyl xanthate complex under the conditions (1*M* hydrochloric acid) used for the extraction of molybdenum. More recent studies have shown that the yellow complex can be completely extracted into chloroform, in three extractions, from 0.1–10*M* hydrochloric acid.[12] The formula of the complex is reported to be $Pd(EX)_2$.[6]

Platinum

The extraction of platinum ethyl xanthate has not been reported previously. However, studies of the reaction of platinum with xanthate have shown that it forms a yellow compound with the formula $Pt(EX)_2$, in which platinum is present in the bivalent state.[75,76]

Recent studies by the author have shown that a yellow complex is partially extracted into chloroform from 0.1–10*M* hydrochloric acid containing 500 μg of platinum(IV).[12] The degree of extraction decreases with increasing acid concentration. Presumably platinum(IV) is reduced by xanthate and reacts in the bivalent state. The probability of platinum(IV) co-ordinating with four ethyl xanthate ions is remote.

Rhenium

References pertaining to the formation or extraction of a rhenium xanthate complex have not been found in the literature. Although solvent extraction of molybdenum xanthate from acid media has been employed for its separation from rhenium before the determination of either rhenium or molybdenum (see molybdenum), recent studies by the author have shown that rhenium is slightly extracted (5% in three extractions), presumably as a colourless ethyl xanthate complex, into chloroform from ~4*M* hydrochloric acid, and appreciably extracted (80%) from the 10*M* acid initially containing 500 μg of rhenium (VII).[12] Possibly complete extraction and separation from molybdenum can be obtained from concentrated hydrochloric acid. The oxidation state of rhenium in the complex is not known.

Selenium

The extraction of selenium has not been reported in earlier reviews of the solvent extraction of metal xanthates. However, it has been reported that selenium is co-extracted during the separation of molybdenum from rhenium by extraction of molybdenum ethyl xanthate into a mixture of carbon tetrachloride and benzene from a dilute hydrochloric acid medium.[55] Recent work by the author, involving the separation of molybdenum from tungsten, has also shown that selenium, initially present as selenium(IV), is completely co-extracted into chloroform from ~1.5*M* hydrochloric acid.[58] More recent studies have shown that a colourless complex is completely extracted into chloroform, in three extractions, from 0.1–10*M* hydrochloric acid containing 500 μg of selenium(IV).[12] The formula of the complex is reported to be $Se(EX)_2$, in which selenium is present in the bivalent state.[6] Presumably xanthate reduces selenium(IV) to selenium(II) and it is the latter that reacts during complex formation.

Silver

According to Pilipenko and Ulko[18] the yellow silver(I) ethyl xanthate complex is not extracted into carbon tetrachloride, chloroform or other non-polar solvents at pH ~ 4–9. However, it has been shown recently that silver is appreciably extracted into chloroform (90–92% in three extractions) from 2–3*M* hydrochloric acid initially containing 500 μg of the element.[12] The complex is not extracted at acid concentrations greater than 3*M*. At acid concentrations below 2*M*, the degree of extraction decreases because of the formation of insoluble silver chloride. Probably more complete extraction of the relatively insoluble complex can be obtained from 2–3*M* hydrochloric acid if larger volumes of chloroform are used. Also it would probably be preferable to extract from a sulphuric acid medium.

Tellurium

The extraction of a mahogany-red tellurium ethyl xanthate complex into diethyl ether in the presence of thiourea was reported almost 50 years ago.[77]

Recently, the author found that like selenium, tellurium(IV) is completely extracted into chloroform from ~ 1.5*M* hydrochloric acid.[58] More recent work has shown that it is completely, or almost completely, extracted into chloroform (97–100% in three extractions) from 0.1–10*M* hydrochloric acid containing 500 μg of tellurium(IV).[12] The formula of the complex is reported to be $Te(EX)_2$,[6] which suggests that tellurium(IV) is reduced to tellurium(II) by xanthate during complex formation, similarly to selenium.

Technetium

Jasim *et al.*[78] found that technetium(IV) or (VII) forms a purple-red ethyl xanthate complex that can be extracted into chloroform or carbon tetrachloride from ~ 1*M* hydrochloric or nitric acid. They used this extraction procedure for the separation of technetium from rhenium on the ultramicro scale.[79] Later, Kiba *et al.*[80] investigated the factors affecting the extraction and separation from rhenium more fully and found that, in the presence of an excess of xanthate, technetium(VII) can be completely, or almost completely (99%), extracted into carbon tetrachloride from solutions 0.1–2*M* in sulphuric, hydrochloric, perchloric or nitric acids, and at pH values up to ~ 2. They found that the best solvents are carbon tetrachloride, chloroform, 1,1,1-trichloroethane, xylene and di-isopropyl ether. Tetrachloroethylene, cyclohexane, amyl acetate, n-hexane, methyl isopropyl ketone and dichloromethane do not extract the complex. Vanadium(V), iron(III), cobalt(II), nickel, copper(II), molybdenum(VI) and uranium(VI) are partially co-extracted under the same conditions. Rhenium(VII) (25 mg) does not interfere with the extraction.

Thallium

The extraction of thallium(I) ethyl xanthate into chloroform from weakly acidic media has been investigated and the extracted species was found to be a 1:1 complex.[81] In later work,[82] a number of xanthates and a variety of solvents were examined. Polar solvents were found to be more efficient extractants than non-polar solvents. This was explained by assuming that the thallium(I) ion is co-ordinatively unsaturated, and that co-ordination sites open after chelation are occupied by water molecules. Because the relative ability of the solvent molecules to replace the water molecules will influence the degree of extraction, more polar solvents will co-ordinate more readily with the chelate and thus result in increased extraction.

Recent studies have shown that a colourless thallium(I) and a yellow thallium(III) ethyl xanthate complex can be partially extracted into chloroform (~ 8 and 50%, respectively, in three extractions) from 0.1*M* hydrochloric acid containing 500 μg of thallium(I) or (III).[12] The degree of extraction of thallium(I) decreases with increasing hydrochloric acid concentration, while that of thallium(III) first decreases, then increases, from ~ 4–6*M* hydrochloric acid, probably because of the extraction of its chloro-complex. The thallium(III) complex is more soluble in di-isopropyl ether than chloroform. The formulae of the complexes are reported to be TlEX and $Tl(EX)_3$.[6]

Tin

It has been reported that yellow tin(II) and tin(IV) ethyl xanthate complexes are extracted into carbon tetrachloride, chloroform and other non-polar solvents from a weakly acid medium (pH ~ 4).[18] Work by the author has shown that tin(IV) is partly extracted into chloroform (~ 75% in three extractions) from 0.1*M* hydrochloric acid containing 500 μg of tin, and that the degree of extraction decreases with increasing hydrochloric acid concentration.[12] Probably quantitative extraction can be obtained at pH values > 1.

Studies of the decomposition of ethyl xanthate solutions in the presence of tin have shown that the composition of the complex corresponds to the formula $Sn(EX)_2$,[36] which suggests that tin(IV) is reduced by xanthate during complex formation.

Uranium

In early work it was reported that the orange-red uranyl ethyl xanthate complex is both extractable[56] and non-extractable by chloroform and other non-polar solvents.[18] Zingaro[83] found that the complex formed in neutral or weakly acidic media is completely insoluble in chloroform and benzene but readily soluble in polar solvents such as alcohols, ethers and ketones. Spectrophotometric studies showed that it is a 1:2 complex.

Extraction of the ethyl xanthate complex into methyl isobutyl ketone at pH 3 has been used for the separation of uranium from thorium.[84] Tests with other alkyl xanthates showed that ethyl, isopropyl, n-hexyl and cyclohexyl xanthates give the best separation, and that dibutyl cellosolve and dibutyl carbitol are the best solvents. The complex has also been extracted into cyclohexanone from neutral solutions.[85] Only trace amounts of uranium(VI) are extracted into chloroform from 0.1–10*M* hydrochloric acid.[12]

Vanadium

The yellow vanadium ethyl xanthate complex can be extracted into chloroform,[56] carbon tetrachloride and other non-polar solvents from a weakly acidic medium.[18] Extraction of the complex has been used for the determination of vanadium in steel after the removal of iron and nickel by electrolysis with a mercury cathode.[61] Vanadium and molybdenum are simultaneously extracted into chloroform from a dilute acid medium and vanadium is subsequently determined by spectrophotometric measurement of the absorbance of the extract at 375 nm.

Recently, it has been shown that vanadium is partially extracted into chloroform (~ 64% in three extractions) from 0.1*M* hydrochloric acid containing

500 μg of vanadium(V).[12] The degree of extraction decreases with increasing acid concentration. Vanadium is not extracted from ~5–10*M* hydrochloric acid.

The formula of the ethyl xanthate complex has not been reported but an n-butyl xanthate compound with the formula $VO(nBuX)_2$ has been prepared and studied.[6] This suggests that vanadium(V) is reduced to vanadium(IV) by xanthate during complex formation.

Zinc

Pilipenko and Ulko[18] have reported that the colourless zinc ethyl xanthate complex can be extracted into carbon tetrachloride, chloroform and other nonpolar solvents from a weakly acid medium (pH ~ 4–7). Hayashi *et al.*[86] investigated the effects of pH, ionic strength and xanthate concentration on the extraction and found that, although it is not complete, optimum extraction occurs at pH 4.5–7.5. The complex is stable in chloroform, and the molar absorptivity is $2.03 \times 10^3\, l\cdot mole^{-1}\cdot mm^{-1}$ at 300 nm, the wavelength of maximum absorption. Zinc and ethyl xanthate were found to combine in a 1:2 ratio. The complex is not extracted into chloroform from 0.1–10*M* hydrochloric acid.[12]

Zinc benzyl xanthate can be completely extracted into chloroform, at pH 1.9–5.2, in the presence of a 100–500-fold excess of reagent.[23]

Although it has been claimed that zinc forms a 1:1 ethyl xanthate complex,[25,26,40] it is generally considered that a 1:2 complex with the formula $Zn(EX)_2$ is formed.[6,7]

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AQUOMOLYBDENUM(III) CHLORIDE AS A REDUCING TITRANT

A POTENTIOMETRIC STUDY

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Summary—The use of aquomolybdenum(III) chloride as a reducing agent for the direct potentiometric titration of Ce(IV), Cr(VI), Fe(III), V(V), Mo(VI), U(VI) and H_2O_2 is described. The variation of the formal redox potentials of Mo(V)/Mo(IV) and Mo(IV)/Mo(III) in varying concentrations of hydrochloric, phosphoric and acetic acids is investigated. Aquomolybdenum(III) chloride is found to be a better reducing titrant than chloromolybdate(III) and gives better breaks in the titration curves. In the titration of molybdenum(VI) in 3*M* HCl the titration curve shows three jumps, corresponding to the reductions of Mo(VI) to Mo(V), and Mo(V) to Mo(IV) *via* an apparently intermediate oxidation state which presumably corresponds to a dimeric mixed-valence species. The aquomolybdenum(III) complex ion is a better reducing titrant than chloromolybdate(III) and has a wider applicability.

In an earlier communication[1] it was shown that green molybdenum(III) solutions contain cationic species and the orange-red solutions of molybdenum(III) contain anionic species.[2] A photometric study of the oxidation of these two species gave indications that the course of the reaction depends on the starting species of molybdenum(III), the nature of the oxidant, and the nature and concentration of the acid used. Of the two species, the cationic aquomolybdenum(III) chloride (green form) is more susceptible to aerial oxidation and more reactive.[3] Chloromolybdate(III) solution (obtained by reduction of molybdate in aqueous media of high hydrochloric acid concentration) has been reported to be a good reducing agent for titration of the common oxidizing agents.[4,5] The end-points of the titrations were determined potentiometrically. The susceptibility of these chloromolybdate(III) solutions to aerial oxidation varies with the concentration of the acid medium.

Except for a few observations[6] on the formal potentials of the Mo(V)/Mo(III) system a detailed study of the formal potentials of the Mo(IV)/Mo(III) system and Mo(V)/Mo(IV) system does not appear to have been made. The object of the present investigation is to determine the formal redox potentials of these systems and to investigate the utility of aquomolybdenum(III) chloride as a reducing titrant.

EXPERIMENTAL

Reagents

Molybdenum(III) chloride solutions (green form) can be obtained either by electrolytic reduction using platinum electrodes or by reduction with amalgamated zinc or aluminium. The electrolytic method is cumbersome and time-consuming. Moreover the molybdenum(III) chloride solutions obtained by electrolytic reduction are quickly converted into the orange-red form and are less green than the solutions obtained through reduction with amalgamated zinc or aluminium. This may be at least partly due to the slow conversion of the green form into the orange-red form. Also, according to Wardlaw *et al.*[7] both forms are oxidized by water when in contact with platinum. Hence the molybdenum(III) solutions used in this investigation were all prepared by reduction in a Jones reductor and standardized as already described.[1] In 1–2*M* hydrochloric acid the reagent shows no significant change in colour in 24 hr if kept under carbon dioxide, but after that period is transformed into the orange-red form.

Cerium(IV) sulphate solutions were prepared and standardized as described by Kolthoff and Belcher.[8] Uranium(VI) solutions were prepared from uranyl acetate. Vanadium(V) solutions were prepared from ammonium metavanadate after conversion into sodium vanadate in the usual manner. Other reagents were prepared by dissolving the analytical-reagent grade materials in the proper acid media, and standardized.

Molybdenum(IV) and molybdenum(V) solutions were prepared by appropriate oxidation of molybdenum(III) solutions with Ce(IV) sulphate.

Apparatus

The potential measurements were made with a platinum-wire indicating-electrode in the titration solution, a saturated calomel reference electrode and saturated potassium chloride bridge. All titrations were done with the solution under a carbon dioxide atmosphere.

RESULTS AND DISCUSSION

From the curves in Fig. 1, it is clear that (1) the formal potentials of Mo(IV)/Mo(III) and Mo(V)/Mo(IV) are influenced by the acid concentration, the values increasing with increasing acid concentration, (2) aquomolybdenum(III) chloride is a more powerful reducing agent than chloromolybdate(III) when oxidized to molybdenum(IV), (3) the molybdenum(IV) species obtained by the oxidation of chloromolybdate(III) is a more powerful reducing agent than that obtained by the oxidation of aquomolybdenum(III) chloride. We have also observed that in titrations with aquomolybdenum(III) chloride the potentials become stable faster than when chloromolybdate(III) is used, in the acid media studied.

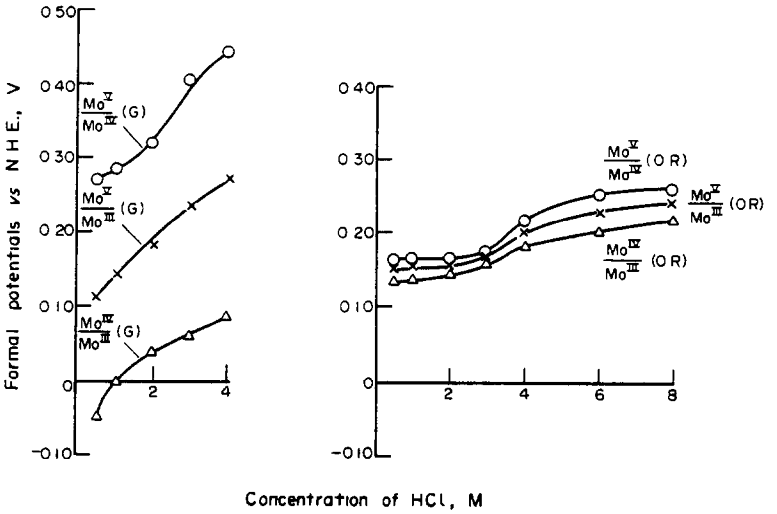

Fig. 1. Formal potentials of Mo(V)/Mo(III), Mo(V)/Mo(IV) and Mo(IV)/Mo(III) in media of varying concentrations of hydrochloric acid, using aquomolybdenum(III) and chloromolybdate(III) solutions as starting materials. A: green aquomolybdenum(III). B: Orange-red chloromolybdate(III).

The complicated nature of these species and their reactivities is also reflected in the results obtained in the photometric study of the oxidation of aquomolybdenum(III) chloride and chloromolybdate(III) by various oxidants.[1] In Fig. 1 the potentials computed[9] for the Mo(V)/Mo(III) system from the potentials of the Mo(IV)/Mo(III) and Mo(V)/Mo(IV) systems are also given. The values of the potentials reported[3,4] for the Mo(V)/Mo(III) system were 0.100 V and 0.300 V in 1.0*M* and 9.0*M* hydrochloric acid media respectively. The formal potentials of these systems in phosphoric and acetic acid media are given in Tables 1 and 2. The potential measurements were made on solutions containing the oxidized and reduced forms prepared in dilute hydrochloric acid medium and diluted with the appropriate acids of required concentration. Hence these solutions contain, in addition to the acids mentioned, hydrochloric

Table 1. Formal potentials (*V*) of molybdenum systems in phosphoric acid medium

Concentration of acid, *M*	Mo(IV)/Mo(III) Green	Mo(IV)/Mo(III) O.R.*	Mo(V)/Mo(IV) Green	Mo(V)/Mo(IV) O.R.	Mo(V)/Mo(III) (computed) Green	Mo(V)/Mo(III) (computed) O.R.
0.17	−0.042	—	0.270	—	0.114	—
0.34	−0.029	—	0.280	—	0.126	—
0.50	—	0.084	—	0.115	—	0.100
0.68	−0.013	—	0.285	—	0.136	—
1.00	−0.002	0.105	0.310	0.134	0.154	0.120
1.35	0.009	—	0.323	—	0.166	—
2.00	—	0.123	—	0.137	—	0.130
2.60	0.016	—	0.333	—	0.175	—
3.90	0.022	0.173	0.348	0.165	0.185	0.169
8.00	—	0.193	—	0.207	—	0.200
12.00	—	0.307	—	0.247	—	0.327

* O.R. = Orange-red

Table 2. Formal potentials (*V*) of molybdenum systems in acetic acid medium

Concentration of acid, *M*	Mo(IV)/Mo(III) Green	Mo(IV)/Mo(III) O.R.	Mo(V)/Mo(IV) Green	Mo(V)/Mo(IV) O.R.	Mo(V)/Mo(III) (computed) Green	Mo(V)/Mo(III) (computed) O.R.
0.495	0.034	0.173	0.664	0.197	0.349	0.185
0.990	0.063	0.163	0.698	0.195	0.381	0.179
1.980	0.082	0.161	0.703	0.198	0.393	0.200
3.96	—	0.193	—	0.208	—	0.201
7.91	—	0.195	—	0.213	—	0.204
11.87	—	0.203	—	0.232	—	0.218

Table 3. Titrations with 0.02*M* aquomolybdenum(III) chloride

Species titrated	[HCl]. *M*	$\Delta E/\Delta V$, *mV*/0.1 *ml* [aquomolybdenum(III) chloride]	Remarks	$\Delta E/\Delta V$, *mV*/0.1 *ml* [chloromolybdate(III) 0.04*M*][4]	Remarks
Ce(IV)	0.5	230	Potentials stable in 5 min	—	—
	1.0	340	Potentials stable in 5 min	—	—
	4.0	—	In >4.0*M* HCl aquomolybdenum(III) chloride is not sufficiently stable	362	—
Cr(VI)	0.5	225	Potentials stable in 5 min	272	—
	1.0	345	Potentials stable in 5 min	—	—
	2.0	320	Stable potentials obtained slowly	388	—
	3.0	250	Potentials first increase, then decrease slowly with time for each addition of the titrant. Stable potentials obtained slowly.	—	—
	4.0	—	—	436	—
Fe(III)	0.1	—	—	39	—
	0.5	30	Potentials stable in 5 min	—	—
	1.0	20	Potentials stable in 5 min	12	Titration in hot medium[4]
	2.0	—	At higher [HCl] stable potentials obtained slowly and the potential jumps are very small	8	
	3.0	—	—	—	
	4.0	—	—	1	
V(V)	0.5	37	Stable potentials obtained quickly at lower acid concentration	—	—
	1.0	80	Stable potentials obtained quickly at lower acid concentration	—	—
	2.0	105	Potentials become stable very slowly, V(V) is reduced to V(IV)	100	—
	3.0	150	—	—	—
	4.0	—	—	192	—
	6.0	—	—	442	—
U(VI)	0.5	—	Potentials not stable even after 30 min	—	Stable potentials not obtained even in 30 min
	1.0	31	Potentials stable within 5–10 min	—	Stable potentials not obtained even in 30 min
	2.0	26	Potentials decrease slowly then stabilize	—	Stable potentials not obtained even in 30 min
	3.0	23	Titration reaction $U(VI) + Mo(III) \rightarrow U(IV) + Mo(V)$	—	Stable potentials not obtained even in 30 min
Mo(VI)	1.0	—	Potentials not stable within 15 min. Mo blue formed at [HCl] <1.0*M*	—	The potentials not stable even after 30 min
	2.0	30	Potentials stable in 5–10 min	—	Mo blue formed at [HCl] <1.0*M*
	3.0	31	Potentials stable in 5–10 min	—	Mo blue formed at [HCl] <1.0*M*
		55		—	Mo blue formed at [HCl] <1.0*M*
		50		—	Mo blue formed at [HCl] <1.0*M*
	4.0	—	—	80	Stable potentials are obtained in 10–15 min
	6.0	—	—	106	The titration is only possible in >4.0*M* acid

Table 3. (*Continued*)

Species titrated	[HCl], M	$\Delta E/\Delta V$, $mV/0.1\ ml$ [aquomolybdenum(III) chloride]	Remarks	$\Delta E/\Delta V$, $mV/0.1\ ml$ [chloromolybdate(III) $0.04M$]^4	Remarks
	8.0	—	—	160	Mo(VI) is reduced to Mo(V) only. No other breaks are observed
H_2O_2	1.0	140	Potentials stable in 5–10 min	75	Stable potentials are obtained in about 10 min
	2.0	—	Potentials not stable even after 30 min	—	The potentials are not stable even after 30 min
	3.0	—	Potentials not stable even after 30 min	—	The potentials are not stable even after 30 min

acid at a concentration of about $0.3M$. The general trend in the formal potentials of these systems with acid strength is similar to that for hydrochloric acid medium. The green solutions of molybdenum(III) obtained in sulphuric acid change rapidly to the orange-red form. Molybdenum(III) solutions are slowly oxidized in $>1.0M$ perchloric acid media.

These formal potentials are in agreement with the earlier observations[3] that molybdenum(III) chloride is a better reducing agent than chloromolybdate(III). Hence it was felt worthwhile to study this reagent as a reducing titrant. The results obtained in titration of common oxidizing agents used in volumetric analysis are summarized in Table 3. Some results for chloromolybdate(III) as reductant are given for comparison.

Titration of Ce(IV) in hydrochloric acid media more concentrated than $2M$ was not attempted owing to the possible oxidation of the medium by the oxidant.[10] In $>4M$ hydrochloric acid media, aquomolybdenum(III) chloride is converted into chloromolybdate(III) rather rapidly.

The results in Table 3 show the following.

(1) The potential break at the end-point is generally at least as steep with aquomolybdenum(III) chloride as with chloromolybdate(III).

(2) Uranium(VI) can be titrated with this new reductant. Uranium(VI) is reduced to uranium(IV) and molybdenum(III) is oxidized to molybdenum(V) in the process. Attempts to titrate uranium(VI) with chloromolybdate(III) failed to give stable potentials and a clear jump at the end-point.

(3) In the titration of molybdenum(VI) with aquomolybdenum(III) chloride in $2M$ hydrochloric acid medium only one clear jump [Mo(VI)–Mo(V)] is observed, while a titration in $3M$ hydrochloric acid medium gives three jumps, one for the reduction Mo(VI)–Mo(V) and two for the reduction Mo(V)–Mo(IV), one of these corresponding to an "intermediate" oxidation state, presumably involving a binuclear Mo(V)–Mo(IV) complex. For the same titration carried out with chloromolybdate(III) in $>4M$ hydrochloric acid medium only one jump, corresponding to Mo(VI)–Mo(V), is observed. At lower acidities no stable potentials are obtained. It may be noted in this connection that earlier workers concluded that this latter titration is possible only at very high acid concentration.[11]

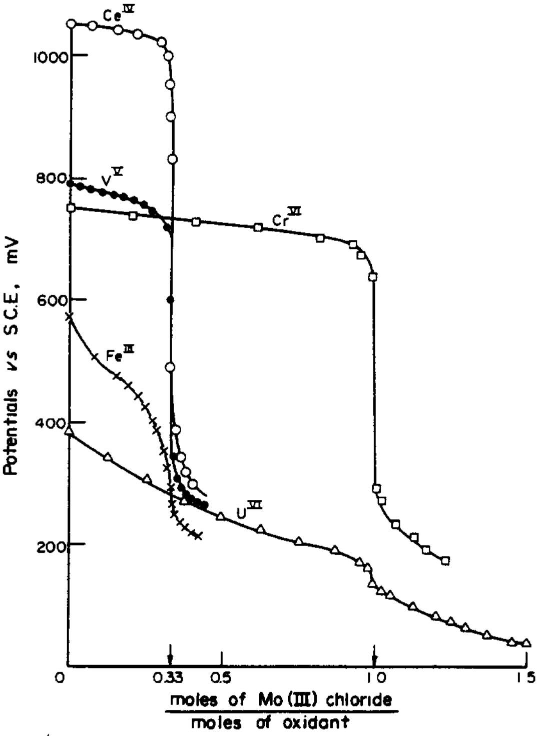

Fig. 2. Potentiometric titration curves. Reduction with aquomolybdenum(III) chloride: (*i*) Ce(IV)—Mo(III) in $1.0M$ hydrochloric acid medium; (*ii*) Cr(VI)—Mo(III) in $1.0M$ hydrochloric acid medium, (*iii*) Fe(III)—Mo(III) in $0.5M$ hydrochloric acid medium; (*iv*) V(V)—Mo(III) in $3.0M$ hydrochloric acid medium; (*v*) U(VI)—Mo(III) in $1.0M$ hydrochloric acid medium.

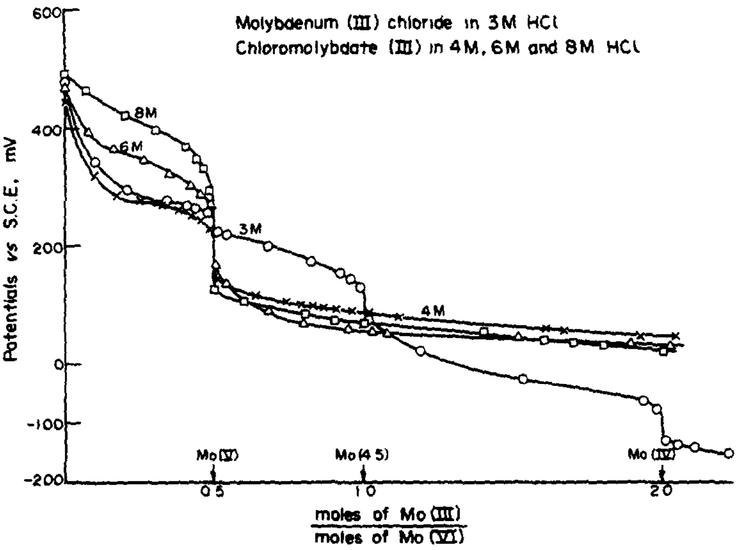

Fig. 3. Potentiometric titration curves for the reduction of molybdenum(VI) with molybdenum

(4) Aquomolybdenum(III) solutions can be used for the reductometric titration of hydrogen peroxide at low acidity.

The recommended concentrations of hydrochloric acid for quantitative titrations with the new reductants are 1.0*M* for Ce(IV), Cr(VI), U(VI) and H_2O_2, 3.0*M* for V(V) and Mo(VI) and 0.5*M* for Fe(III). The errors in these titrations are not more than 0.8%. Representative titration curves are given in Figs. 2–4.

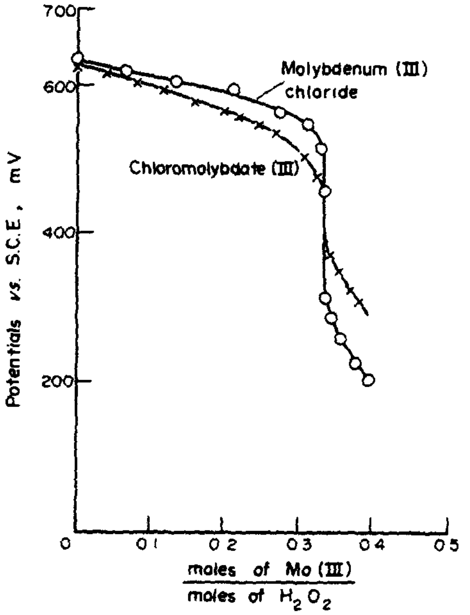

Fig. 4. Titrations of hydrogen peroxide with molybdenum(III).

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USE OF *p*-DIETHYLAMINOPHENYLMERCURIC ACETATE FOR THE DETERMINATION OF THIOL GROUPS IN BIOLOGICAL SAMPLES

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Summary—A simple titrimetric method for the determination of thiol and disulphide groups in biological samples with *p*-diethylaminophenylmercuric acetate as titrant, is suggested. Milligram amounts of cysteine (1–25 mg) are determined with a relative standard error not higher than 1%. The lowest determinable amount of cysteine is 0.1 mg (relative standard deviation 3%). The accuracy and the sensitivity are the same as in amperometric titration with mercuric chloride. The method has been successfully used for the determination of thiol groups in various biological samples.

In a number of studies in biochemistry, physiology, cytology and radiobiology, the thiol groups in proteins taking part in fundamental physiological processes[1–4] are to be determined. In the present paper, the commonest methods for determination of thiol groups are reviewed and the *p*-diethylaminophenylmercuric acetate method for the visual titration of SH-groups[5] is recommended.

For the determination of SH-groups amperometric titration with mercuric chloride is commonly used, with rotating platinum electrodes.[6,7] The main disadvantage is that mercuric chloride, like other inorganic compounds of mercury and silver, has a tendency to form a variety of mixed-ligand complexes containing a thiol group. Because of the technical difficulties mentioned above, a modification has been suggested[8–10] for tracing the effect of radioprotectors on the total concentration of SH-groups in the body tissues: the sample is homogenized in the presence of a substoichiometric amount of mercuric chloride solution and the reaction mixture is then titrated amperometrically with mercuric chloride.

This modification was used to solve a specific problem, that of finding the relative difference in the number of SH-groups in the tissues of an animal subjected to the influence of the protector and in those of a control animal, and was adequate for the purpose. The original method has been considerably simplified. According to our results, the relative standard deviation in analysis of a homogenized spleen by this modified method was 23% (the mean concentration of SH-groups being 1.2–1.5 μmole per 100 mg of tissue), compared with 10% by Kolthoff's method.[6,7]

The most common reagents for thiol groups are monofunctional organomercuric compounds, which react with different thiols strictly in 1:1 proportion.[11–13]

$$RHg^+ + R'S^- \rightarrow RHgSR'$$

The determination is usually carried out titrimetrically with indicators, and is the simplest, quickest and most convenient method.

A comparative study[14–16] of silver nitrate, mercuric nitrate and organomercuric compounds as titrants for thiol groups showed that polyfunctional organomercuric reagents are more selective with respect to SH-groups. An organomercuric cation (RHg^+) forms stepwise complexes with thiol groups to a far less extent than do Hg(II) and Ag(I), which accounts for the more accurate results. The visual titration with organomercuric reagents is as sensitive as the amperometric titration with mercuric compounds and is simple and reliable.[5]

Among organomercuric reagents, *p*-chloromercuribenzoic acid,[17–36] first suggested by Hellerman,[37–39] has become widely accepted; it can be obtained 99% pure. In one study[40] it was recrystallized three times, but in others, unfortunately, no attention was paid to the purity. Aqueous 0.005*M* solutions of *p*-chloromercuribenzoic acid in 0.01*M* sodium hydroxide are known to remain stable for less than a month, and regular standardization is necessary.

There are no reliable data on interferences. Judging by other organomercuric reagents,[5] chlorides in large quantities would be expected to interfere, so titration in physiological saline solution (0.9% NaCl) may yield erroneous results. The end-point is determined visually or spectrophotometrically. In the first case sodium nitroprusside is used as indicator for titrations done at pH 3.2–5.3, but it has low selectivity for thiol groups. Since the titration reaction is not instantaneous a back-titration with cysteine is used.[18,26,27,29]

A spectrophotometric method is based on the increase in absorption at 250–255 nm, when the thiol-compound reacts with *p*-chloromercuribenzoic acid.[41] The method is rather sensitive, and gives reliable results with $10^{-5}M$ concentration of thiol group. It can be used for photometric titration. The optimal pH range for photometric titration was not indicated. The increase in absorbance is measured at 250 nm (pH 7.0) or 255 nm (pH 4.6). The thiol groups of phosphorylase were also titrated photometrically in a more acidic medium at pH 2.3.[42]

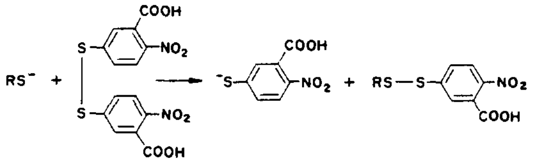
Various authors give different reaction times in their procedures. Since the rate of reaction of an organomercuric cation with different proteins varies, the time of colour development should be sufficient for constant absorbance to be reached.

The method used in the original study is somewhat unclear, and the authors of the papers that followed do not explain how the determination was carried out. Since the molar absorptivity for different mercaptides of *p*-chloromercuribenzoic acid varies, photometric titration is recommended.[4,43] The concentration of thiol groups has been found from a calibration curve[44] or from the molar absorptivity of the mercaptide,[45] but even under the most favourable conditions, the molar absorptivity varies and accurate determinations are difficult to obtain.

Because in photometric titration the same amount of *p*-chloromercuribenzoic acid is added to both the control solution and the active solution, it seems more reasonable to have a number of measuring flasks with equal amounts of protein to which increasing amounts of the organomercuric reagent are added. For each flask the absorbance is then measured, each time with respect to a similar solution containing an equivalent amount of water instead of protein. Titration can be carried out in a suitable vessel or in the cuvette of the spectrophotometer, and the dilution should be taken into consideration. Boyer seems to have used the first method, though he never stated it specifically. His report stating that one measurement of the absorbance is sufficient, once the excess of organomercuric reagent has been found, is open to criticism. In that case it would have been necessary to calculate the concentration of thiol from the molar absorptivity or to plot a calibration graph. Individual amino-acids would have been required and a calibration graph would have to be plotted for each one, since different mercaptides of *p*-chloromercuribenzoic acid have different absorption intensities. Another disadvantage of Boyer's method is that only pure solutions, free from the remnants of homogenized tissues, can be analysed. The different reaction rates of *p*-chloromercuribenzoic acid with thiols may yield low results in determination of the total number of thiol groups. Another point that gives rise to doubts is that for complete binding of thiol groups an excess of *p*-chloromercuribenzoic acid is required.[46] It is for this reason that back-titration of excess of organomercuric reagent is often used. Other organomercuric reagents have been suggested, but they have not found wide application.[47]

Because the titrimetric methods are not sensitive enough, photometric methods with organomercuric reagents have been explored,[47–56] but addition of a thiol only slightly affects the electronic structure of the reagent, and the spectra of the organomercuric reagents and the products are similar.[12,41]

For direct photometric determination of thiol groups 5,5′-dithio-bis(2-nitrobenzoic) acid is used (at pH 7.8–8.0).[57]; it forms a product absorbing in the neighbourhood of 412 nm.



Ellman's reagent is selective for a thiol group and the sensitivity of his method is the same as for photometric titration with *p*-chloromercuribenzoic acid. Ellman recommended measuring the absorbance 2 min after the beginning of the reaction, but in his later works[58,59] the time of measurement varies from 5 to 15 min. The method requires the removal of the remnants of the homogenized material from the solution before the analysis, and also that a correction be made for the absorbance of the excess of reagent.[58] The analysis of proteins which absorb in the region of 412 nm also proves rather difficult. The disadvantage of the method is the lower reactivity, compared to organomercuric reagents.[59]

A simple titrimetric method for thiols of different classes, using *p*-dimethyl- or *p*-diethylaminophenylmercuric acetate as titrant has been suggested.[5] The reagents are synthesized by simple mixing of solutions of mercuric acetate and the alkylaniline. Recrystallization from ethanol gives 100% pure substance. The reaction with thiols in an alkaline medium is almost instantaneous. Diphenylcarbazone is used as indicator (colour change pink → violet). In the determination of 1–50 mg amounts of thiols of different classes the relative standard deviation is 0.1–1.7% in slightly acidic, neutral and alkaline media. For titration of coloured thiols or samples containing sediments, an alkaline solvent, consisting of a saturated solution of sodium acetate in a mixture of benzene and ethanol (2:3) is added to improve end-point detection. The colour change is easily seen in the upper benzene layer.

EXPERIMENTAL

Reagents

p-Diethylaminophenylmercuric acetate was synthesized[60] and recrystallized from hot ethanol. Solutions were prepared by dissolving a precisely weighed amount in the minimal amount of warm ethanol, and then diluting with water. The titre stays constant for at least two months if the solution is kept in a dark bottle at room temperature. The solid remains stable for not less than two years, if stored in darkness and at room temperature.

A 0.2% solution of diphenylcarbazone in ethanol was used as indicator.

An 8*M* solution of urea was prepared in 1*M* ammonium acetate buffer medium at pH 8.5–10.0. In order to prevent the catalytic effect of metallic ions on oxidation of thiol groups, $10^{-6}M$ EDTA was added.

Test samples included cystine and cysteine hydrochloride monohydrate, lyophilized human serum albumin, with not less than 95% of albumin, lyophilized ox albumin, powdered egg albumin, crystallized pancreatic ribonuclease, crystalline trypsin, papain, a suspension of crystalline aldolase in 2.0*M* ammonium sulphate. Chromatographically pure reduced glutathione was used for preparing a standard solution.

Spleens from sacrificed mongrel white mice were quickly cut out and homogenized by hand in a glass homogenizer, in buffer solution for the determination of SH-groups and in 8*M* urea for the determination of disulphide bonds.

Solutions of cysteine (10^{-2}–$10^{-4}M$) in distilled water were prepared on the day of use. Weighed portions of cystine and proteins were dissolved in 8*M* urea at pH 8.5–10.0. A saturated solution of chemically pure sodium sulphite was prepared every 30 min. For the two-phase titrations, 10 g of sodium acetate trihydrate were dissolved in 400 ml of benzene and 600 ml of ethanol.

Gluten was obtained from first-grade flour by a standard method and frozen instantly. Later it was freeze-dried. The dry gluten was ground in a porcelain mortar into a fine powder containing 87% protein and 4% moisture. Gluten and egg protein were dispersed in 8*M* urea.

Ammonium acetate buffer solution was prepared from 1*M* acetic acid and ammonia solutions.

Procedures

Thiol-groups. Place 5–15 ml of a solution of 0.4–20 mg of substance in water or 8*M* urea in a 50-ml conical flask, add 0.5–1 ml of buffer solution, 5–15 ml of the benzene–ethanol solvent and 1–3 drops of indicator, and titrate with aqueous ethanolic solution of *p*-diethylaminophenylmercuric acetate until a permanent violet colour appears in the benzene layer.

Total number of thiol groups and disulphide bonds. Disperse an accurately weighed portion of raw egg protein or dry powdered gluten (lyophilized) in 8*M* urea at pH 9.0–10.0 on a water-bath at 35–40°C and add 0.2 ml of saturated sodium sulphite solution. After 2 min add 2–10 ml of benzene–alcohol solvent and titrate as above.

Thiol-groups in spleen. Add 2–10 ml of benzene–alcohol solvent and 1–3 drops of indicator to the homogenate, and titrate as above.

Amperometric determination of SH-groups. Place the sample solution, containing 0.08–15 mg of substance in water or in 8*M* urea, in a titration cell, add 15 ml of ammonium acetate buffer (pH 7.0–7.5) as background electrolyte, and titrate amperometrically with *p*-diethylaminophenylmercuric acetate solution 20–40 times as concentrated as the sample, at 0.7 V, using a wax-impregnated rotating graphite electrode and a saturated calomel reference electrode.

RESULTS AND DISCUSSION

The pH range for determining cysteine varies with the concentration of the titrant (Table 1). The optimal reagent concentration was found to be 5×10^{-3}–$2 \times 10^{-4}M$.

The lowest determinable amount of cysteine depends on the volume of $2 \times 10^{-3}M$ titrant that will give a definite change in the colour of 1–3 drops of the indicator.

The visual titration is as accurate and sensitive as the amperometric method.[61,62] Cysteine (1–25 mg) in the presence of cystine can be determined with a relative standard deviation of less than 1%. The lowest determinable amount is 0.1 mg (relative standard deviation 3%). Cystine (1–50 mg) was determined with a relative standard deviation of 0.1–3.5%. The results are presented in Table 2.

Table 1. The pH interval for cysteine titration by *p*-diethylaminophenylmercuric acetate, for different concentrations of the titrant

Titrant concentration, *M*	pH interval
1×10^{-2}	7.5–11.0
5×10^{-3}	8.0–11.0
1×10^{-3}	9.0–11.0
5×10^{-4}	9.5–11.0

The presence of disulphides, organic sulphides and sodium sulphite (0.5 ml of saturated solution) does not interfere. The effect of other foreign ions was studied earlier.[5] When cysteine hydrochloride was titrated, the indicator colour change at the equivalence point was more pronounced.

The methods used for determining disulphide bonds usually amount to determining the SH-groups after the disulphide bonds have been reduced.[15,63] The reduction of cystine by sodium sulphite, which is reversible to a certain extent, has been studied in great detail.[63] The excess required not only for reducing disulphide bonds but also for preventing thiol groups from oxidizing, was found.

The method proposed here can be used for determining cysteine in the presence of cystine as well as for determining their total amount after the cystine has been reduced.

Cysteine reacts rather slowly with aromatic mercury compounds, which makes it somewhat difficult to find the equivalence point. This fact is usually overlooked when thiol groups are directly titrated with *p*-chloromercuribenzoic acid or other organomercuric reagents. In the case of *p*-diethylaminophenylmercuric

Table 2. Titrimetric determination of cysteine and cystine with *p*-diethylaminophenylmercuric acetate

Substance	Mean found,* *mg*	Relative std. devn. %
Cysteine	24.22	0.07
	6.05	0.3
	2.42	0
	0.76	0
	0.61	0
	0.31	3.0
Cystine	46.46	0.1
	23.23	0.3
	5.82	0.7
	2.33	2.2
	1.62	3.5

* Five determinations.

Table 3. Determination of thiol groups and disulphide bonds with p-diethylaminophenylmercuric acetate (average number of groups per molecule)

Sample	Found by visual titration (this method)		Literature data		Literature method	Reference
	SH	SS	SH	SS		
Ox albumin	1.4	15.2	1.4	15.4	Titrimetric, $AgNO_3$, 8*M* urea	65
Human serum albumin	2.8	15.1	1.0	17.0	Titrimetric, p-CMB-acid,† decyl sulphate	66
Egg albumin	2.6	3.4	2.7	—	Ellman's method, dodecyl sulphate	67
Ribonuclease	—	4.0	—	4.0	Titrimetric, $HgCl_2$, p-CMB acid, 8*M* urea	68
Trypsin	—	3.2	—	3.0	—	69
Papain	3.0	—	3.0	—	Amperometric, CH_3HgI, 8*M* urea	70, 71
Aldolase	20	—	7 and 28	—	Boyer's method, p-CMB acid, 8*M* urea	41
Glutathione reduced	0.81*					
Cysteine	0.72*					

* Similar results were obtained by a control iodometric method.

† p-Chloromercuribenzoic acid.

acetate the reaction also slows down near the equivalence point, when the concentrations of the reacting substances decrease. Therefore, near the equivalence point the flask should be shaken briskly for some time between additions of titrant. Titration in the presence of the benzene–alcohol solvent overcomes this disadvantage. The amount of mixed solvent is sufficient to give a separate benzene layer when shaking is stopped. In determining cystine after its reduction, an excess of p-diethylaminophenylmercuric acetate should be added, and the surplus back-titrated with cysteine under the same conditions. The results from back-titration do not differ from those of direct titration.

We have used the proposed method for determining SH- and disulphide groups in certain amino-acids, proteins and in some biological samples. The results obtained were checked by the method of standard additions. Reduced glutathione was used as a standard solution. The number of thiol groups in glutathione was checked iodometrically.[64] The experimental results and those found in the literature are presented in Table 3.

The number of thiol groups in certain proteins was determined by amperometric titration with p-diethylaminophenylmercuric acetate. Conditions for the titration of thiols were found earlier.[5] In the present study, the optimal pH range for proteins was found to be 7.0–7.5 (ammonium acetate supporting electrolyte). Titration at pH values outside this range gives erroneous and irreproducible results. Results are given in Table 3. The amperometric method cannot be recommended in practice, since it has no advantages over the much simpler visual titration.

For determination of disulphide bonds in biological samples dispersion was effected by shaking with 8*M*

Table 4 Amount of SH-groups in the spleen of mongrel white mice according to results obtained by different methods of determination

	Visual titration with p-diethylaminophenylmercuric acetate	Amperometric titration by mercuric chloride	
		Kolthoff's method	Graevskii's modification
Mean SH content, μmole/100 mg of tissue	1.48	1.24	1.39
Number of determinations	112	111	15
Relative standard deviation, %	8.8	10.2	23.0

urea at pH 9.0–10.0 on an automatic mixer. Urea not only evenly disperses protein, but also encourages dissolution of S–S bonds.[73]

No free SH-groups were found in gluten protein. The content of disulphide sulphur was 0.56% of the total amount of protein. In raw egg protein the content of thiol sulphur was found to be 0.0149 ± 0.0006% and that of disulphide sulphur 0.0522 ± 0.0008%. In a comparative visual titration with *p*-diethylaminophenylmercuric acetate of SH-groups in 10 μmole of cysteine and an amperometric titration with mercuric chloride the relative standard deviations were 0–3.2% and 4.6–8.9% respectively.* Results for thiol groups in the spleens of mice, by both methods, are given in Table 4.

In 112 determinations, 1.48 μmole of SH-group were found, on average, per 100 mg of spleen, by visual titration with *p*-diethylaminophenylmercuric acetate, relative standard deviation 8.8%. In 15 amperometric titrations with mercuric chloride, the mean number of SH-groups per 100 mg of spleen was 1.24 μmole, relative standard deviation 10.2%. In the amperometric titration by the Graevskii modification,[8,9] the relative standard deviation was 23.0%.

The results prove that the visual titrimetric determination of SH-groups is somewhat more accurate than Kolthoff's amperometric titration with mercuric chloride, and greatly superior to the modification of this method.

It should be pointed out that not all organomercuric reagents react in a similar way with protein thiol groups. Thus, for example, the error of the titrimetric determination of cysteine with *p*-dimethylaminophenylmercuric acetate is higher than that with the *p*-diethyl analogue even though the reagents differ only in the substituent on the nitrogen atom.

Therefore, *p*-dimethylaminophenylmercuric acetate should not be used for determining cysteine though it is successfully used for determining thiols of other classes.

When the number of thiol groups is small, an indirect extractive photometric method seems to be the most effective for cysteine.[72] It is based on reacting a thiol with *p*-diethyl- or *p*-dimethylaminophenylmercuric acetate and subsequent extractive photometric determination of the excess of organomercuric reagent, by means of diphenylcarbazone in benzene. Amounts of 5–120 μg of cysteine ($6 \times 10^{-6}M$ and higher) are determinable with a relative standard deviation of 2–6%. This method is slightly more accurate that Ellman's photometric method using 5,5'-dithiobis(2-nitrobenzoic) acid.

Urea, sulphate, nitrate, phophate, 10-fold amounts of disulphide and 300-fold amounts of organic sulphides do not interfere. As in this case excess of the organomercuric reagent is added, all thiol groups have a chance of reacting. Much less time is required for the analysis than for Boyer's photometric titration. The extractive photometric method also makes it possible to do the determination with turbid homogenates and in the presence of coloured proteins, because the absorbance of the benzene extract is measured, which excludes substances insoluble in benzene. The extraction of other coloured substances into the benzene layer is of no consequence, since the absorbance is measured against a blank solution containing all the reactants except the organomercuric reagent.

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ON THE COPPER(II)–EDTA–PAR SYSTEM FOR VISUAL AND PHOTOMETRIC END-POINT DETECTION IN IRON(III)–EDTA TITRATIONS

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Summary—The copper(II)–EDTA–PAR system is proposed as indicator for direct EDTA titration of 0.2–20 mg of iron(III) in acetic acid medium. The precision and accuracy have been evaluated by spectrophotometric titration. Microtitrations determine down to 10 μg of iron. A logarithmic concentration diagram has been constructed to present the complex equilibria involved. In an interference study the masking agent ammonium fluoride was found to improve the end-point detection. The method has been applied successfully to practical standard samples and compares favourably with other EDTA titrations of iron.

The direct complexometric titration of iron(III) in routine analysis is a problem not yet satisfactorily resolved. The formation of the iron(III)–EDTA complex is slow at room temperature and heating is advisable, but not above 40–50° or hydrolysis may occur. Moreover, the end-point is not sharp when an indicator for iron(III) is used. Many procedures for the titration have been reported, some quite recently,[1–7] including an excellent review of the indicators available[6] in which 57 compounds were investigated. Undoubtedly, sulphosalicylic acid is among the most widely used,[6–12] but its colour transition depends greatly on the pH of the solution, and the colour disappears gradually and a little before the equivalence point. In addition, a large excess of the indicator is needed (this is generally the case for phenolic indicators in this titration). For these reasons, the problem seemed to us to be worth further investigation.

In our previous work[13] it was shown that the system Cu(II)–EDTA–PAR can be successfully used for direct EDTA titration of barium. The precision of the end-point prompted us to try the same reaction for titration of iron(III).

Iwamoto[8,14] used Cu(II)–EDTA–PAN and Cu(II)–EDTA–PAR system as indicators in his work on tartrate as an auxiliary complexing agent and buffer in the chelatometric determination of iron(III) and aluminium, but Momoki and Sekino[15] found the Cu(II)–EDTA–PAN end-point sluggish in EDTA titration of iron(III) in acetate buffer medium, because of hydrolysis. For the present study PAR was chosen because of its highly sensitive colour reaction with copper(II).

THEORY

The replacement equilibrium (omitting charges for simplicity) is

$$\mathrm{Fe} + \mathrm{CuY} + \mathrm{In} \rightleftharpoons \mathrm{FeY} + \mathrm{CuIn} \qquad (1)$$

It is possible to find the optimum conditions for this reaction provided the formation constants of the various species are available. Ringbom's data[16] for $K^{\mathrm{H}}_{\mathrm{MHL}}$ and K_{ML} for iron(III)–EDTA and copper(II)–EDTA were used; the conditional stability constant of copper(II)–PAR, $\log K'_{\mathrm{CuIn}} = 6.4$ at pH 3, was calculated from the data in our previous work.[17] These values were used to establish the following parameters.

(*a*) $\mathrm{pCu}_{\mathrm{trans}}$, needed to calculate $\Delta\mathrm{pFe}'$, which in turn is included in the equation for the titration error:[16,18]

$$\text{Relative error } \% = (10^{\Delta\mathrm{pM}'} - 10^{-\Delta\mathrm{pM}'})/(C_{\mathrm{M}}K'_{\mathrm{MY}})^{1/2} \qquad (2)$$

(*b*) The best Cu(II)–EDTA concentration according to the equation:[16,19]

$$\mathrm{pFe}' = \mathrm{pCu}_{\mathrm{trans}} + \log K'_{\mathrm{FeY}}/K'_{\mathrm{CuY}} + \log\,[\mathrm{CuY}]'/[\mathrm{FeY}]' \qquad (3)$$

where the side-reaction coefficient $\log \alpha_{\mathrm{Fe(Ac^-)}} = 0.8$ at pH 3 and $[\mathrm{Ac^-}] = 5 \times 10^{-2}M$, $\log \alpha_{\mathrm{Fe(OH)}} = 0.4$, $\log \alpha_{\mathrm{CuY(H)}} = 0.3$ and $\log \alpha_{\mathrm{Y(H)}} = 10.8$ were taken into account. Hence $\log K'_{\mathrm{FeY}} = 13.4$ and $\log K'_{\mathrm{CuY}} = 8.3$ were obtained and used in further calculations.

Accordingly, when 10^{-2} and $10^{-3}M$ iron(III) solutions are titrated, suitable values of $[\mathrm{CuY}]'$ are $10^{-5.8}$ and $10^{-6}M$ respectively. For practical application a concentration about ten times as great, *i.e.*, $10^{-5}M$ was always used. Thus, in titration of $0.01M$ iron(III) $\Delta\mathrm{pFe}'$ was 0.8 and the titration error only 0.001%, whereas for $10^{-3}M$ iron(III) $\Delta\mathrm{pFe}'$ was 1.3 and the error 0.01%.

To represent more clearly the rather complicated ionic equilibria in this study and offer an easy way of surveying the conditions of the complexometric titration in question, we constructed the logarithmic diagram shown in Fig. 1. Construction details will not be given, since they are described clearly elsewhere.[18,20–24]

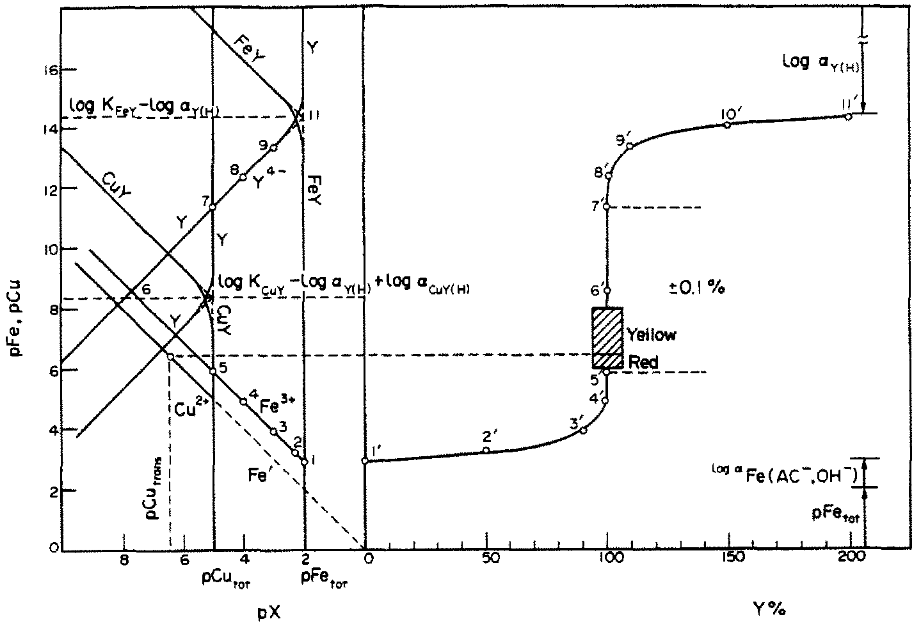

Fig. 1. Logarithmic-concentration diagram for the system Fe^{3+} + Cu^{2+} + EDTA and PAR as metallochromic indicator for Cu^{2+}. $C_{Fe} = 10^{-2}M$; $C_{CuY} = 10^{-5}M$; log $K_{FeY'} = 14.3$; log $K_{CuY'}$ + log $\alpha_{CuY(H)} = 8.3$; log $\alpha_{Fe(Ac^-, OH^-)} = 0.9$.

The diagram allows us to read the points needed to construct the titration curve and to evaluate directly the accuracy of the titration. The large break corresponding to ±0.1% error is obviously due to the high stability of the iron(III)–EDTA complex (log $K_{FeY} = 25.1$). Taking into account the sensitivity of the human eye, the indicator interval (shown only approximately) is asymmetric about $pCu_{trans} = 6.4$ in a direction favourable for titration. It is also evident that the transition interval of the indicator PAR coincides satisfactorily with the 0.1% error section of the titration curve, the equivalence point of the system Cu^{2+}–Y^{4-} being near the transition point of the colour change interval.

These considerations indicate convincingly that accurate results should be expected on a thermodynamic basis. However, in view of the tendency of iron(III) to form kinetically inert complexes, the reaction has been examined to prove experimentally the validity of these conclusions. Spectrophotometric titrations were performed to evaluate the precision of equivalence point detection[16,25] and the sensitivity and selectivity of the method.

EXPERIMENTAL

Reagents

Iron(III) chloride solution, 0.1*M*. Prepared from ferric chloride and standardized gravimetrically via ferric oxide. A 0.01*M* solution was prepared by dilution and checked potentiometrically with EDTA, a bright platinum indicator electrode being used.[8,10] Solutions of lower concentration were prepared by further dilution.

EDTA, 0.01 *and* 0.02*M solutions*. Prepared by dissolving the free acid.[8]

Copper(II)–EDTA solution, $10^{-3}M$. Prepared by dissolving the Koch-Light reagent and checked for free copper(II).

4-(2-Pyridylazo)resorcinol (*PAR*). A $1.00 \times 10^{-4}M$ aqueous solution was used for spectrophotometric titrations, and an aqueous 0.05% solution for visual titrations.

Acetic acid, 0.5*M and ammonia solution* were used for pH adjustment.

Ammonium fluoride, p.a. 0.1*M solution.*

Ammonium acetate, p.a., 10% *solution.*

All other inorganic chemicals used were of analytical-reagent grade.

Spectrophotometric titrations

Place the test solution in the titration cell, add 6 drops of copper(II)–EDTA solution, 2 ml of 0.5*M* acetic acid and 2 ml of $1.00 \times 10^{-4}M$ PAR*. A red-violet colour develops immediately. Dilute with distilled water to about 20 ml, stir (magnetic stirrer), and measure the absorbance at 520–530 nm after each addition of 0.002*M* EDTA, continuing the titration until the absorbance remains nearly constant during addition of 0.2–0.3 ml of titrant. Locate the end-point graphically.[26,27] The second intersection point corresponds to the amount of iron present. A typical titration curve is shown in Fig. 2 and results in Table 1.

Visual titration

Transfer a portion of test solution containing 0.25–5.5 mg of iron into a 100–150 ml beaker. Add 0.5 ml of copper(II)–EDTA solution, 2 ml of 0.5*M* acetic acid and if necessary adjust the pH to 2.7–2.9 with dilute acetic acid or ammonia solution, then dilute the solution to 50 ml with distilled water. Add indicator (2 or 3 drops of 0.05% solution) and titrate at room temperature with standard EDTA solution, with magnetic stirring. Near the end-point titrate slowly until the colour changes from red-violet to pure yellow (this takes 1 or 2 drops of titrant). The intense pink colour of the solution a little before the end-point gives useful warning. Typical results are given in Table 2.

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* Preliminary tests might be performed to establish the best PAR concentration.

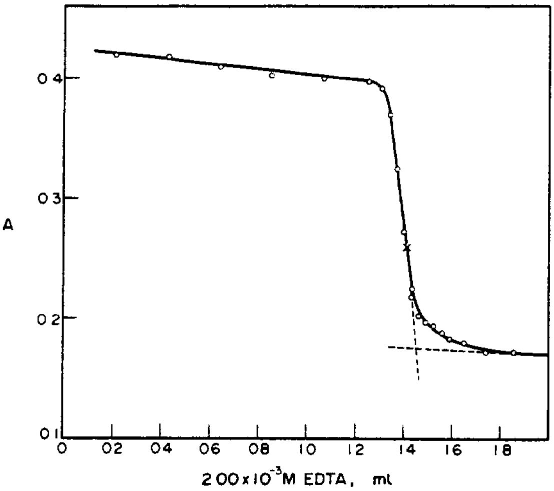

Fig. 2. Spectrophotometric titration of iron(III) with EDTA, using copper(II)–EDTA–PAR system as indicator. Fe 162 μg, $10^{-5}M$ CuY, 2 ml of 0.5M acetic acid and 2 ml of $10^{-4}M$ PAR are added. Total volume about 20 ml. Titrated with 0.002M EDTA at 530 nm.

RESULTS AND DISCUSSION

Spectrophotometric titration

The optimal difference in the absorptivities of the coloured species contributes to an abrupt change in absorbance after the end-point has been reached. Figure 2 shows the well-defined intersection and the absorbance jump of at least 0.2 units.

Ringbom's procedure applied to the spectrophotometric data gives the absorbance at the equivalence point by means of the equation:

$$A_{eq} = (A_{In}^{max} + A_{MIn}^{max}[M]'_{eq}K'_{MIn})/(1 + [M]'_{eq}K'_{MIn}) \qquad (4)$$

With $[Cu]'_{eq} = 10^{-6.65}$ and $[Cu]'_{eq} \cdot K'_{CuIn} = 0.56$, A_{eq} is found to be 0.261. By interpolation the equivalence point should occur at a consumption of 1.409 ml of titrant. The indicator correction is given by:

$$[MIn]_{eq} = C_{Ind}(A_{eq} - A_{In}^{max})/(A_{MIn}^{max} - A_{In}^{max}) \qquad (5)$$

where C_{Ind} is the total indicator concentration. The value $[MIn]_{eq} = 3.6 \times 10^{-6}M$ is obtained. The volume of 0.002M EDTA corresponding to this correction is 0.036 ml. Hence, the volume of EDTA reacted at the equivalence point is 1.445 ml, compared with the 1.448 ml required for the 162 μg of iron in the solution tested. The same quantity was obtained more easily by graphical extrapolation as can be seen from Fig. 2.

Table 1. Spectrophotometric titrations

Iron (III), μg	EDTA, M	n	EDTA consumed, *ml* Theoretical	Experimental ($\bar{x} \pm S$)
269	0.005	7	0.965	0.966 ± 0.004
162	0.005	3	0.579	0.579 ± 0.002
	0.002	7	1.448	1.452 ± 0.007
108	0.005	3	0.386	0.393 ± 0.007
	0.002	5	0.965	0.965 ± 0.004
54	0.002	5	0.483	0.494 ± 0.02
27	0.001	5	0.483	0.473 ± 0.01
11	0.001	5	0.193	0.206 ± 0.01

Table 2. Visual titration of iron(III)

Iron (III), *mg*	EDTA, M	No. of titns.	EDTA consumed, *ml* Theoretical	Experimental ($\bar{X} \pm S$)
5.39	0.01	5	9.65	9.68 ± 0.03
3.77	0.01	5	6.76	6.75 ± 0.02
2.69	0.01	10	4.825	4.837 ± 0.009
1.62	0.01	5	2.895	2.914 ± 0.007
1.08	0.01	7	1.930	1.937 ± 0.006
0.269	0.005	8	0.965	0.962 ± 0.015

The results in Table 1 show that good precision is attainable for 10–270 μg of iron.

Visual titration

The concentration range of iron(III) for visual titration was selected (Table 2) to ensure suitable volume of EDTA consumed, and to utilize the high sensitivity of the indicator reaction. The visual titration is less precise than the spectrophotometric titration of the same amount of iron. With the larger amounts of iron, the colour of the indicator complex is screened by the iron(III) species. Hence, the starting solution was yellowish and the pink colour appeared only when most of the iron(III) was complexed with EDTA. The addition of fluoride (see later) improves the colour characteristics of the solution.

Interferences

Synthetic mixtures were prepared with cations commonly found with iron. Most interferences are prevented by masking with ammonium fluoride and use of a relatively high acidity where few other metals form complexes with PAR and EDTA. The presence of fluoride improves the detection of the end-point. Results are shown in Table 3.

Of the cations studied which under these conditions could react with PAR, nickel, cobalt(II), zinc and cadmium interfere strongly, but as Table 3 shows, elements that generally appear in silicate materials do not.

Preliminary investigations have proved ammonium fluoride to be the best masking agent, the presence of which favours the titration by increasing the apparent intensity of the indicator-complex colour, first by formation of the colourless fluoride complexes of iron(III), and secondly perhaps by formation of a ternary copper(II)–PAR–fluoride complex, in which the unidentate halide ion occupies the fourth position in the inner co-ordination sphere of copper(II) (it was recently again proved[28] that PAR co-ordinates as a terdentate ligand). Fluoride is known to form ternary complexes with some metal–indicator complexes, giving an increase in absorption intensity and a small

Table 3. Interference of foreign ions in visual EDTA titration of iron(III) (1.62 and 5.13 mg of Fe were taken; 2–5 titrations were performed for every ratio studied)

Metal ion	Iron–metal ion ratio (tolerance limit)	Iron found, *mg* (mean value)
Al(III)	1:1	1.62 ± 0.01
	1:2	1.65
	1:50*	1.54
	1:30	5.15
Ti(IV)	10:1*	1.63 ± 0.01
	1:0.6	5.15
Zr(IV)	10:1	1.60
	5:1	1.64
Ca(II)	1:1	1.62
	1:50	1.62
	1:1000	1.55
Ba(II)	1:1	1.62
	1:200	1.65
	1:150	5.11
Sr(II)	1:500	1.55
Mg(II)	1:200	1.65
	1:500	1.55
	1:150	5.16
Cr(III)	1:10	1.55
V(V)	100:1	1.56
Mn(II)	1:6	5.14
	1:20	5.17
SO_4^{2-}	1:30	5.10
PO_4^{3-}	10:1	1.52
	30:1	5.08

* Masking with NH_4F.

bathochromic effect,[29] as observed here, this effect presumably being due to the strong electrophilic character of the fluoride influencing the π-electron system of the dye.[12]

Effect of acetate concentration

Because acetate forms rather stable complexes with iron(III), its effect was investigated and found to be dependent on both the acetate concentration and the pH. Acetate did not interfere provided the overall concentration was less than 0.1*M*, and the pH was not more than 2.9.

Determination of iron in standard samples

The usefulness of the procedure outlined above was tested by applying it to: (*a*) a Czechoslovak standard sample (1-01-002) with the following certified composition: Fe 69.16%, SiO_2 0.48% and Al_2O_3 0.55%, and (*b*) two standard talc samples (DDR) with the composition (*i*) moisture 0.1%, loss on ignition 25.0%, SiO_2 32.2%, TiO_2 1.5%, Fe_2O_3 6.52%, MgO 33.4%, CaO 1.1%, CO_2 23.2%; (*ii*) moisture 0.9%, loss on ignition 8.3%, SiO_2 48.1%, Al_2O_3 2.5%, Fe_2O_3 9.70%, MgO 30.5%, CaO 0.2%, K_2O 0.04%, Na_2O 0.03%, CO_2 0.2%.

The results are given in Table 4.

Procedure for Czech standard

Treat 0.2–0.4 g of the finely ground material in the usual way with concentrated hydrochloric acid and fusion of the residue with sodium carbonate in a platinum crucible.[18] Take special care not to use too great an excess of hydrochloric acid. Combine the solutions in a 250-ml volumetric flask and take a 10–20 ml fraction. Add 1 ml of copper(II)–EDTA solution, 3–5 drops of PAR, 1–2 ml of 0.1*M* ammonium fluoride and adjust the pH by first adding dilute ammonia (or sodium hydroxide solution) till the pH is about 2 and then ammonium acetate solution to pH 2.7–2.9. If necessary, use acetic acid to lower the pH. Titrate at room temperature, slowly near the end-point.

Procedure for talc

Weigh accurately about 0.5 g of the powdered air-dried sample and follow the procedure as described for analysis of a limestone.[30] Transfer the residue after ignition to a small porcelain dish and treat as usual. Filter off the silica, collect the filtrate and washings in a 100-ml volumetric flask, and titrate aliquots of appropriate volume in the same way as for the Czech Standard.

The results obtained for the standard samples indicate that the method has good accuracy and precision, sensitivity and selectivity, which allow a simple determination of iron in materials with similar composition.

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Table 4. Determination of iron in standard materials

					Titration values, *ml*				
Samples	Weight, *g*	Fraction, *ml*	Number of titns.	EDTA, *M*	Average consumed	Theoretical		Found, % $\bar{X} \pm S$	Certificate value, %
Czechoslovak Standard	0.1522	20	5	0.01	15.05	15.08	Fe	69.05 ± 0.19	69.16
	0.4120	10	7	0.01	20.39	20 41		69 11 ± 0.08	
	0.1382	20	3	0.02	13.68	13 69		69 10	
	0.4037	20	1	0.02	19.97	20.00		69.06	
		20	1	0.02	19.94	20.00		68.96	
	0.4120	10	1	0.02	10.25	10.21		69.47	
		10	1	0.02	10.23	10.21		69 33	
Talc Standards	0.5032	10	7	0.01	3.097	3.056	Fe_2O_3	9.77 ± 0.06	9 70
	0.4975	15	5	0.01	3.001	2.921		6.42 ± 0.06	6 25

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ELECTROCHEMICAL DETERMINATION OF HYDROGEN SULPHIDE IN AIR

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Summary—A new method for the quantitative analysis of sub-ppm and high ppm levels of hydrogen sulphide is reported. The technique is based on the electrochemical oxidation of hydrogen sulphide at a potentiostatically-controlled, Teflon-bonded diffusion electrode. Two instruments (one portable and one a fixed-location instrument) were constructed and their operating characteristics evaluated. They were sensitive and selective, responded rapidly to the gas, and gave a linear relationship between steady-state signal and gas concentration. Excellent zero and signal stability indicate that the electrochemical sensor is not poisoned by the H_2S.

Hydrogen sulphide is a toxic, malodorous and corrosive gas which produces severe effects on the nervous system at low concentrations and causes fatalities at higher concentrations. It is produced by the anaerobic digestion of all types of excreta, in oil-fields and refineries, during the synthetic production of fibres, during heavy-water production, and during the Kraft pulping process. The concentrations met in practical situations, and hence the instrument range, will depend on the application. For example, the concentration in ambient air is 1–5 ppM,* v/v, the threshold limit for industrial exposure, set by the American Conference of Governmental Industrial Hygienists, is 10 ppm, and concentrations as high as 200 ppm over a short time are met on oil-drilling rigs. Clearly the analysis technique must not be paralysed by these high concentrations.

A large number of methods have been reported for the determination of hydrogen sulphide. The standard method for environmental samples involves collection by passage through a $Cd(OH)_2$ suspension followed by reaction with *p*-amino-*N*,*N*-dimethylaniline to form Methylene Blue.[1–3] The most widely used method involves collection by passing through a paper tape[4] impregnated with lead acetate,[5,6] mercuric chloride,[7] silver nitrate,[8] or potassium dicyanoargentate.[4] A more precise technique utilizes gas chromatography with a flame photometric detector,[9] but these instruments are limited by their inability to monitor continuously, by their complexity, and by the requirement of a.c. power and support gases.

Recently we described an electrochemical technique for the quantitative determination of carbon monoxide,[10–12] ethanol[13] and the oxides of nitrogen.[14] We now report the extension of this method to the measurement of hydrogen sulphide in the atmosphere. The method is based on the electrochemical oxidation of hydrogen sulphide at a Teflon-bonded diffusion electrode.[15] Two experimental monitoring systems were fabricated and tested to show the feasibility of this electrochemical technique for the measurement of hydrogen sulphide; one was a portable unit while the other was more suitable for continuous operation in corrosive and contaminated environments. We now report on the operating characteristics of these analysers.

EXPERIMENTAL

The smaller portable unit was 7 × 11 × 7 in., weighed 9 lb, and could be operated from a.c. mains or batteries. The larger, fixed-location instrument was 15 × 12 × 6 in., weighed 32 lb, and was mains-operated.

Each instrument comprised a pump, a flowmeter, an electrochemical sensor, and electronic circuitry. The fixed-location instrument also contained a water-bottle (250 ml). Test gases were passed over the surface of the water before entering the sensor, to adjust the water content of the sample gas approximately to the water vapour pressure of the 28% sulphuric acid electrolyte in the sensor. This permitted continuous operation with minimal change in the electrolyte concentration in the sensor.

The electronic circuitry (Fig. 1) consisted of a potentiostat to maintain the sensing electrode at 0·4 V *vs.* the reference electrode, impedance-matching circuitry for a low output-impedance (10 ohm), and provision for battery recharge. The low output-impedance rendered the system compatible with any commercial potentiometric recorder. The low power-requirements of the pump (0·3 W) and of the electronic components (0·25 W) enabled the portable instrument to be operated continuously on a "D" size nickel–cadmium battery for approximately 10 hr.

The same sensor was used in both instruments: it is similar to that previously described for the carbon monoxide analyser.[11,12] Sensing (W), counter (C) and reference (R) electrodes were Teflon–bonded diffusion electrodes.[15] The backs of these electrodes are open to the surrounding air,[11,12] and the electrochemical reaction occurs by gaseous diffusion to the electrocatalytic sites on the front (electrolyte) side of the electrode.[12] The reference electrode was catalysed with platinum, and although this is not a truly reversible electrode, its potential remained sufficiently constant during operation of the cell at 1·0 ± 0·03 V[12] Sensing and counter-electrodes contained a proprietary noble-metal catalyst material (Energetics Science, Inc.)

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* ppM = parts per milliard, *i.e.* parts in 10^9.

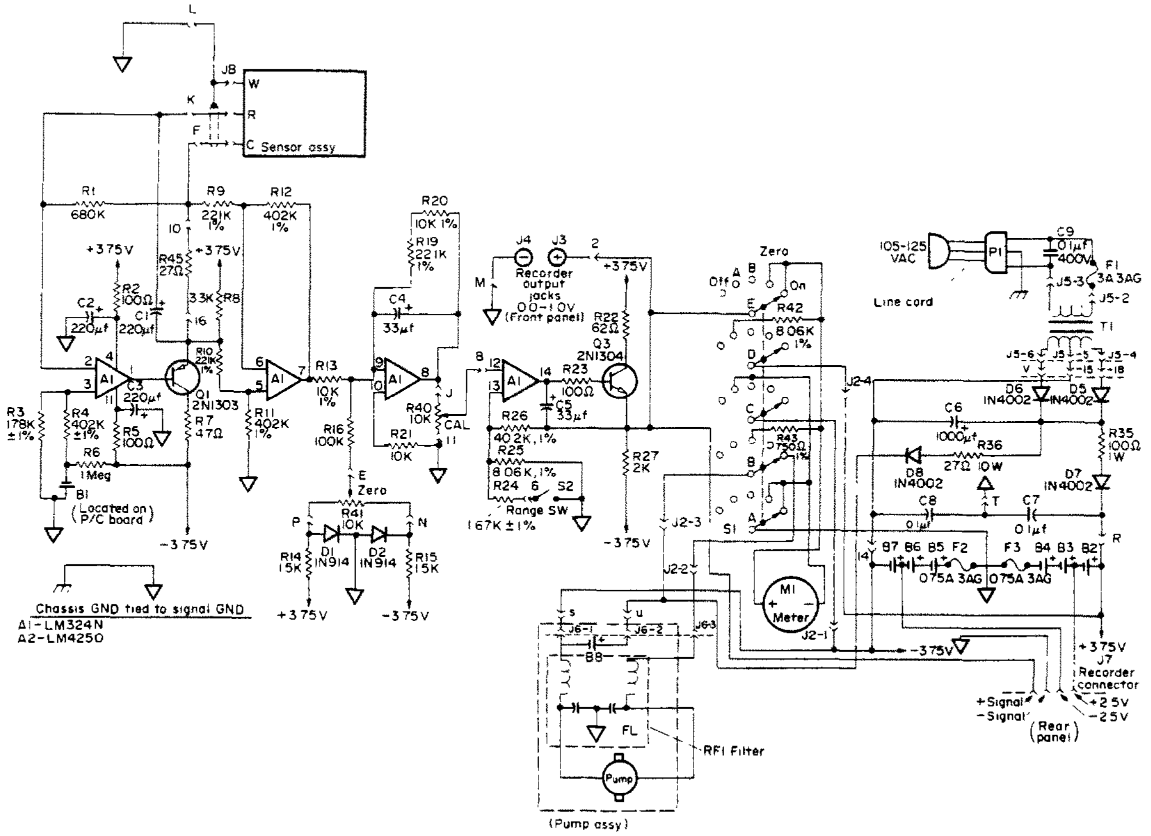

Fig. 1. Circuit diagram for portable hydrogen sulphide analyser. W—working electrode; C—counter-electrode; R—reference electrode.

The systems were set to zero either with pure air or by merely turning off the gas pump. The difference between these two methods was equivalent to less than 0·03 ppm H_2S, and therefore the use of purified air is only necessary when measuring low H_2S-levels. Response characteristics were determined by passing air with various hydrogen sulphide concentrations into the sensor at a fixed flow-rate of 0·7 l./min. The current generated by the electrochemical oxidation of the hydrogen sulphide was displayed on a panel voltmeter calibrated in ppm H_2S and recorded on a Hewlett-Packard Model 680 potentiometric recorder.

Standard gas concentrations were obtained either from cylinders or from permeation tubes. Cylinders of natural gas, CO, N_2O and COS diluted with air were obtained from Matheson Gas Products Co., H_2S and NO diluted with N_2, NO_2 and SO_2 diluted with air, and pure air ("zero air") were obtained from Airco Inc. Permeation tubes of H_2S, CH_3SH, C_2H_5SH and $(CH_3)_2S$ were obtained from Metronics Associates, Inc.

RESULTS AND DISCUSSION

The operating characteristics of both instruments and of the twenty electrochemical sensors used at one time or another in these instruments were similar. The data presented here are typical. Of necessity the larger instrument was always operated from a.c. while the smaller was operated from a.c. or d.c. No difference was observed between a.c. or d.c. operation as long as the batteries were maintained in a state of charge.

Instrument response time

Hydrogen sulphide is oxidized electrolytically in the instruments, and after introduction of a sample, the current generated rapidly reaches a steady-state value, i_l. Table 1 lists the elapsed times between admittance of the test gas and the attainment of 95% of i_1 (t_r), and between removal of the test gas and the decay of the steady-state signal to 5% of i_1 (t_d). The response was observed to quicken as the hydrogen sulphide concentration was increased.

The reaction of hydrogen sulphide at the catalytic surface comprises a series of discrete steps with several possible intermediates. Both SO_2 and SO_3^{2-} were readily electro-oxidized when introduced into the sensor, and therefore, it was concluded that the final reaction product of electro-oxidation of hydrogen sulphide was sulphuric acid, the reaction at the sensing electrode being

$$H_2S + 4H_2O \rightarrow H_2SO_4 + 8H^+ + 8e \qquad (1)$$

Table 1. Signal response and decay times

n_0, ppm H_2S	t_r, sec	t_d, sec	t_d/t_r
0·38	39	28	0·72
11	17	12	0·71
130	11	8	0·73

The reaction at the counter-electrode was

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad (2)$$

thus giving an overall reaction of

$$H_2S + 2O_2 \rightarrow H_2SO_4 \qquad (3)$$

Previous work[12] showed that the response of the diffusion electrode to carbon monoxide followed a first-order law according to equations (4) and (5)

$$\text{signal rise: } i = i_1(1 - e^{-\lambda t}) \qquad (4)$$

$$\text{signal decay: } i = i_1 e^{-\lambda t} \qquad (5)$$

where i is the current (signal) at any time t, and λ is the sensor response-time constant. With carbon monoxide[11] λ was similar for signal rise and decay, and independent of the concentration.

In contrast, i–t results for 0·38, 11 and 130 ppm of hydrogen sulphide could not be fitted to either equation (4) or equation (5). The signal rise and decay for hydrogen sulphide were therefore described in terms of a second-order rate-law subject to boundary conditions) signal rise: $i = 0$ at $t = 0$ and $i = i_1$ as $t \rightarrow \infty$; signal decay: $i = i_1$ at $t = 0$ and $i = 0$ as $t \rightarrow \infty$. Then the sensor response characteristics are:

$$\text{signal rise: } di/dt = k_r(i_1 - i)^2 \qquad (6)$$

$$\text{signal decay: } di/dt = k_d i^2 \qquad (7)$$

As discussed below, i_1 was directly proportional to the hydrogen sulphide concentration, n_0. Thus, i_1 and n_0 can be substituted for one another without loss of generality except that the units of the rate constants k_r and k_d will change. Integration of equations (6) and (7) yields

$$\text{signal rise: } \frac{i_1}{i} = \frac{1}{n_0 k_r t} + 1 \qquad (8)$$

$$\text{signal decay: } \frac{i_1}{i} = n_0 k_d t + 1 \qquad (9)$$

Least-squares analyses of rise and decay data for a 0.38-ppm H_2S sample yielded equations (10) and (11)

$$\frac{i_1}{i} = 0.987 + 0.204/t; \qquad k_r = 1.29\,\text{sec}^{-1}.\text{ppm}^{-1} \qquad (10)$$

$$\frac{i_1}{i} = 0.982 + 0.744t; \qquad k_d = 1.96\,\text{sec}^{-1}.\text{ppm}^{-1} \qquad (11)$$

which are in good correspondence with theoretical equations (8) and (9). The instrument response to 11-ppm and 130-ppm H_2S samples was too fast for accurate abstraction of i–t data points from recorder traces. However, the variation of t_r and t_d with n_0 (Table 1) also suggests that k_r and k_d are dependent on n_0.

The linearity of the i_1/i *vs.* $1/t$ plots, and the observations that $t_d < t_r$ (Table 1) and that t_r and t_d decrease with increasing n_0 (Table 1) demonstrate that the overall electrochemical process is indeed a second-order reaction and that the rate can be represented by equations (6) and (7). This is in contrast to the first-order kinetics observed for electro-oxidation of carbon monoxide.

The rapid response of these instruments to hydrogen sulphide is important since high levels of this gas can be fatal in a short time (seconds). We have no explanation for the invariance of the t_d/t_r ratio with the concentration (Table 1). However, this does demonstrate the consistency of the data.

Relationship between signal and H_2S concentration

The relationship between signal and hydrogen sulphide concentration was studied in the concentration ranges 0–0·277 ppm and 0–153 ppm.

Seven concentrations in the range 0–0·277 ppm were prepared by using a permeation tube. The instrument was calibrated with the 0·277 ppm mixture, and readings were taken with the more dilute samples. Y (ppm H_2S found) was fitted to the following least-squares line as a function of X (ppm H_2S taken):

$$Y = 0{\cdot}0003 + 0{\cdot}9702\,X \qquad (11)$$

The standard deviation of the points from the line was only ±0·007 ppm H_2S.

A more elaborate set of measurements was taken over the 0–153 ppm range. Twenty-five (X, Y) data points obtained with four different sensors were fitted to the least-squares line

$$Y = 1{\cdot}02 + 0{\cdot}944\,X \qquad (12)$$

In this case the standard deviation was ±0·97 ppm H_2S. Both standard deviations include the uncertainties of sample preparation.

It is evident, therefore, that the signal is directly proportional to the H_2S concentration in the range tested.

Signal stability

Figure 2 shows the zero drift (expressed as ppm H_2S) of an instrument over 23 days. During this period the instrument was operated continuously on laboratory air and measurements were made only in the periods marked in the figure.

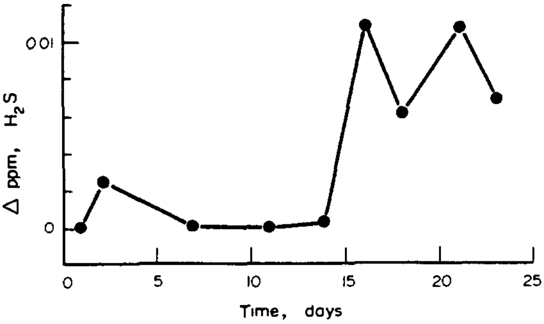

Fig 2. Cumulative zero drift on portable hydrogen sulphide analyser (no rezeroing of instrument during the 23-day period).

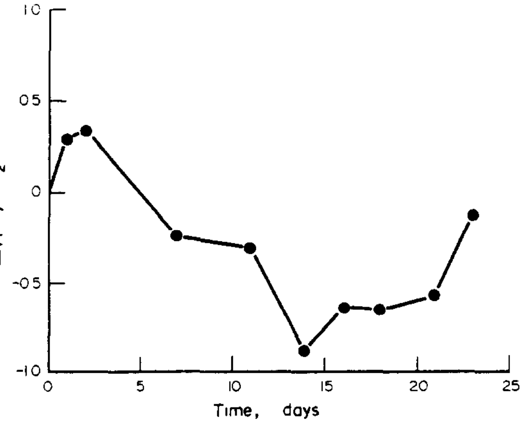

Fig. 3. Cumulative span drift on portable hydrogen sulphide analyser (no recalibration of instrument during the 23-day period). The same 30-ppm H_2S test gas was used for all measurements.

The results show that zero drift was insignificant over this period. In fact for a 0–1-ppm H_2S instrument the maximum zero drift was 0·5% of full scale per 24 hr (clearly the relative drift would be even lower for higher range instruments).

On the first day of these tests, the signal was also recorded for a mixture with 30 ppm hydrogen sulphide, and this measurement was repeated during the test period. The drift in the sensitivity is shown in Fig. 3. The weighted average signal, $\bar{n}_0$, was 29·7 ppm H_2S over the complete testing interval. The maximum change in sensitivity over a 24-hr period was always less than 1% of the signal.

In a series of short-term measurements, a 130-ppm hydrogen sulphide mixture was passed into the instrument for 20 min (maximum time possible with the Mylar sample bag used). The bag was then removed and within 3 sec a new one was connected. Forty-eight measurements were made on the recorder traces from a 90-min period to assess steady-state current-output fluctuations. The standard deviation of i_1 was ±0·54 ppm or ±0·42% relative.

These results show that the instrument does not need to be zeroed and calibrated frequently to ensure a satisfactory degree of accuracy.

Specificity of instrument response

The instrument is quite selective towards hydrogen sulphide, as shown by the results of interference studies shown in Table 2. These other gases are either common atmospheric pollutants or may be present at H_2S sources.

TABLE 2. RESPONSE TO SELECTED INTERFERENTS

Interference gas	Concentration tested, *ppm*	Concentration required to give signal equivalent to 1 ppm H_2S, *ppm*
CO_2	3000	No signal obtained
CH_4	95%	No signal obtained
C_2H_2	10	27
C_2H_4	15	No signal obtained
NO	41	7
NO_2	4	40
N_2O	100	No signal obtained
SO_2	11	8
CO	900	2000
CH_3SH	2	3
C_2H_5SH	1	3
$(CH_3)_2S$	1	No signal obtained
COS	22	No signal obtained

The potential interferent gas was introduced at a known concentration into the instrument under the same conditions used for the measurement of hydrogen sulphide. Further, a sample of natural gas was spiked with 0·5 ppm of hydrogen sulphide, and then was found to give the same signal as a 0·5-ppm mixture in air or nitrogen. None of the gases listed in Table 2 is as electrochemically active as hydrogen sulphide in the sensor and no gas filter was required to obtain this specificity.

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ION-EXCHANGER COLORIMETRY—I

MICRO DETERMINATION OF CHROMIUM, IRON, COPPER AND COBALT IN WATER

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Summary—A new, sensitive, colorimetric method based on the direct measurement of light-absorption by an ion-exchange resin phase, which has sorbed the sample complex species, has been developed. Determinations of chromium(VI) with diphenylcarbazide, iron(II) with 1,10-phenanthroline, copper with Zincon and cobalt with thiocyanate have more than ten times the sensitivity obtainable with conventional solution colorimetry. The present method can be applied to natural water samples containing very low levels of these metals.

A spot-test with ion-exchange resin beads has been proposed by Fujimoto,[1] and by Kakihana and his co-workers.[2] This technique has various advantages for qualitative microanalysis. In this method, concentration and selective sorption of the chemical species to be identified may occur simultaneously. In some cases, the sample species are converted into complex anions of higher ligand number within an anion-exchange resin phase, leading to remarkable enhancement of the sensitivity.

In spite of a number of publications on the resin spot-test[3–8] and on the interpretation of resin-phase absorption spectra of the inorganic complexes,[9–13] no papers on the quantitative analytical application of these resin-phase spectra could be found. A new spectrophotometric microanalytical method, based on the direct measurement of the resin-phase absorbance after the sorption of sample species, has been developed for the determination of some transition metals.

In acid solution[14] diphenylcarbazide forms a soluble, red-violet cationic complex with sexivalent chromium, having a metal-ligand molar ratio of 3:2. This reaction has been utilized for the micro determination of chromium.[15] 1,10-Phenanthroline is known as a sensitive reagent for the colorimetric determination of iron. The very stable red complex cation $\mathrm{Fe(phen)_3^{2+}}$ is formed in weakly acidic, neutral and weakly alkaline media. A sensitive colorimetric method for copper with Zincon (2-hydroxy-5-sulphophenylazobenzylidenehydrazinobenzoic acid) was reported by Rush and Yoe.[16] They succeeded in determining zinc and copper in mixtures by appropriate adjustment of the pH. The spot-test for cobalt(II) with anion-exchange resin beads and ammonium thiocyanate was proposed by Fujimoto.[1] This test was very sensitive and specific.

The present paper describes the application of these colour reactions to quantitative studies on ion-exchange resins.

EXPERIMENTAL

Absorption measurements on the resin phase

The following ion-exchange resins were used, depending upon the mechanism of the colour development: Dowex 50 W-X2, $\mathrm{H^+}$-form (50–100 mesh and 100–200 mesh); Dowex 1-X2, $\mathrm{Cl^-}$-form (100–200 mesh). The mixture of resin, sample solution and reagent was shaken mechanically. The coloured resin beads were separated from the bulk solution and packed together with a small volume of the solution into a 1-mm quartz cell, by means of a pipette. The absorbance was measured with a Hitachi recording spectrophotometer, Model EPS-3T, a perforated metal plate being used as a neutral density filter (of absorbance 2.0) in the reference beam to balance the light intensities.

From the observed absorbance A at a given wavelength, the net absorbance A_{RC} of the complex species sorbed on the resin can be obtained from the equation

$$A_{\mathrm{RC}} = A - A_{\mathrm{soln}} - A_{\mathrm{R}} - A_{\mathrm{RL}} \qquad (1)$$

where A_{soln} represents the absorbance of the interstitial solution between the resin beads, A_{R} that of the resin background and A_{RL} that of the reagent in the cell. The absorbance due to the sample complex in the interstitial liquid may be neglected. The values of A_{RC}, A_{R} and A_{RL} are affected by the packing of the resin beads because of the change in path-length or scattering behaviour in the cell. The packing should therefore be reproducible. The following procedure was found to be adequate. The absorption spectrum of a resin layer containing no coloured species was measured against pure water. The absorbance at two different wavelengths, one corresponding to the absorption maximum of the coloured species and the other in a region where the resin alone absorbs (700–800 nm) was read from the chart. The absorbance difference may be assumed to be constant under the similar packing conditions. In practice, A_{R} at 700 or 800 nm was constant to within ±0.025. The value of A_{R} at the absorption maximum, in equation (1), was calculated from the absorbance difference and the measured value of A_{R} at 700 or 800 nm. Thus the net absorbance A_{RC} can be obtained by subtracting A_{R} from the overall absorbance. When A_{RL} cannot be neglected, $A_{\mathrm{RC}} + A_{\mathrm{RL}}$, instead of A_{RC}, is obtained by the same treatment.

Procedure for the determination of chromium(VI) with diphenylcarbazide

To a 200-ml water sample containing 0.01–0.3 μmole of chromium(VI), enough $5N$ sulphuric acid was added to make the concentration of this acid approximately $0.05N$. Then 5 ml of 0.25% acetone solution of diphenylcarbazide and 0.50 g of Dowex 50W-X2 (100–200 mesh) in the hydrogen form were added. The mixture was stirred for 15 min and the supernatant solution discarded, the residual resin slurry transferred to the cell and the absorbance measured at 550 nm.

Procedure for the determination of iron with 1,10-phenanthroline

To a 200-ml water sample containing 0.1–2 μmole of iron, 5 ml of $0.01M$ 1,10-phenanthroline, 5 ml of 10% hydroxylamine solution, 5 ml of $0.5M$ acetic acid–sodium acetate buffer (pH 5) and 0.50 g of Dowex 50W-X2 in the hydrogen form (100–200 mesh) were added and the mixture was stirred for 30 min. The coloured resin was collected and its absorbance measured at 514 nm.

Procedure for the determination of copper(II) with Zincon

To a 200-ml water sample containing 0.1–1 μmole of copper(II), 10 ml of $0.2M$ potassium hydrogen phthalate–sodium hydroxide buffer (pH 5.2) and 0.50 g of Zincon-treated resin were added and the mixture was stirred for 30 min. The resin was collected and its absorbance measured at 630 nm. The Zincon-treated resin was prepared by shaking 30 g of Dowex 1-X2 in the chloride form (100–200 mesh) with 50 ml of 0.1% Zincon–$0.02M$ sodium hydroxide solution for 1 hr.

Procedure for the determination of cobalt(II) with thiocyanate

To a 1000-ml water sample containing 2–20 μmole of cobalt(II), 20 ml of 50% ammonium thiocyanate solution and 0.50 g of Dowex 1-X2 in the chloride form (100–200 mesh) were added and the mixture was stirred for 30 min. The blue resin was collected and its absorbance measured at 630 nm.

All chemicals used were of analytical grade and all experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Absorption spectra in resin and solution

The complex of chromium(VI) with diphenylcarbazide can be sorbed on cation-exchange resins and to some extent on anion-exchange resins by molecular interaction as well as by ion-exchange. The net absorbance curve of the sorbed complex was constructed from the difference between the resin phase curve and the resin background curve. The net resin-phase absorption spectrum of the complex is similar to that obtained in solution but the maximum is shifted to longer wavelengths (550 nm), as shown in Fig. 1. For quantitative studies the cation-exchange resin Dowex 50W-X2 (100–200 mesh) was used in $0.05N$ sulphuric acid medium.

Only cation-exchange resins sorb the iron(II)-1,10-phenanthroline complex and give the same absorption spectrum as that of an aqueous solution.

The Zincon complex of copper(II) has a molar ratio of 1:1 and has an absorption maximum at 600 nm in solution. The maximum for free Zincon is at 470 nm. When both species are sorbed on anion-exchange resins, the maxima shift to 630 and 570 nm respectively (Fig. 2). These maxima are so close that the combined spectrum usually exhibits only a shoulder at 630 nm. Consequently the absorbance at 630 nm may include a contribution from free Zincon. The copper–Zincon complex is not sorbed on anion-exchange resins from acidic solution, but the Zincon reagent is sorbed irreversibly from alkaline solution. The resin containing presorbed Zincon reagent was therefore added to acidic water samples. The excess

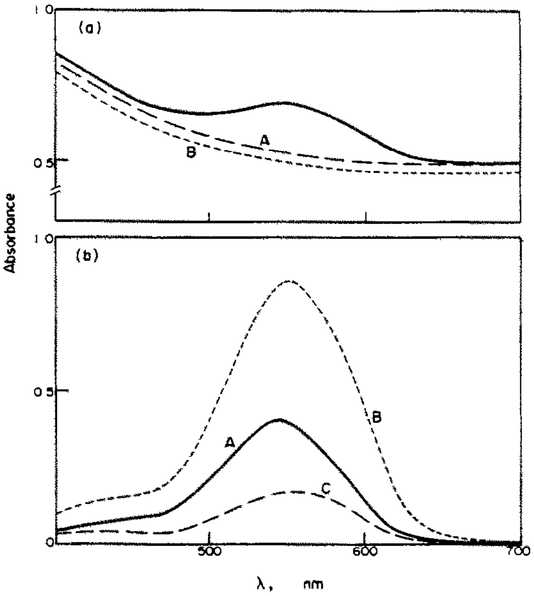

Fig. 1. (*a*) Absorption spectra of Dowex 1-X2 resin containing chromium complex of diphenylcarbazide. A, assumed resin background of sample; B, reference resin spectrum; (*b*) Net absorption spectra of chromium complex of diphenylcarbazide. A, solution spectrum; B, Dowex 50 W-X2 resin spectrum; C, Dowex 1-X2 resin spectrum.

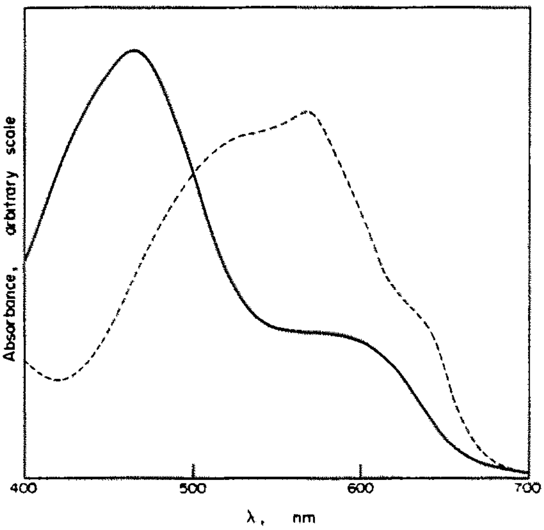

Fig. 2. Absorption spectra of copper–Zincon complex and free Zincon. ——, solution spectrum; ...., Zincon presorbed on Dowex 1-X2 resin.

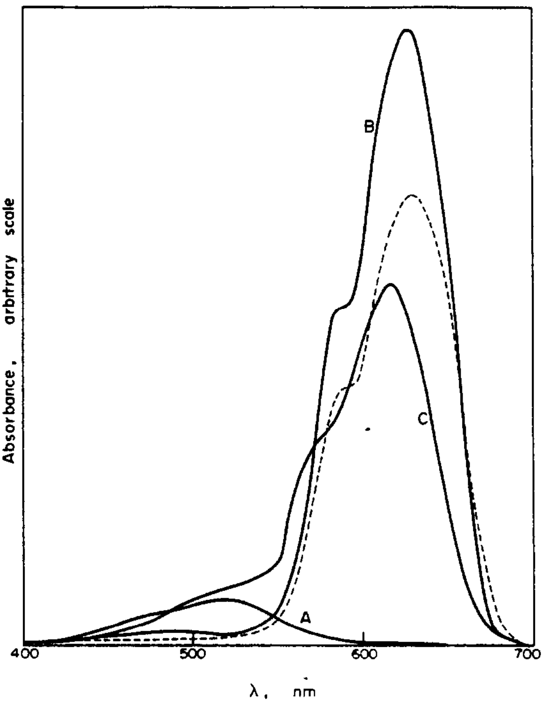

Fig. 3. Absorption spectra of cobalt–thiocyanate complexes. ——, solution spectra, A, $0.7M$ $NH_4SCN + Co(II)$; B, $0.7M$ $NH_4SCN + Co(II)$, 1:1 acetone–water; C, $8M$ $NH_4SCN + Co(II)$; ...., spectrum of Dowex 1-X2 (100–200 mesh, Cl^--form) equilibrated with solution A.

of uncomplexed Zincon was not desorbed during the equilibration.

Figure 3 shows the absorption spectrum of the cobalt(II)-thiocyanate complexes sorbed on the anion-exchange resin, together with spectra of the solutions for comparison. It may be seen that the resin spectrum is similar to that obtained with solutions in which the thiocyanate concentration is as high as $8M$ even when the thiocyanate concentration in the equilibrating solution is as low as $0.7M$. The tendency of the complex to change to one with higher ligand numbers in the anion-exchange resin phase may be exploited.

Time-dependence of colour development

Almost all of the chromium in 200 ml of sample solution is sorbed on the resin within 15 min equilibration (Fig. 4). The presence of other electrolytes, such as sodium chloride (at the concentration level found in sea-water) has no effect on the sorption rate of the complex. The chromium concentration can be determined with the aid of a calibration curve constructed by use of a fixed equilibration time, even though the sorption of chromium is not complete. Figure 4 also shows that the use of resin particles of larger size leads to a slower sorption rate. Equilibrium with Dowex 50W-X1 (50–100 mesh) and 200 ml of solution took more than 1 hr to reach.

The complete sorption of copper requires a long time, probably because of the slow rate of internal diffusion of the complex in the particles (Fig. 5). For rapid analysis it is convenient to equilibrate until just after the early sorption stage.

A study of the rate of development of the colour of the cobalt-thiocyanate complex indicates that with large sample volumes a longer equilibration time is required for quantitative sorption, but the sensitivity is increased (Fig. 6). There is no limitation upon the size of sample volume taken, but a large volume requires a longer equilibration time. The calibration curve should be prepared under the conditions used for the sample to be analysed.

Calibration

The calibration graph for chromium is reasonably linear in the concentration range 5×10^{-8}–$1.5 \times 10^{-6}M$, that for iron in the range

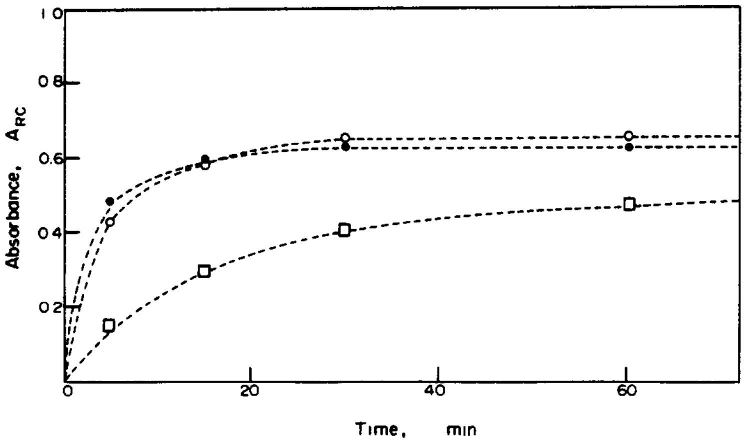

Fig. 4 Colour development of chromium–diphenylcarbazide complex in the cation-exchange resin phase. Resin, □ Dowex 50W-X2 (50–100 mesh, H^+-form) 0.50 g, ●, ○ Dowex 50W-X2 (100–200 mesh, H^+-form) 0.50 g. Solution, □, ● 0.15 μmole Cr(VI), 200 ml + $5N$ H_2SO_4, 2 ml. ○ 0.15 μmole Cr(VI) + $0.6M$ NaCl, 200 ml + $5N$ H_2SO_4, 2 ml.

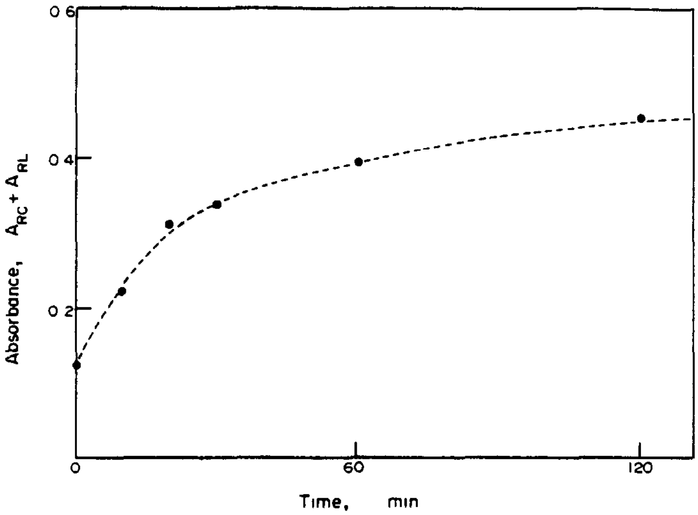

Fig. 5. Colour development of copper–Zincon complex in the anion-exchange resin phase. Resin, Dowex 1-X2 (100–200 mesh, Cl^--form, Zincon presorbed) 0.50 g. Solution, 0.50 μmole Cu(II), 200 ml + 0.2*M* phthalate buffer (pH 5.2), 10 ml.

5×10^{-7}–$1 \times 10^{-5}M$, that for copper in the range 5×10^{-7}–$5 \times 10^{-6}M$ and that for cobalt in the range 2×10^{-6}–$2 \times 10^{-5}M$. Deviations are about ±5–10%.

Sensitivity

In Table 1 the sensitivity for each system is compared with that obtained with a conventional colorimetric method. The concentrations giving an absorbance of 0.50 are listed. In each case the sensitivity was about ten times that for conventional colorimetry.

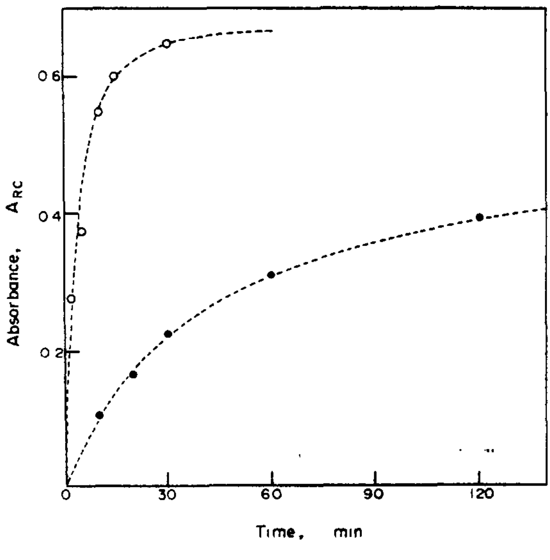

Fig. 6. Colour development of cobalt–thiocyanate complexes in the anion-exchange resin phase. Resin, Dowex 1-X2 (100–200 mesh, Cl^--form) 0.50 g. Solution, ● 6 μmole Co(II), 1000 ml + 50% NH_4SCN, 20 ml, ○ 6 μmole Co(II), 100 ml + 50% NH_4SCN, 10 ml.

Effects of foreign ions

Most metals which interfere in the colorimetric determination of chromium, such as vanadium(V), iron(III) and molybdenum(VI) did not interfere when present in up to one hundred times the concentration of chromium(VI). Table 2 shows that, with the exception of copper, errors in the range of 5–10% are obtained.

Iron(III), cobalt(II) and nickel(II) ions were found to interfere in the determination of copper when their concentrations exceeded ten times that of the copper (Table 3).

Table 4 shows the effects of several ions on the determination of cobalt(II). Iron(III) and high concentrations of alkali caused considerable interference.

Applications of ion-exchanger colorimetry

The present method may be applied to the analysis of natural water samples such as sea, river and lake water. The error of 5–10% is not excessive for the

Table 1. Comparison of sensitivity of ion-exchanger colorimetry and conventional colorimetry (metal concentration giving a final absorbance of 0.50)

	Ion-exchanger colorimetry, *M*	Conventional colorimetry*, *M*
Cr(VI)	6.2×10^{-7}†	1.8×10^{-5}
	6.7×10^{-7}§	1.8×10^{-5}
Fe	2.9×10^{-6}	3.9×10^{-5}
Cu	2.5×10^{-6}	2.2×10^{-5}
Co	9.4×10^{-6}	3.0×10^{-3}

* 1-cm cell.
† 0.05*N* H_2SO_4 medium.
§ 0.05*N* H_2SO_4 and 0.6*M* NaCl medium.

Table 2. Effect of foreign ions on the determination of chromium(VI)

	Added, molar ratio to Cr	Cr taken $10^{-7}M$	A_{RC}	Cr found, $10^{-7}M$	Relative error, %
		1.0	0.092	1.1	+10
		5.1	0.395	4.9	− 4
V(V)	100	5.1	0.435	5.4	+ 6
	1000	5.1	0.260	3.2	−37
Cr(III)	100	5.1	0.429	5.3	+ 4
	1000	5.1	0.498	6.2	+22
Fe(III)	100	5.1	0.434	5.4	+ 6
	1000	5.1	0.425	5.3	+ 4
Cu(II)	1	5.1	0.375	4.7	− 8
	10	5.1	0.299	3.7	−27
Mo(VI)	100	5.1	0.376	4.7	− 8
	1000	5.1	0.401	5.1	0

Table 3. Effect of foreign ions on the determination of copper(II)

	Added, molar ratio to Cu	Co taken, $10^{-6}M$	$A_{RC} + A_{RL}$	Co found, $10^{-6}M$	Relative error, %
		3.0	0.722	2.8	− 7
Fe(III)	8	2.5	0.687	2.6	+ 4
	80	2.5	undeterminable		
Co(II)	8	2.5	0.623	2.3	− 8
	100	2.0	0.661	2.5	+25
Ni(II)	8	2.5	0.671	2.5	0
	100	2.0	0.664	2.5	+25
Zn(II)	100	2.0	0.552	2.0	0
	800	2.5	0.204	0.41	−84

Table 4. Effect of foreign ions on the determination of cobalt(II)

	Added, molar ratio to Co	Co taken, $10^{-5}M$	A_{RC}	Co found, $10^{-5}M$	Relative error, %
		0.10	0.057	0.11	+ 10
		0.50	0.265	0.50	0
		1.5	0.769	1.4	− 7
Cr(III)	10	1.0	0.525	1.0	0
	100	1.0	0.532	1.1	+ 10
Fe(III)	0.1	1.0	0.508	0.96	− 4
	1	1.0	1.142	2.2	+120
Ni(II)	10	1.0	0.478	0.91	− 9
	100	1.0	0.550	1.2	+ 20
Cu(II)	1	1.0	0.473	0.90	− 10
	10	1.0	0.375	0.71	− 29
NaCl	10^4	1.0	0.512	0.97	− 3
	10^5	1.0	0.451	0.86	− 14
NaOH	10^4	1.0	0.000	0.00	−100
HCl	10^4	1.0	0.523	0.99	− 1

micro determination of metals in practical environmental analysis. The technique can be extended to the determination of other metals which give complexes having characteristic absorption maxima.

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SHORT COMMUNICATIONS

COMPARISON OF FIGURES OF MERIT FOR FLUORIMETRIC ANALYSIS OF RHODAMINE COMPLEXES OF GALLIUM AND INDIUM BY EXCITATION WITH PULSED LASER AND BY XENON ARC SOURCES[*]

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There are several reviews concerning the absorption and fluorescence spectrometric determination of gallium and indium by means of Rhodamine dyes.[1-3] The sensitivity of measurement of these complexes[4-6] and the optimum conditions for extraction and measurement of trace concentrations of indium *via* Rhodamine complexes[2, 7-9] have also been reported. Hitherto, there have been no reports on the optimization of experimental conditions in fluorimetry in order to obtain the best detection limits. In the present study, two different arrangements are used to determine analytical figures of merit for indium and gallium Rhodamine dye complexes: (*i*) a commercial spectrophotofluorimeter with a special high-intensity xenon source, and (*ii*) a fluorimetric system with a pulsed nitrogen laser as the excitation source (at 337·1 nm).

EXPERIMENTAL

Reagents

Rhodamine B and Rhodamine 6G were purified;[10] 1·5 × 10^{-5}*M* solutions of each dye in either water or 6*M* hydrochloric acid were prepared Hydrochloric (6*M*) and sulphuric acid (7·5*M*) solutions were prepared from the reagent grade concentrated acids; hydrobromic acid was redistilled and diluted with distilled water to prepare a 2*M* solution. Thiophene-free benzene was used for the extraction studies.

A standard gallium stock solution was prepared by dissolving 116·2 mg of gallium metal (99·999% pure) in 20 ml of 6*M* hydrochloric acid and diluting to 50·0 ml. A more dilute standard solution containing 0·02 ppm of gallium was prepared by dilution of the stock solution with 6*M* hydrochloric acid.

A standard indium stock solution was prepared by dissolving 388·5 mg of indium metal (99·999% pure) in 20 ml of hydrobomic acid with heating, and then diluting to 50·0 ml. A more dilute standard solution containing 0·02 ppm of indium was prepared by dilution of the stock solution with 2*M* hydrobromic acid.

Apparatus

Spectrofluorimeter. An Aminco–Bowman spectrophotofluorimeter with a 10-mm sample cell was used. An EIMAC (VIX-150-UV, Eimac Division, San Carlos, CA 94070) xenon arc lamp with integral reflector and powered by an EIMAC power supply replaced the conventional AMINCO source assembly. A potted Hamamatsu 1P21 multiplier phototube was powered by a separate high-voltage power supply. The photoanodic currents were measured with a low-noise nanoammeter.[11]

The pulsed nitrogen laser fluorescence system consisted of a 100-kW pulsed nitrogen laser (C950, AVCO Research Lab.) focussed onto the solution in a 10 × 10 mm quartz cuvette placed directly in front of a 250-mm focal length monochromator (EU-700, GCA/McPherson Instrument). An RCA 1P28 photomultiplier tube and boxcar integrator (Model 160, Princeton Applied Research Corp.) were used to process the pulsed signals, and a potentiometric recorder (Servoriter II, Texas Instrument), was used for the read-out. Flat, front-surface mirrors were used to obtain an additional pass of the laser pulse through the sample solution and to increase the fluorescence signal. In Fig. 1, a block diagram of the system is given.

Procedures

Determination of gallium. The analytical calibration curve is prepared by adding gallium (0·02, 0·04, 0·06, 0·08 μg) to 60-ml separating funnels, adding 0·5 ml of Rhodamine B (or Rhodamine 6G) solution in 6*M* hydrochloric

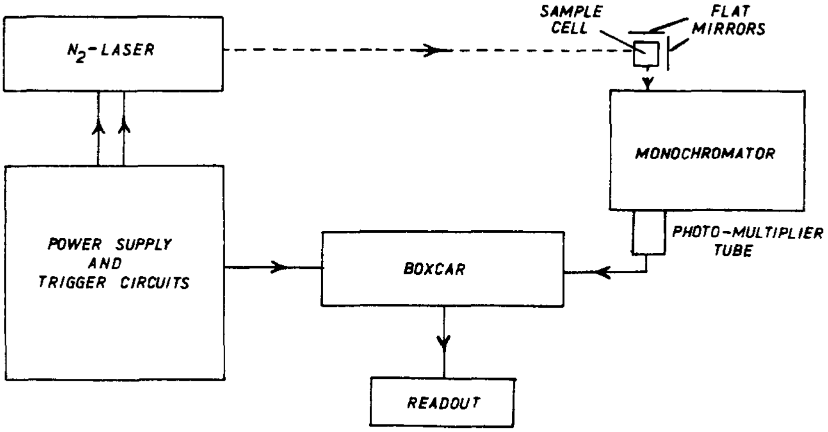

Fig. 1. Block diagram of N$_2$-laser-excited fluorimeter.

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Table 1. Analytical figures of merit for fluorescence of Ga and In Rhodamine complexes

		Modified Aminco-Bowman spectrophotofluorometer					
		Wavelength, *nm*		Analytical curve			
Element	Dye	Excitation	Emission	*a*, *μA*	*b*, *μA ml μg*$^{-1}$	Blank standard deviation, *μA*	Limit of detection *ng/ml*
Ga	Rhodamine B	563	584	0·073	0·18	0·017	0·94
	Rhodamine 6G	527	548	0·76	0·92	0·19	0·21
In	Rhodamine B	564	578	0·059	0·35	0·028	0·90
	Rhodamine 6G	525	551	0·65	0·90	0·11	0·12

		Nitrogen laser		
		Wavelength, *nm*		
Element	Dye	Excitation	Emission	Limit of detection *ng/ml*
Ga	Rhodamine B	337	584	1·1
	Rhodamine 6G	337	548	0·10
In	Rhodamine B	337	578	1·3
	Rhodamine 6G	337	551	0·16

acid and then sufficient $6M$ hydrochloric acid to make the final volumes about 5 ml. The solutions are shaken to mix them thoroughly, then 5 ml of benzene are added, and the mixture is again thoroughly shaken for 1 min. After the organic solvent phase separates (about 10 min), the mixture is centrifuged at 3000 rpm for 4 min. The fluorescence signal of the benzene extract is measured (1 × 1 cm quartz cuvette).

Determination of indium. The analytical calibration curve is prepared by adding indium (0·1, 0·02, 0·03, 0·04 μg) to 60-ml separating funnels, followed by 0·5 ml of Rhodamine B (or Rhodamine 6G) solution in water, 5 ml of $7{\cdot}5M$ sulphuric acid and enough hydrobromic acid to make the final volume 7·5 ml. The solution is shaken to mix it thoroughly, 5 ml of benzene are added, and the mixture is thoroughly shaken for 1 min; the mixture is centrifuged as for gallium, and the fluorescence signal of the resulting benzene layer is measured.

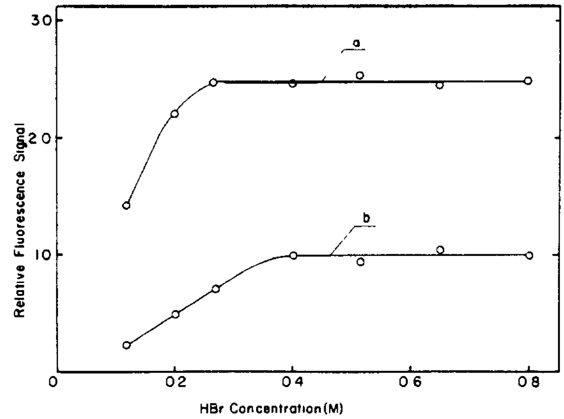

Fig. 2. Fluorescence signal of extracts of bromide complexes of indium with Rhodamine 6G (a) and Rhodamine B (b) as a function of hydrobromic acid concentration.

RESULTS AND DISCUSSION

Optimum conditions for extraction and measurement of gallium and indium

The extraction and measurement conditions for gallium were identical to those given previously,[12] but those for the indium complexes were examined in the present work.

Effect of acidity. The maximum fluorescence signal was obtained with Rhodamine B when the indium solution was made $5M$ in sulphuric acid before extraction; similar results were previously[13] obtained with Rhodamine 6G.

Effect of bromide concentration. The influence of hydrobromic acid concentration on the measured fluorescence signals of the indium-Rhodamine complexes is given in Fig. 2. For hydrobromic acid concentrations greater than about $0{\cdot}4M$, the fluorescence signals reached a plateau. For further comparative studies, a hydrobromic acid concentration of $0{\cdot}53M$ was chosen.

Fluorimetric limits of detection for gallium and indium

The limits of detection for gallium and indium Rhodamine B and Rhodamine 6G complexes obtained with the xenon arc source as well as with the pulsed nitrogen laser were determined and are listed in Table 1. For the continuum xenon source, the slope a and intercept b for the straight line analytical curves ($y = a + bx$) were determined as well as the standard deviation of the blanks (signal level), and these values are also listed in Table 1. The limits of detection for gallium and indium with Rhodamine 6G are lower by a factor of 5–8 than those of the best fluorimetric methods previously reported.[4,14] The two different excitation–detection methods that were used give comparable detection limits. However, the work of Smith *et al.*[15] and the present work with the simple nitrogen laser[16] system indicates the potential usefulness of laser excitation sources for fluorimetric measurements of molecules in the condensed phase.

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Summary—Optimum conditions have been established for formation and extraction of indium–Rhodamine complexes, and limits of detection found for fluorimetric determination of gallium and indium by means of Rhodamine dyes, using the excitation with pulsed laser and xenon arc sources.

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ANALYTICAL APPLICATIONS OF ORGANIC REAGENTS IN HYDROPHOBIC GEL MEDIA—II

SELECTIVE PRECONCENTRATION OF MERCURY(II) WITH DITHIZONE OR THIOTHENOYLTRIFLUOROACETONE GEL[*]

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(*Received* 3 *September* 1975. *Accepted* 9 *October* 1975)

In a previous paper,[1] we reported the potential use of dithizone gel beads for the selective trapping of mercuric ion from aqueous samples. Although dithizone is labile, its zinc chelate is very stable during prolonged storage on gel beads. In this easily prepared form it is a good extractant for mercuric ion. Other sulphur ligands, such as thiothenoyltrifluoroacetone (STTA)[2], are also effective for gel extraction of the same metal ion.

Mercury trapped on the gel-bead column can be back-extracted with a hydrogen halide solution, with a concentration factor of 100–200.

In this paper, we report a more detailed study on dithizone and STTA gel columns, and the back-extraction of mercury. Mercury in synthetic or natural sea-water at the ppm or ppM level, has been successfully preconcentrated by the proposed procedure.

EXPERIMENTAL

Reagents

Thiothenoyltrifluoroacetone [1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one] obtained commercially was used without further purification. Dithizone (analytical grade) and zinc dithizonate (laboratory preparation[3]) were recrystallized from chloroform. All other reagents were of analytical grade.

Procedures

Preparation of the gel beads and the column. Polystyrene beads (2% divinylbenzene)[§] were washed with acetone until the extract became colourless, dried at 110° for 24 hr and finally sieved to yield 80–100 mesh particles. The dry polymer beads (2 g) were soaked in 10 ml of a chlorobenzene solution containing 0·05–0·07% zinc dithizonate [$Zn(HDz)_2$] or 0·05% thiothenolytrifluoroacetone, for 24 hr at room temperature. The gel beads, after centrifugation, were suspended in water and packed into a glass tube (1·1 cm^2 × 25 cm) to give a column of 10 cm height. The interstitial volume of the column was 5·5–6 ml. Thus, the ratio of stationary to mobile phase is approximately 1, implying that the gel column extraction may be regarded as a multi-step extraction process between equal volumes of the two phases.

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Thiothenoyltrifluoroacetone [1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one] obtained commercially was used without further purification. Dithizone (analytical grade) and zinc dithizonate (laboratory preparation[3]) were recrystallized from chloroform. All other reagents were of analytical grade.

Procedures

Preparation of the gel beads and the column. Polystyrene beads (2% divinylbenzene)§ were washed with acetone until the extract became colourless, dried at 110° for 24 hr and finally sieved to yield 80–100 mesh particles. The dry polymer beads (2 g) were soaked in 10 ml of a chlorobenzene solution containing 0·05–0·07% zinc dithizonate [$Zn(HDz)_2$] or 0·05% thiothenolytrifluoroacetone, for 24 hr at room temperature. The gel beads, after centrifugation, were suspended in water and packed into a glass tube ($1{\cdot}1\ cm^2 \times 25\ cm$) to give a column of 10 cm height. The interstitial volume of the column was 5·5–6 ml. Thus, the ratio of stationary to mobile phase is approximately 1, implying that the gel column extraction may be regarded as a multi-step extraction process between equal volumes of the two phases.

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§ Polymer beads were obtained by courtesy of Mitsubishi Kasei Kogyo Co., to whom the authors' thanks are due.

Column operation. All aqueous solutions to be passed through the column were presaturated with chlorobenzene.

The aqueous solution containing a known amount of metal ions was passed through the column at a given rate, and the effluent was collected in 10-ml fractions, which were analysed for metal ions (mercury with dithizone,[4] copper and zinc by atomic-absorption spectrophotometry at 324·7 and 213·9 nm respectively).

Mercury was back-extracted from the column with either 1*M* hydrobromic acid or 8*M* hydrochloric acid in the case of dithizone gel, and with sulphuric acid–potassium bromide solution (40 ml of 0·05*M* H_2SO_4 plus 10 ml of 10% KBr solution) in the case of STTA gel. The effluent was collected in 10-ml fractions, in which the mercury was determined with dithizone at pH 5–6.[4]

RESULTS AND DISCUSSION

The purpose of this investigation was to concentrate mercuric ion selectively from a very dilute aqueous solution onto the gel-bead column containing chelating agents of high selectivity for mercuric ion, and to recover it from the column by back-extraction into the aqueous phase for the final mercury determination.

Since our preliminary report on the use of the dithizone gel column,[1] we have used polystyrene gel beads rather than dibenzalsorbitol gel particles, because they result in more reproducible column performance.

Dithizone and thiothenolytrifluoroacetone[2] were chosen as the chelating agents because these were known to be highly selective for mercuric ion at low pH, and to have a high distribution ratio.

Dithizone gel

The poor durability of the free dithizone gel used earlier has been improved by using the zinc chelate.

At pH 1, the reactions proceed in two steps:

$$[Zn(HDz)_2]_g + 2[H^+]_w = [H_2Dz]_g + [Zn^{2+}]_w$$

$$[H_2Dz]_g + [Hg^{2+}]_w = [Hg(HDz)_2]_g + 2[H^+]_w$$

where H_2Dz represents dithizone, and suffixes g and w indicate the gel and aqueous phases, respectively. The colour change on the column and the analysis of the effluent support this reaction scheme.

The original pink colour of the zinc dithizonate gel turned to blue instantaneously as the acidic sample solution flowed through the column, then an orange zone of mercury dithizonate appeared gradually from the top of the column. Almost all the zinc on the column was eluted in the first few fractions of effluent, whereas the breakthrough of mercury was observed after conversion of the gel into the mercury complex form was complete, as shown in Fig. 1.

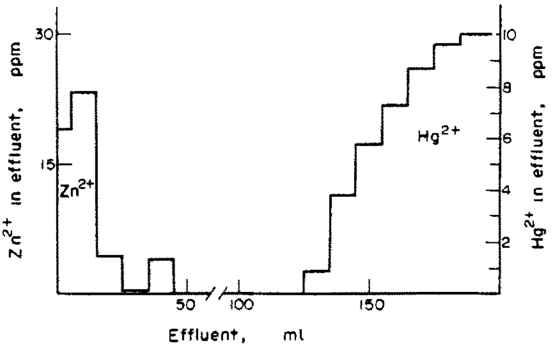

Fig. 1. Extraction of mercury(II) with zinc dithizonate gel column at pH 1.
Gel soaked with 0·068% $Zn(HDz)_2$ solution, flow-rate 1·5 ml/min.

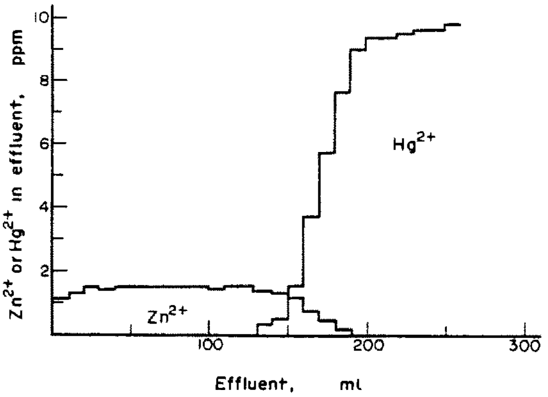

Fig. 2. Extraction of mercury(II) with zinc dithizonate gel column at pH 5·6.
Gel soaked with 0·046% $Zn(HDz)_2$ solution; flow-rate 1·5 ml/min.

At higher pH (5·6), however, the mercuric ion was extracted by direct exchange:

$$[Zn(HDz)_2]_g + 2[Hg^{2+}]_w = [Hg_2Dz_2]_g + [Zn^{2+}]_w + 2[H^+]_w$$

As the reaction proceeded, zinc ion was gradually released from the column whilst the mercuric ion was being extracted mainly as the secondary complex. Accordingly, the original pink colour of the column turned to orange-red from the top. This reaction scheme is also supported by the results shown in Fig. 2.

Mercuric ion extracted as the primary complex at low pH could be easily back-extracted by simply eluting with 1*M* hydrobromic acid or 8*M* hydrochloric acid, by analogy with the batch extraction process.[4] However, mercury extracted as the secondary complex, could not easily be back-extracted with these eluents.

Thus, extraction at low pH was preferable for preconcentration of traces of mercury, because of the higher selectivity as well as the quantitative recovery of mercury by the back-extraction, although the extraction capacity is only about half that at the higher pH.

The selectivity of dithizone for mercury becomes higher as the pH is decreased, and only metal ions such as palladium, silver, copper and mercury are complexed in a fairly acid (0·1–0·5*N*) solution.[4] On the other hand, the interference from halide ions becomes serious with decreasing pH. For example, the extraction of mercury from sea-water is quantitative at pH 2 but incomplete at pH 1.

Table 1 illustrates the preconcentration of mercury from synthetic and natural sea-waters spiked with a trace level of mercury. Sample solution, adjusted to pH 2 with sulphuric acid, was passed through the column, and after extraction, the column was treated either with 1*M* hydrobromic acid or 8*M* hydrochloric acid. As shown in the table, hydrobromic acid is more effective as a back-extractant than hydrochloric acid, because less is required for the quantitative recovery of mercury.

Under these conditions, copper may also be extracted by the gel. However, it remains on the column when mercury is back-extracted with 1*M* hydrobromic acid, because of the relatively low formation constant of tetrabromocopper(II) ($\beta_4 = 10^8$ for $CuBr_4^{2-}$ and $\beta_4 = 10^{21}$ for $HgBr_4^{2-}$).[5]

STTA gel

The extraction behaviour of mercuric ion with STTA has been investigated in some detail,[6,7] and the selectivity of STTA for heavy metal ions was found to be similar

Table 1. Extraction at pH 2 and back-extraction of mercury (dithizone gel column)

	Synthetic sea-water			Natural sea-water		Synthetic sea-water		Natural sea-water		
Concn. of Hg, *ppm*	1	0·6	0·1	0·1	0·05	1	0·1	0·5	0·1	0·05
Amount passed, *ml*	125	500	1000	1000	2000	250	1000	500	1000	2000
Flow-rate, *ml/min*	2·1	3·3	4·2	4·2	5·0	1·7	2·3	3·8	2·3	2·1
Total amount of Hg, μg	120	296	99	99	99	250	100	250	100	100
Eluent	$1M$ HBr (flow-rate 1 ml/min)					$8M$ HCl (flow-rate 1 ml/min)				
Volume, *ml*	30	10	20	20	10	50	30	30	40	40
Hg recovered, μg	115	290	95	100	96	254	106	251	95	101
Recovery, %	97	99	96	102	98	102	106	100	95	101
Concentration factor	4	50	50	100	200	5	33	17	25	50

Table 2. Extraction at pH 4 and back-extraction of mercury (STTA gel column, flow-rate 1·5 ml/min)

	Synthetic sea-water				Natural sea-water			
Concn. of Hg, *ppm*	1·0	0·1	0·05	0·02	0·1	0·05	0·02	0·01
Amount passed, *ml*	500	1000	2000	2500	2000	2000	2500	2500
Total amt. of Hg, μg	500	100	100	50	200	100	50	50
Volume of eluent, *ml*	50	25	10	10	25	10	10	10
Hg recovered, μg	483	99	86	34	192	84	32	27
Recovery, %	96·6	99·0	86·0	68·0	96·2	84·0	66·0	54·0
Concentration factor	10	40	200	250	80	200	250	500

to that of dithizone. Thus, mercuric ion can be selectively extracted with STTA from $\geq 1N$ sulphuric acid.

The capacity of the STTA gel column increased linearly with increasing concentration of STTA in the range 6–20 × $10^{-3}M$, indicating the formation of a 1:2 (metal: ligand) chelate. With $0{\cdot}02M$ STTA gel, an extraction capacity of 4·5 μeq/ml of gel bed was obtained. At a much higher STTA concentration, such as $0{\cdot}1M$, some STTA tends to leak into the aqueous phase during the column operation, although a higher extraction capacity such as 19 μeq/ml is attained, a value comparable with that obtained on the dithizone-impregnated polyurethane foam column.[8]

The stability constant of Hg–STTA seems to be slightly lower than that of mercury dithizonate, because mercury can be back-extracted from the STTA gel column with a mixture of 40 ml of $0{\cdot}05M$ sulphuric acid and 10 ml of 10% potassium bromide solution. This eluent will not back-extract mercury from the dithizone gel.

When up to 500 μg of mercury on the column is eluted with this mixture at a flow-rate of 1·5 ml/min, all the mercury is found in the first 50 ml of effluent.

The lower stability constant of the mercury STTA complex also means that the interference from halide ions is more serious. Thus, with the STTA gel quantitative extraction and recovery of mercury from sea-water required a pH $\geq$ 4.

Table 2 shows the result of the preconcentration of mercury from synthetic and natural sea-waters spiked with a low level of mercury. Samples were adjusted to pH 4 with sulphuric acid and passed through the column at a flow-rate of 1·5 ml/min. The rather poor recovery for 0·05 ppm Hg or less may be due to loss of mercury from the sample solution during storage, which is often experienced with very dilute mercury solutions.[9]

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Summary—Mercury(II) at the sub-ppm level is selectively trapped on a column packed with cross-linked polystyrene gel beads soaked with zinc dithizonate or thiothenoyltrifluoroacetone. Mercury trapped on the beads can be back-extracted into the aqueous phase with a hydrogen halide solution. Mercury in sea water at ppm or ppM level has been successfully preconcentrated by this procedure.

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PICOLINALDEHYDE 4-PHENYL-3-THIOSEMICARBAZONE AS A SPECTROPHOTOMETRIC REAGENT FOR THE SELECTIVE DETERMINATION OF SMALL AMOUNTS OF COBALT IN THE PRESENCE OF IRON

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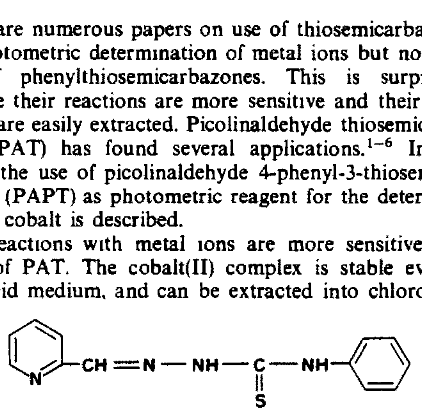
There are numerous papers on use of thiosemicarbazones for photometric determination of metal ions but none on use of phenylthiosemicarbazones. This is surprising, because their reactions are more sensitive and their complexes are easily extracted. Picolinaldehyde thiosemicarbazone (PAT) has found several applications.[1–6] In this paper, the use of picolinaldehyde 4-phenyl-3-thiosemicarbazone (PAPT) as photometric reagent for the determination of cobalt is described.

Its reactions with metal ions are more sensitive than those of PAT. The cobalt(II) complex is stable even in very acid medium, and can be extracted into chloroform.



PAPT

The classical reagents[9] for determining cobalt have various disadvantages. In recent years, numerous spectrophotometric determinations of cobalt have been proposed[10,11] but none has entirely solved the problem.

EXPERIMENTAL

Reagents

Picolinaldehyde 4-phenyl-3-thiosemicarbazone solutions. Make 0.1 and 0.05% w/v solutions in dimethylformamide, and 0.05% in chloroform.

Standardized cobalt solution.

Buffer solution, pH 4.7. Dissolve 56.0 g of sodium acetate and 25.0 ml of glacial acetic acid in water and dilute to a litre.

Dowex 50-X8 resin, sodium form.

All solvents and reagents were of analytical grade.

Synthesis of the reagent

4-Phenyl-3-thiosemicarbazide (4.6 g) was dissolved in 150 ml of hot ethanol and added to 3.0 g of picolinaldehyde in 35 ml of ethanol. The mixture was refluxed for 2 hr, and allowed to cool to room temperature. The yellow crystalline product was filtered off and recrystallized from ethanol. The yield was >80% (m.p. 204–205°: found C 60.8%, H 4.6%, N 21.8%, S 12.8%; calculated for $C_{13}H_{12}N_4S$; C 60.91%, H 4.71%, N 21.85%, S 12.50%).

Properties of the reagent

PAPT is sparingly soluble in water, moderately soluble in chloroform (4.01 g/l.), ethanol (2.91 g/l.), methanol (4.43 g/l.) and nitrobenzene (9.36 g/l.), and very soluble in dimethylformamide (168.20 g/l.) at room temperature.

Infrared spectra were obtained (KBr discs), and the bands assigned (cm^{-1}) to the stretching vibrations of —NH— (3300 s and 3110 m) >C=N (1595 s and 1540 s), and >C=S (1105, 1075, 1040 m and 835 w).

The ultraviolet spectrum of an aqueous solution of the reagent, in neutral medium, shows an absorbance maximum at 318 nm. This band undergoes a bathochromic shift to 356 nm in acidic medium, and in alkaline medium to 330 nm. Phillips and Merritt's method[12] was used for determination of the ionization constants, in 2% ethanol–water medium (1 ml of $2 \times 10^{-3}M$ PAPT solution in ethanol, diluted to 50 ml with distilled water). The values found were $pK_1 = 3.66$, $pK_2 = 10.47$.

Reactions with metal ions

The reactions of 36 ions with PAPT were tested at various pH values. The samples were prepared in 50-ml volumetric flasks, with 2 or 10 ppm of metal ion, 20 ml of 0.05% PAPT solution in dimethylformamide, 10 ml of buffer solution and dilution to 50 ml with distilled water; the spectrum from 350 to 700 nm was measured against a reagent blank. The most important results are summarized in Table 1.

Recommended procedures for the determination of cobalt(II)

In weakly acid medium. To a cobalt solution (10–100 μg of Co) in a 50-ml volumetric flask, add 20 ml of 0.05% PAPT solution in dimethylformamide, 10 ml of pH 4.7 acetate buffer, 10 ml of 0.5*M* potassium chloride and dilute to the mark with water. Measure the absorbance in 1-cm cells at 390 nm against a reagent blank.

In strongly acid medium. Place the cobalt solution (25–100 μg of Co in not more than 10 ml) in a 50-ml standard flask. Add 0.1 g of ascorbic acid, 10 ml of 0.1% PAPT solution in dimethylformamide, 10 ml of 2*M* hydrochloric acid and 10 ml of 0.5*M* potassium chloride and dilute to volume. Measure the absorbance, in 1-cm cells, at 430 nm against the reagent as blank.

By extraction of the complex. Place the sample solution, containing up to 20 μg of Co, in a separating funnel. Add 2 ml of pH 4.7 acetate buffer, 2 ml of 0.5*M* sodium perchlorate and dilute to 10 ml with water. Extract with 10 ml of 0.05% PAPT solution in chloroform, with vigorous shaking for 2 min; transfer the chloroform layer into a 25-ml calibrated flask, dilute to the mark with chloroform and dry with anhydrous sodium sulphate. Measure the absorbance at 400 nm against a blank obtained by extraction in the same way.

Determination of cobalt in steels. Dissolve 0.25 g of steel in 30 ml of *aqua regia* under reflux. Dilute the solution to 100 ml in a standard flask with distilled water. Analyse an aliquot of this solution by the "strongly acid medium" method. Any silica or tungstic acid precipitated should be filtered off.

RESULTS AND DISCUSSION

PAPT is amphoteric, with protonation of the ring nitrogen atom, and/or dissociation of a proton from the

Table 1. Characteristics of PAPT complexes in solution

Metal ion	pH	λ_{max}, *nm*	$10^{-3} \times \varepsilon$, *$l \cdot mole^{-1} \cdot cm^{-1}$*	p*D**	Colour
Ag	10	384	1.2	3.6	yellow
Hg(I)	4.5	380	19.1	5.1	yellow
Hg(II)	4.5	384	31.0	5.3	yellow
Au(III)	10	370–380	25.6	5.2	yellow
V(V)	4.5	440	7.1	5.9	orange–yellow
Pb	4.5	380–390	10.8	5.6	yellow
Pd(II)	10	390	21.5	5.3	yellow
Zn	4.5	390–400	32.7	6.1	yellow
Pt(IV)	4.5	400–410	23.4	5.3	orange–yellow
Cu(II)	4.5	400–410	18.4	6.3	yellow–green
	10	380–390	31.8	6.3	yellow–green
Cd	4.5	390	39.5	5.6	yellow
Co(II)	4.5	390	29.9	7.6	yellow
Co(II)	4.5	390	29.9	7.6	yellow
Ni	4.5	380–390	32.3	7.6	yellow
Fe(III)	4.5	390–400	35.6	6.6	yellow
Fe(II)	4.5	380	38.7	6.8	yellow
		620	6.0	6.6	green
	3.0	530–560	4.1	6.0	red–violet

* p*D* = −log *D*; *D* = detection limit, *g/ml*.

thiol group. It is stable in dimethylformamide–water solution. Reducing agents do not affect it, but oxidizing agents, such as potassium persulphate and hydrogen peroxide, destroy it.

The benzene ring substituted on the thiosemicarbazone produces an auxochromic effect for the complexes formed, giving better sensitivity than other thiosemicarbazones.[2,13]

Reaction with cobalt

PAPT forms a yellow cobalt(II) chelate at pH 5 and 1, the wavelengths of maximum absorption being 390 and 420 nm, respectively (Fig. 1). The complex is formed rapidly and its absorbance remains stable for at least 24 hr. Reducing and oxidizing agents do not affect the cobalt-complex spectrum.

The complex is retained on a cationic ion-exchanger resin in weakly acidic but not in alkaline medium, probably[14] because of the equilibrium:

$$\mathrm{Co(HPAPT)_2^{2+} = Co(PAPT)_2 + 2H^+}$$

The absorbance–pH graph for the cobalt complex is shown in Fig. 2. The optimum pH range for complex formation is 4.4–6.9, so an acetate buffer is proposed.

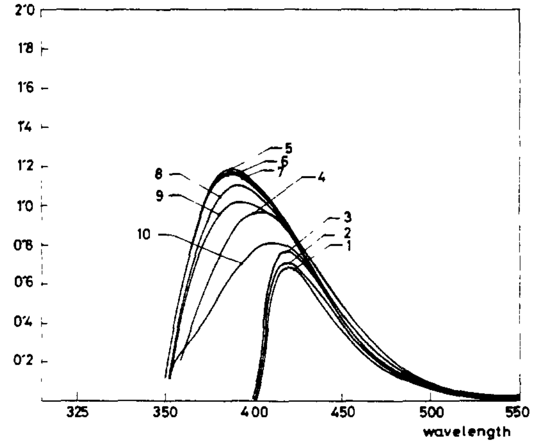


Fig. 1. Absorption spectra of solutions of the PAPT–cobalt complex (2 ppm) at the pH values indicated.

The stoichiometry of the complex is shown by the continuous variations method to be 1:2 metal:ligand at both pH 4.7 and 1.0. Therefore, two different species exist, each having the same cobalt:PAPT ratio. At low pH values the absorbance decreases because of the bathochromic shift of the reagent.

The optimum pH range for extraction of the complex into chloroform is 4–7 and sodium perchlorate is the best salting-out agent.

Analytical applications

In acetate buffer. Beer's law is obeyed at pH 4.7 for 0.2–2 ppm of cobalt and the molar absorptivity is 29.9×10^3 l·mole^{-1}·cm^{-1} (at 390 nm). The optimum concentration range, evaluated by Ringbom's method, is

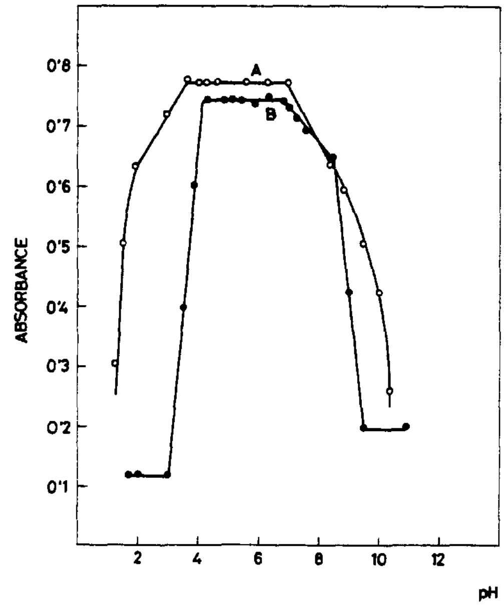


Fig. 2. Absorbance–pH graphs of the PAPT–cobalt complex: A, extracted into chloroform, 2 ppm cobalt (λ_{max} 400 nm); B, in homogeneous medium, 2 ppm of cobalt (λ_{max} 400 nm).

Table 2. Influence of foreign ions in cobalt determination at pH 1

Interference level, *ppm*				
1	2	5	25	50
Au(III)	Sn(II)	Hg(I)	Cr(III)	Pb
Cu(II)		Hg(II)	Ni	
V(V)				
Ag				
Pd(II)				
Pt(IV)				

Bi, W(VI), Ca, Fe(II), Mo(VI), Cd, Sr, Ce(III), Ba, Zn, Mn(II), Be, Al, Li, Rb do not interfere at the 100-ppm level.

Table 3. Determination of cobalt in steel

Steel type	Cobalt, %	
	Added	Found
Cr–Ni Steel I	1.95	1.86
Cr–Ni Steel I	0.97	0.90
Cr–Ni Steel I	0.46	0.43
Cr–Ni Steel I	0.23	0.22
AISI-316T	1.91	1.95
AISI-316T	0.95	0.98
AISI-316T	0.45	0.43
AISI-316T	0.24	0.25
AISI-316E	1.89	1.92
AISI-316E	0.96	0.89
AISI-316E	0.47	0.45
AISI-316E	0.23	0.21

0.2–2 ppm. The relative error (95% confidence limits) is ±0.2%.

The interferences for 1 ppm of cobalt were investigated: 100 ppm of W(VI), Mo(VI), As(III), Th, U(VI), Ca, Ba, Be, Sr, Mg, Rb, Li, PO_4^{3-}, SCN^-, citrate and tartrate, and 50 ppm of Mn(II) and Al ions did not interfere. Ag, Pb, Hg(I), Hg(II), Cd, Bi, Sn(II), Sn(IV), Au(III), Pd(II), Fe(II), Fe(III), Cu(II), Ni, Zn and V(V) ions interfere when they are present in concentrations below 1 or 2 ppm, and Cr in 10 ppm concentration.

In strongly acid medium. This is the most interesting procedure because it removes numerous interferences and, more importantly, the determination of cobalt in the presence of iron is made possible. Beer's law is obeyed between 0.2 and 2 ppm of cobalt. The molar absorptivity at 430 nm is 15.1×10^3 $l \cdot mole^{-1} \cdot cm^{-1}$. Ringbom's method shows that 0.8–1.5 ppm is the minimum-error range. The relative error (95% limits) is ±1.0%.

The interferences at the 1-ppm cobalt level have been investigated; the results are summarized in Table 2. The reaction is selective for cobalt(II) in the presence of up to 1000 ppm of iron.

By extraction. The optimum conditions have been indicated in the *Experimental* section. Beer's law is obeyed between 0.2 and 2 ppm of cobalt and the molar absorptivity at 400 nm is 29.5×10^3 $l \cdot mole^{-1} \cdot cm^{-1}$. A Ringbom graph shows that 0.8–2 ppm of cobalt(II) is the minimum-error range. The relative error (95% limits) is ±0.8%. The interferences are analogous to those observed in the acetate-buffer method.

Determination of cobalt in steels. The technique described above has been applied to the determination of cobalt in spiked samples of Hoepfner Gebr. Chromium Nickel Steel I, AISI 316-T Steel and AISI 316-E Steel*. The results are shown in Table 3 (average of 10 determinations).

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*Chromium Nickel Steel I: Fe 68.15%, Ni 11.84%, Cr 17.77%, Mo 2.15% and C 0.09%. AISI 316-T Steel: Fe 65.1%, Cr 20.7%, Ni 11.4% and Mo 2.8%. AISI 316-E Steel: Fe 64.4%, Cr 19.8%, Ni 13.4% and Mo 2.4%.

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Summary—The characteristics and analytical applications of picolinaldehyde 4-phenyl-3-thiosemicarbazone are described. This compound gives coloured reactions with cobalt(II), iron(II) and (III), nickel(II), copper(II), palladium(II) and other ions, that are much more sensitive than those with picolinaldehyde thiosemicarbazone. The 1:2 yellow cobalt(II) complex has been used for the spectrophotometric determination of cobalt in the presence of iron, and applied to steel analysis.

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STUDY OF LIQUID–LIQUID EXTRACTION OF PERRHENATE WITH CYCLOHEXANONE IN DIFFERENT MEDIA

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The liquid–liquid extraction of ReO_4^- by means of different ketones has been the subject of a number of investigations.[1–15] The advantage of this extraction is that it can be carried out in acidic as well as in neutral or alkaline medium. Only a few investigations on the mechanism of this extraction are available[1,11,13] and it has not been completely elucidated. Cyclohexanone (Ch), which is one of the most useful ketones, has been used in this study. The purpose of the present work was to carry out a more detailed study of ReO_4^- extraction with cyclohexanone, elucidate some aspects of the extraction mechanism, and to show the possibility of separating molybdenum in determination of rhenium in molybdenum ores, concentrates and preparations.

EXPERIMENTAL

Reagents

Stock solutions of rhenium and molybdenum were prepared from $KReO_4$ and $(NH_4)_6Mo_{24}.4H_2O$. Cyclohexanone, b.p. fraction 155–156° was used. Its purity was checked by gas chromatography. All other reagents were of analytical grade.

Apparatus

Absorbance was measured with a CΦ-4 spectrophotometer. Radiometric measurements were carried out with Vakutronic V20 counting equipment. Atomic-absorption measurements were carried out with a Pye-Unicam SP 90B spectrophotometer.

Procedure

Distribution coefficients of rhenium were determined in two ways: radiometrically with ^{186}Re and photometrically by the thiocyanate method.[16] The concentration of rhenium in both phases was measured. Distribution coefficients of molybdenum were determined by means of atomic absorption. Equal volumes of the aqueous and organic phases (5 ml) were shaken in glass centrifuge tubes fitted with ground-glass stoppers. Equilibrium was attained after 5 min and the two phases were separated by centrifugation. The volume changes of the two phases for each point of the extraction curves have been taken into consideration when calculating the distribution coefficients.

RESULTS AND DISCUSSION

Extraction of ReO_4^- from different media

Curves for extraction of ReO_4^- with Ch from aqueous solutions of some mineral acids are shown in Fig. 1. Corresponding curves for aqueous solutions of the corresponding sodium salts and sodium hydroxide are shown in Fig. 2. No data for phosphate medium are presented, because of the low solubility of alkali metal phosphates.

The importance of the salting-out agent is evident. Ions interact with water in different ways depending on their electric charge and radius, affecting the structure of water and its activity[17] to different extents. The non-hydration of NO_3^- and Cl^- helps their own extraction, thus influencing unfavourably the ReO_4^- extraction. Probably, the decrease in extraction at higher acid concentrations is connected with the competitive extraction of the corresponding anions or condensation of perrhenate in the presence of the acids.[18,19]

There is no information about the extraction of ReO_4^- with Ch from solutions of phosphoric acid, hydrochloric acid, sodium carbonate and sodium hydroxide. Distribution coefficients for some other media (sodium sulphate, ammonium sulphate) determined by us differ from the reported values[1] by approximately one order of magnitude but we found their salting-out efficiencies to be in the same order as reported by Gerlit *et al.*,[1] except for the changed places of OH^- and Cl^-.

Choice of diluent

Some "inert" diluents were tested. The most suitable appeared to be benzene and chloroform. Rhenium was extracted with 50% solution of Ch in the latter diluents

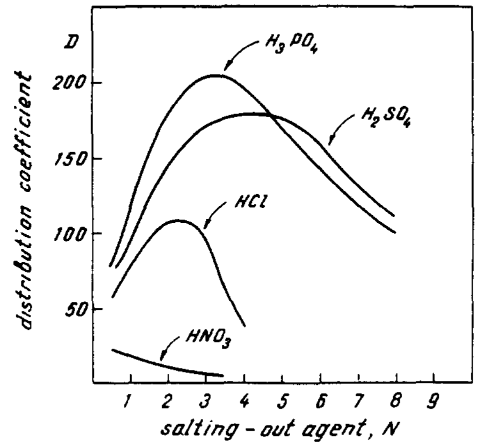

Fig. 1. Distribution of ReO_4^- by extraction with cyclohexanone from aqueous solutions of inorganic acids.

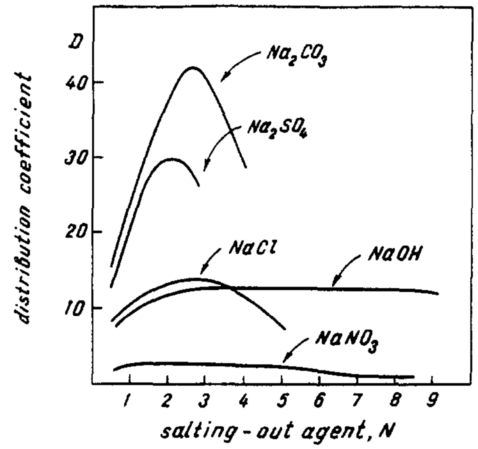

Fig. 2. Distribution of ReO_4^- by extraction with cyclohexanone from neutral and alkaline media.

from 2*N* sulphuric acid with $D = 0{\cdot}17$ and from 2*N* sodium hydroxide with $D = 0{\cdot}004$. The experimental data show that it is possible to carry out back-extraction of Re by adding diluent to the organic phase after the extraction.

Determination of solvation and hydration numbers

Solvation numbers were determined graphically from plots of log *D* *vs.* log [Ch] for different concentrations of the investigated media, using benzene and chloroform as diluents. The fact that irrespective of the nature of the diluent straight lines with equal slopes were obtained is regarded as evidence of the reliability of the result. The same value of the mean solvation number, namely $\bar{s} = 9{\cdot}6 \pm 0{\cdot}6$, with statistical certainty of 95%, was obtained when ReO_4^- was extracted with Ch from solutions of sulphuric acid, lithium sulphate, sodium sulphate and sodium hydroxide of different concentrations. When the extraction is performed from potassium sulphate medium $\bar{s} = 6{\cdot}0 \pm 0{\cdot}1$. Therefore when the cation and anion are both "positively" hydrated,[17] the extraction process proceeds by means of solvation with a greater number of Ch molecules than in the cases when the cation is "negatively" hydrated as in the case of the potassium ion.

Hydration numbers were determined by a modified Fischer method. Titrations were carried out in the presence of small concentrations of methanol and high concentration of pyridine.[20] Thus, the side-reaction between ketone and methanol, causing a liberation of an additional amount of water, was eliminated. The results show that in extraction of 0·02*M* solution of ReO_4^- in the presence of potassium sulphate, sodium sulphate and sodium hydroxide, the solvates which pass into the organic phase are not hydrated. The amount of water in the rhenium-containing extracts is equal to that found in blank tests. Thus, it may be deduced that cyclohexanone solvates the corresponding perrhenate directly without participation of water.

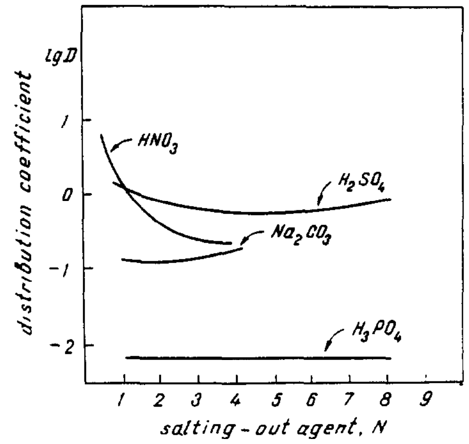

Fig. 3. Distribution of Mo(VI) by extraction with cyclohexanone from aqueous solutions of acids and sodium carbonate.

The extract obtained after extraction of ReO_4^- from sodium sulphate and sodium hydroxide medium was evaporated and the content of sodium and rhenium in the dry residue was determined. The two ions were present in amounts corresponding to their stoichiometric quantities in $NaReO_4$. Other evidence of the solvate mechanism of extraction of ReO_4^- from neutral and alkaline medium is the fact that anhydrous $NaReO_4$ is very soluble in cyclohexanone. The proposed solvate extraction mechanism does not agree with the suggestions of some other authors.[13]

When the extraction is carried out from 2*N* sulphuric acid, the differences in the water content of the blank test extracts and of those containing rhenium are statistically significant (according to Kaiser and Specker's criterion) and the hydration number found is 7. In this case, solvation of the protons takes place by means of bridge water molecules.

Extraction of Mo(VI) from different media

Similar investigations were carried out with Mo(VI) and nitric acid, sulphuric acid, phosphoric acid and sodium carbonate media. Extraction curves are shown in Fig. 3. It is seen that phosphoric acid solutions provide the best conditions for separation of rhenium from molybdenum. The separation coefficient in 3–4*N* phosphoric acid is $\beta = 3 \times 10^4$.

Rhenium is completely and selectively extracted from concentrates of high molybdenum content if extraction is carried out from sodium sulphate medium in the presence of the solid phase obtained after the decomposition of the sample with peroxide.

Determination of rhenium in molybdenum concentrates

A sample of molybdenum concentrate containing 5–10 μg of rhenium is mixed with 1 g of sodium peroxide in an iron or nickel crucible and the mixture is kept for 30 min in a molten state in a muffle furnace. When the melt is cool, 5 ml of water are added and the crucible is left for 30 min on a boiling water-bath. Then the contents of the crucible are transferred by means of 5 ml of 10% sodium sulphate solution into a centrifuge tube fitted with a ground-glass stopper. Extraction is carried out with 10 ml of Ch from sodium carbonate and sodium sulphate solution in the presence of the solid phase containing the major part of the molybdenum in the form of slightly soluble molybdates. The phases are separated by centrifugation. The organic phase is transferred into a separatory funnel, 10 ml of water are added and rhenium is back-extracted after addition of an equal volume of chloroform. Rhenium is determined in the aqueous phase by the thiocyanate method. The method has been applied to the determination of rhenium in non-standard molybdenum concentrates. A mean Re value of 92·8 μg/g was obtained with relative standard deviation 2·4% (9 replicates). The absence of a methodical error was checked by standard addition. The results for rhenium content are in very good agreement with the results obtained by other techniques for decomposition of the concentrate and extraction of rhenium.

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TITRATION OF METHYLENE BLUE WITH CHLOROMOLYBDATE(III)

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Knecht and Atack[1] titrated molybdenum(III) with a standard solution of Methylene Blue, the colour of the dye indicating the end-point. According to them the molybdenum(III) is oxidized to molybdenum(IV) and then to molybdenum(V). On the other hand Treadwell and Nieriker,[2] in their potentiometric titration of molybdenum(III) with Methylene Blue, observed only one break, corresponding to the oxidation of molybdenum(III) to molybdenum(V). The titration curve showed no indication of formation of molybdenum(IV) as an intermediate stage. Molybdenum(III) is known to exist in two forms (green and orange-red). According to Sagi and Rao[3,4] the green form is cationic aquomolybdenum(III) chloride and the orange-red form is anionic chloromolybdate(III). The type of molybdenum(III) obtained depends upon the method of preparation. Aquomolybdenum(III) chloride has a lower formal redox potential than chloromolybdate(III).[5,6] The two species behave differently with different oxidants.[3,7] The green form is stable only at hydrochloric acid concentrations $<4M$ whereas the orange-red form is stable in all concentrations of the acid.

The reaction of the two forms of molybdenum(III) with Methylene Blue has now been re-examined.

EXPERIMENTAL

Reagents

Methylene Blue solutions were standardized with a standard solution of titanium(III) chloride.[8,9]

Aquomolybdenum(III) chloride and chloromolybdate(III) solutions were prepared by reducing ammonium molybdate solution in $3M$ and $8M$ hydrochloric acid respectively, in a Jones reductor, and stored under carbon dioxide. They were standardized against standard cerium(IV) sulphate *via* oxidation with excess of ferric alum solution and titration of the iron(II) with ceric sulphate, with ferroin as indicator.[10]

Procedure

Known volumes of chloromolybdate(III) and aquomolybdenum(III) chloride were titrated with standard Methylene Blue solution in 1–$8M$ and 0.5–$4M$ hydrochloric acid media respectively, until the solution showed the colour of Methylene Blue. The orange-red form first became straw yellow, then pale green and finally blue; the green form first became reddish brown, then pale bluish green and finally blue. The end-points for the orange-red form were

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The titrations were repeated potentiometrically. Titration of chloromolybdate(III) in 6–8*M* hydrochloric acid was best, because stable potentials were obtained in 2-3 min after each addition of titrant and a potential jump of 100 mV was obtained exactly at the visual end-point, whereas in 2–5*M* hydrochloric acid stable potentials were obtained only after waiting for 5–10 min after each addition of titrant and the potential jump was only 50–60 mV. With aquomolybdenum(III) chloride no potential jump was obtained until the solution had become blue, and 5–10 min were required for the potential to become stable after addition of the titrant, so satisfactory titrations could not be carried out.

Titrations of Methylene Blue with chloromolybdate(III) and aquomolybdenum(III) chloride in similar acid conditions by visual and potentiometric methods gave results similar to those for the titrations described above.

RESULTS AND DISCUSSION

The results obtained in the visual and potentiometric titrations of chloromolybdate(III) (*e.g.*, Fig. 1) showed that in 6–8*M* hydrochloric acid media the Methylene Blue is reduced to leuco-Methylene Blue and molybdenum(III) is oxidized to molybdenum(V) only. In less concentrated acid (2–5*M*) a fraction of the molybdenum(V) formed is oxidized to molybdenum(VI), the fraction increasing with decrease in acid concentration. This is expected from the variation of the formal redox potential of the Mo(VI)/Mo(V) couple in media of low hydrochloric acid concentration,[11] and confirms the results obtained by Sagi and Rao.[12] The results of the reverse titrations confirm these conclusions.

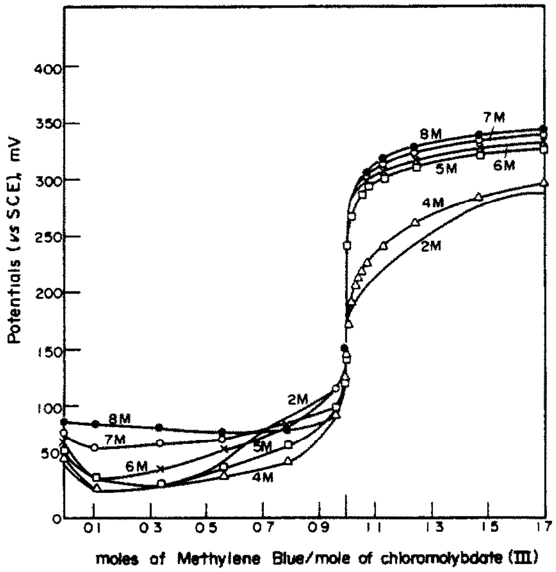

Fig. 1. Potentiometric titrations of chloromolybdate(III) with Methylene Blue in hydrochloric acid media.

The results obtained in the visual titration of aquomolybdenum(II) chloride with Methylene Blue show that oxidation to molybdenum(V) is incomplete even though aquomolybdenum(III) chloride is a more powerful reductant than chloromolybdate(III) (according to the formal redox potentials).

We consider that only 6–8*M* hydrochloric acid media are suitable for titration of Methylene Blue with molybdenum(III), which itself must be in the form of chloromolybdate(III).

Other reductometric reagents available for the direct titration of Methylene Blue are titanium(III) chloride,[8,9] chromium(II) sulphate,[13,14] iron(II) sulphate[15] and ascorbic acid.[16] Of these the titration with iron(II) is done slowly, with a 1-min wait after each addition of titrant. The titrations with ascorbic acid and titanium(III) require higher temperatures. Titanium(III) chloride and chromium(II) sulphate are highly susceptible to atmospheric oxidation whereas chloromolybdate(III) is less susceptible,[17] and the titrations with chloromolybdate(III) now proposed can be carried out at room temperature.

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Summary—The reaction of Methylene Blue with aquomolybdenum(III) chloride and chloromolybdate(III) in hydrochloric acid media has been investigated. Chloromolybdate(III) can be satisfactorily used as a reductometric titrant for Methylene Blue in 6–8*M* hydrochloric acid medium. The end-point can be detected either potentiometrically or visually. Aquomolybdenum(III) chloride is not useful as a titrant for this estimation.

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SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM WITH ERIOCHROME CYANINE R IN ANALYSIS OF SILICATES

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Samples containing large amounts of Ca and Mg are sometimes analysed by the classical technique, but this is prone to errors because of co-precipitation and solubility effects.[1] The alkaline earth metals are so easily co-precipitated with the ammonia group precipitate that reprecipitation and adequate washing of the precipitate is essential if high results for alumina and low results for Mg and Ca are to be avoided. Careful control of pH is also essential during the ammonia group precipitations to avoid alumina escaping precipitation and then being brought down in the oxalate or, more probably, the phosphate precipitations. For this reason the method is inconvenient in a routine laboratory.[2]

Most complexometric methods involve the determination of lime and of lime plus magnesia, the magnesia being obtained by difference, but difficulties arise in the lime determination and the complexometric determinations are not completely satisfactory either.[2–4]

The determination of small amounts of magnesium is often based on lake formation or indirect photometric determination.[3,4] Dyes used include Titan Yellow,[5–7] curcumin, 1,2,5,8-tetrahydroxyquinone, *etc.* It is very difficult to obtain accurate and reproducible results with lake-forming compounds because of variations in dyestuff samples, impurities in protective colloids, precipitation of the lake, rapid fading of the colour, and the uncertain effect of other metals.[3] The indirect photometric procedures are mostly based on the gravimetric methods, but so many manipulations are involved that there is a very great possibility of error.[3]

The development of the EDTA titration of magnesium with Eriochrome Black T as indicator suggested the use of this dye for a photometric procedure.[8] Interference by the alkaline earth metals is eliminated by precipitating them with sodium tungstate. Interference by Zn, Cu, Cd and Co is eliminated with potassium cyanide. Fluoride, phosphate, sulphate and oxalate should be absent.[3] Similar methods which utilize the formation of a coloured magnesium complex employ 2-[2-hydroxy-3-(2,4-xylylcarbamyl]-1-naphthylazophenol and its sulphonate as reagents.[9,10] Iron, copper and aluminium interfere by reacting with the reagent.

Magnesium can be determined in low concentration by spectrophotometric measurement of its 8-hydroxyquinoline complex. The magnesium must be almost completely isolated by extraction before its determination although the interference due to small amounts of Ni, Co, Cu, Ag, Au and Pt can be eliminated by masking with sodium cyanide.[3,11,12]

This paper describes an alternative method that is applicable to silicate materials that are low in iron and aluminium and is more sensitive and less subject to interference from common diverse ions. In a previous paper[13] we have shown that Mg and Eriochrome Cyanine R ERCR form a true solution of a well-defined coloured complex and that the reaction is complete in the pH range 11.0–11.5. The same reaction has now been used for direct magnesium determination in silicate analysis.

EXPERIMENTAL

Reagents

ERCR solution 0.01*M*. Dissolve 5.36 g of ERCR in 10 ml of nitric acid (1 + 1) and add 100 ml of water, 8 g of sodium chloride, 8 g of ammonium nitrate and dilute to 1 litre with water. This solution is stable for months.[14]

Standard magnesium solution, 0.001*M*. Dissolve 0.2033 g of $MgCl_2 \cdot 6H_2O$ in 1 litre of distilled water and standardize gravimetrically if necessary.[1]

Buffer solution. Mix 0.2*M* ammonia and 0.2*M* ammonium chloride in 32:1 ratio and add 25 ml of 25% ammonia solution (sp.gr. 0.91) per litre.

Spectral characteristics and optimum conditions

In Fig. 1 curves A and B show the absorption spectrum of ERCR in the presence and absence of magnesium at pH 11.5 in ammonium buffer solution. As shown earlier,[13] complex formation is complete in this medium and the absorbance is independent of pH in the range 11.0–11.5. The order of addition of reagents is immaterial. At pH 11.5 (chosen for the present work), a 1.5-fold molar excess of reagent is sufficient for complete complex formation, but it is better to use at least a 30-fold excess. The colour is essentially completely developed in 10 min and then remains unchanged for at least 1 hr.

Calibration curve and procedure

Weigh accurately a 0.5-g ground sample into a platinum dish. Decompose the sample and determine the silica.[1] After removal of the silica with hydrofluoric acid fuse the residue with 2 g of potassium pyrosulphate. Cool, add

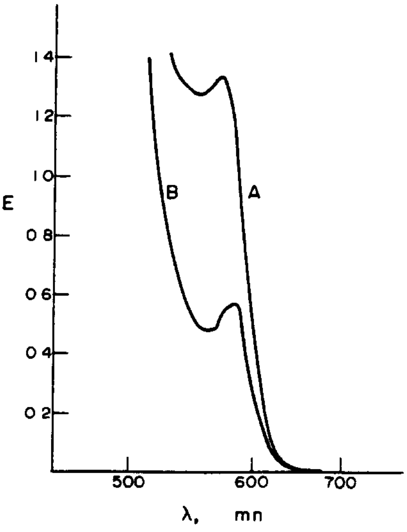

Fig. 1. Absorption spectra of (A) $1.5 \times 10^{-3}M$ ERCR/$1.5 \times 10^{-4}M$ Mg(II); (B) $1.5 \times 10^{-3}M$ ERCR.

water and 10 ml of 5% sulphuric acid to dissolve the fusion cake. Add the solution to the filtrate from the silica determination in a 500-ml volumetric flask. Dilute to the mark and pipette 100 ml into a 250-ml beaker. Add 1 or 2 drops of conc. nitric acid, boil for 1–2 min, add 1–2 g of ammonium chloride, precipitate R_2O_3 by adding ammonia solution (1 + 1) dropwise (pH ~ 8, universal indicator), keep warm for about 10 min and filter (coarse paper) collecting the filtrate in a 250-ml volumetric flask, cool and dilute to volume. Pipette an aliquot of 1 or 5 ml, depending on the magnesium content, into a 50-ml volumetric flask, add 7.5 of 0.01*M* ERCR, 25 ml of buffer solution and dilute to volume. Determine the absorbance of the solution at 570 nm against a blank as reference, using 30-mm cells.

To prepare the calibration curve transfer 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 ml of the standard magnesium solution to 50-ml volumetric flasks, add to each flask 5 ml of the reagent blank, 7.5 ml of ERCR solution, 25.0 ml of buffer solution and dilute to volume with water. Determine the absorbance of each solution at 570 nm against a blank as reference, using 30-mm cells. Find the equation of the line $\Delta A = a + bC_{Mg}$ and test the constant a for equality to zero.[15,16]

The calibration curve should be linear over the range 2×10^{-5}–$10^{-4}M$ magnesium.

RESULTS AND DISCUSSION

Accuracy

The accuracy was tested in two principal ways: (*a*) by the absolute method in which a synthetic sample was employed, and (*b*) by the use of standard samples. Various amounts of magnesium were used because the determinate errors in the procedure may be a function of the amount present.[17,18] Many replicate analyses for Mg in synthetic samples, covering the range of concentration over which the method is applicable, when analysed by the method of least squares gave a linear relation between amount found and amount added, passing through the origin, with a slope equal to unity. Statistical analysis[15,16] showed the procedure to be free from both a constant bias and an error of relative type, *i.e.*, one that increases with the amount of Mg.

Determination of the accuracy of a method by use of pure solutions is only the first step in evaluation of the accuracy.[17] The effect of accompanying species in varying amounts must also be examined. Such a programme is so laborious that it is rarely, if ever, carried out to its full extent.[17] One way of reducing the labour is to consider the determination in a specified concentration range in a material of more or less fixed composition, both with respect to the elements which may be present and their relative amounts. By the use of suitable synthetic samples the effect of foreign elements on the Mg determination was thus systematically evaluated. We analysed four samples containing 12, 18, 24 and 48 μg of Mg, and various amounts of the elements to be studied for possible interference. The amounts of magnesium found from five separate determinations were compared by the *Student* criterion with the amount of magnesium taken. The investigation showed that the effect of the foreign substances is a function of their relative contents; there was no effect when the concentrations (in a notional "sample") were less than: CaO ~ 16%, MnO ~ 2%, ZnO ~ 2.0%, Al_2O_3 ~ 1%, Fe_2O_3 ~ 1.0% and TiO_2 ~ 1%. Thus we may conclude that our procedure is applicable to silicate glasses containing sodium, potassium, calcium and magnesium as major constituents as well as to feldspars, clays and others low in alumina and iron oxides.

The use of liquid synthetic samples does not always suffice, however.[17] We therefore also used standard samples of glass, clay, feldspars, china clay and sands. The results for glass are given in Table 1. The distribution was normal and a statistical analysis should be compatible with these data. We thought at first that the existence of a relative type of error in the data was related to the amounts taken for analysis. Therefore, to determine the adequacy of the sample size we tested statistically the significance of the differences between the mean values of different subsample volumes for each glass. For this purpose we compared the standard deviations of the subsamples by the Cochran criterion. The estimates were so close [see Table 2, data for the *G*-criterion—$G_{found} < G(95, k = 4, f = 4) = 0.68$] that the differences could have arisen by chance. Since our results were classified into more than two groups we also utilized analysis of variance.[16] The *F*-values showed (see Table 1) that there is no evidence for bias at the four levels of concentration [$F_{found} < F(95, f_1 = 3, f_2 = 16) = 3.24$]. Finally, the mean values for each subsample size were compared with the true composition by means of the *t*-criterion. The difference appears not to be greater than can be attributed to chance, since $t_{found} < t(95, f = 19) = 2.09$. As mentioned, since the different subsamples correspond to samples of different sizes, the results of Table 1 reveal that there were no determinate errors in the determination of MgO in glasses. These data were also used to test the accuracy of the method, expressed by the difference ΔX between the contents found and the true values μ (given in Table 1 as $\Delta X/\mu\%$). The precision of the procedure was measured by the coefficient of variation V_x, also given in the Table.

The proposed method was applied to the analysis of a series of samples. Table 2 shows the results of five repli-

Table 1. Effect of the subsample volume on the results of the magnesium determination

Sample	1 ml %MgO	3 ml %MgO	5 ml %MgO	7 ml %MgO	S %MgO	V_x %	$\Delta X/\mu$, %	Mean value found, %	True value, %	G_{found}	F_{found}	t_{found}
Glass A	3.95	3.95	3.91	3.89	0.076	1.9	0.51	3.92 ± 0.09	3.90 ± 0.08	0.28	0.71	1.1
Glass B	2.75	2.77	2.81	2.78	0.051	1.8	0.36	2.78 ± 0.06	2.77 ± 0.07	0.38	1.28	0.79
Glass C	4.54	4.54	4.51	4.53	0.038	0.8	0.00	4.53 ± 0.05	4.55 ± 0.06	0.58	0.70	0.00

Composition of the samples

	A	B	C
SiO_2	72.6	72.4	71.8
Al_2O_3	1.05	2.38	1.16
Fe_2O_3	0.07	0.15	0.11
CaO	7.20	5.50	6.56
MgO	3.90	2.77	4.53
Na_2O	14.96	14.96	14.68
K_2O	trace	0.96	0.66
SO_3	0.32	0.27	0.45

Table 2. Comparison of the results obtained by the proposed method with the complexometric determination of MgO in different materials

Sample	True value, %	The proposed method					Complexometric method				
		x, %	s, %	V_x, %	$\Delta X/\mu$, %	Total error, %	x, %	s, %	V_x, %	$\Delta X/\mu$, %	Total error, %
Clay	0.63 ± 0.02	0.65	0.027	4.0	3.2	12	0.72	0.220	30.0	14.4	84
Feldspar	0.19 ± 0.01	0.20	0.013	6.5	5.3	19	0.27	0.028	10.4	42.0	72
Sand	0.15 ± 0.01	0.15	0.014	9.4	0.0	19	0.16	0.067	42.0	6.7	96
China clay	0.06 ± 0.007	0.06	0.009	15.0	0.0	30	0.09	0.009	10.0	3.4	80

cate magnesia determinations in these samples by the proposed method and by the complexometric method. The standard deviation of the first method s_1 was compared with that of the other, s_2, in order to compare the precisions of the two procedures. The variance ratio F exceeded the tabulated values. Hence there is evidence of a real disparity between the two estimates and the precision of the proposed method is superior to that of the other (see also the coefficient of variation V_x). The evidence for a positive bias of the volumetric method may here be regarded as conclusive. The results of Table 2 also give a view of the total errors of both procedures.[19] They were calculated as the ratio of the sum of the absolute error and twice the standard deviation to the true value.

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Summary—A simple and sensitive method for determining magnesium in silicates low in aluminium and iron (glass, clay, feldspars, *etc.*) is presented. The method is applicable in the classical procedure of silicate analysis and magnesia is determined with Eriochrome Cyanine R in an ammonium buffer solution at pH 11.5. There is no interference by elements likely to occur in such samples. The accuracy and the precision of the proposed method are superior to those of the complexometric method. The limit of detection is 0.007% MgO.

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LIQUID ION-EXCHANGE MEMBRANE ELECTRODE FOR LITHIUM

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(*Received* 14 *July* 1975. *Accepted* 14 *October* 1975)

During our work on liquid-membrane ion-selective electrodes it was observed that n-decanol alone showed a slight potentiometric selectivity for lithium ion relative to sodium ion. The electrode, while exhibiting linear near-Nernstian response over three decades of activity, has a relatively poor selectivity with respect to univalent cations. However, the observed potentiometric selectivity coefficient for lithium relative to sodium is 0.33 which is the same as that of the recommended ion-selective electrode for the direct determination of lithium in the presence of

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Sample	True value, %	The proposed method					Complexometric method				
		x, %	s, %	V_x, %	$\Delta X/\mu$, %	Total error, %	x, %	s, %	V_x, %	$\Delta X/\mu$, %	Total error, %
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LIQUID ION-EXCHANGE MEMBRANE ELECTRODE FOR LITHIUM

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During our work on liquid-membrane ion-selective electrodes it was observed that n-decanol alone showed a slight potentiometric selectivity for lithium ion relative to sodium ion. The electrode, while exhibiting linear near-Nernstian response over three decades of activity, has a relatively poor selectivity with respect to univalent cations. However, the observed potentiometric selectivity coefficient for lithium relative to sodium is 0.33 which is the same as that of the recommended ion-selective electrode for the direct determination of lithium in the presence of

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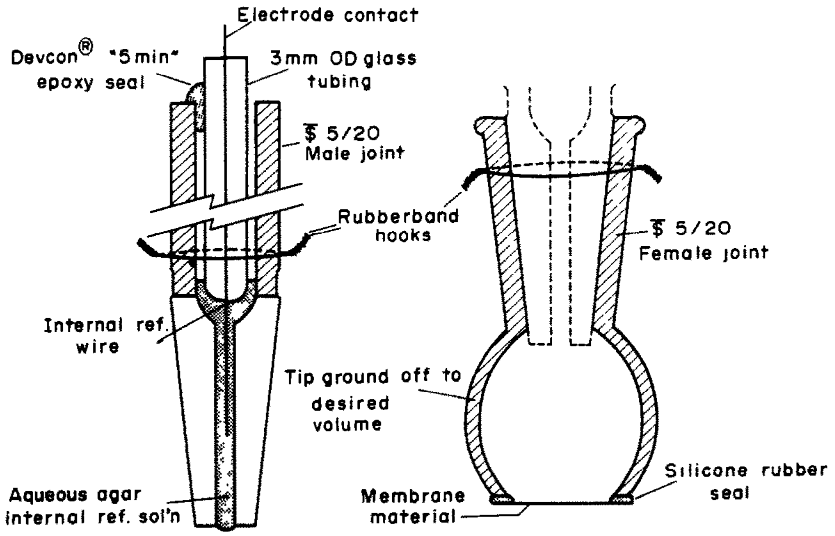

Fig. 1. Construction details of the versatile liquid ion-exchange electrode body.

sodium, a glass-membrane electrode made from LAS 15-25 glass.[1,2] This response should be of interest to researchers using liquid ion-exchange membrane electrodes with long-chain alcohols as the ion-exchanger solvent.

A good approximation to the EMF of an electrochemical cell containing an ion-selective electrode with a fixed internal electrode is given by an extended Nikolsky equation[3]

$$E_{\mathrm{cell}} = E' + \frac{RT}{z_i F} \ln \left[a_i + \sum_{j=1}^{N} K_{i,j}^{\mathrm{Pot}} a_j^{z_i/z_j} \right]$$

where E_{cell} is the measured potential of the cell containing the ion-selective electrode, E' is constant for a particular electrode–reference pair and includes contributions from the internal and external reference electrodes and junction potentials, R, T, F, and z_i have the usual meanings, a_i is the activity of the primary ion in the sample solution, $K_{i,j}^{\mathrm{Pot}}$ is the potentiometric selectivity coefficient and a_j is the activity of an interfering ion in the sample solution.

The electrode body developed during this study allows easy removal of the tip for exchanging membranes, rinsing and refilling of exchanger, and removing water or bubbles. The exchanger volume can be reduced by grinding down the tips, which is useful if the exchanger material is expensive or difficult to obtain. If stocks are kept of internal reference units and tips with several types of membranes, an electrode can be assembled and in use within 5 min. The electrodes cost <$5 each to make.

EXPERIMENTAL

Instrumentation

Cell potentials were measured with a Vibron Model 33B-2 Vibrating Capacitor Electrometer as a null detector and impedance matcher to a Rubicon Type B High Precision Potentiometer. Response times were monitored by connecting a Sargent SRL recorder to the output of the electrometer. The electrode and a saturated KCl reference electrode (Corning 476050) were immersed in the test solution in a 125-ml jacketed beaker maintained at 25° ± 0.02° by circulating water, and stirred by a magnetic stirrer, all placed inside a Faraday cage, except the water pump.

Reagents

Reagent-grade chemicals were used without further purification. All solutions were prepared in doubly distilled water and stored in polyethylene bottles. Halide solutions were standardized against silver nitrate. n-Decanol was distilled at 0.15 mmHg and 60–61°, the middle third being taken for use. The purity was checked by infrared spectroscopy, GLC, and refractive index. Phase-separating membranes for the liquid ion-exchanger electrodes were cut from "Millipore" HA 0.45 μm plain white cellulose acetate filters. Lithium chloride–4% agar internal filling solutions were prepared by adding 1 g of Difco "Bacto-Agar" to 25 ml of 0.1*M* lithium chloride, and heating, with stirring, in a container placed in boiling water, until all the agar had dissolved.

Electrode construction

The electrodes were made in two parts from ₮5/20 ground-glass joints (Fig. 1). A silver wire was sealed into a 3-mm o.d. glass tube, either with epoxy glue or by melting the glass tube directly around the wire. The exposed end of the silver wire was coated electrolytically with silver chloride to form the internal reference electrode, which was inserted into the male joint and attached at the side on top, leaving an air gap for filling the joint with the lithium chloride–agar solution. Devcon "5-Minute Epoxy" was used so that immersion in boiling water allowed easy disassembly. The tube was filled by dipping into hot agar solution. It was found that if a small amount of agar was allowed to solidify outside the tip, it was easier to assemble the complete electrode without trapping air-bubbles at the tip. Grinding a small flat on the ground-glass surface of the male joint resulted in a vented reservoir which minimized the hydrostatic pressure differences across the membrane and allowed easy replacement of the solvent-exchanger medium lost by dissolution in test solutions. The membrane tip was made by grinding down the ₮5/20 female joint until the desired exchanger volume was obtained. The membrane was attached with silicone rubber sealant, which provided a flexible and inert seal. The electrode was assembled by filling the tip with the ion-exchanger solution and slowly inserting the internal reference unit, taking care that no air-bubbles were trapped. The two pieces were then held together by two rubber bands.

Procedures

Repeated additions of standard stock solutions were made to a known volume of doubly distilled water until little significant change in cell potential was observed. When caesium hydroxide was used to raise the pH of test solutions to approximately 9.4 in some studies, the following procedure was used. A known volume of doubly distilled water was transferred to the beaker (thermostatically controlled) and allowed to come to thermal equilibrium. A small syringe needle connected to plastic tubing was used to bubble a stream of nitrogen through the solution for 40 min to remove acidic gases such as carbon dioxide. A known amount of standard caesium hydroxide solution was then added by micropipette to raise the pH to the desired value. The nitrogen flow was maintained over the top of the solution during the experiment to ensure that carbon dioxide would not be reabsorbed.

Single-ion activity coefficients were estimated from the Davies equation[4]

$$\log_{10}\gamma_i = -0.51\,z_i^2[I^{1/2}/(1 + I^{1/2}) - 0.3\,I]$$

where γ_i is the single-ion activity coefficient at 25° in water, I the ionic strength of the test solution, and z_i the charge on the ion.

RESULTS

New electrodes made with freshly distilled n-decanol exhibited either zero response or very slight response to anions, but after soaking in $0.1M$ lithium chloride for 18–24 hr gave increasingly cationic response until the Nernstian slope was reached. When the decanol in the electrode was replaced or small amounts were added to replace losses due to dissolution and leakage, the electrode again needed a presoaking period to establish full response.

Figure 2 shows the response of an electrode, already soaked in lithium chloride solution, to lithium, sodium, and potassium chloride solutions. Each curve is based on 35 data points. Caesium hydroxide was added to raise the pH of the test solutions to 9.4. The tailing of response at low activity for both lithium and sodium is due to the caesium ion interference, and starts where the ion concentrations are approximately equal to the $2 \times 10^{-5}M$ of the caesium. A 90% response was reached in ~15 sec and equilibrium potentials were usually obtained within 1 min, with a drift of less than 0.2 mV/hr. Potentials could be measured to within ±0.1 mV at higher concentrations and ±1.0 mV at concentrations of approximately $10^{-5}M$. The "noise" of the electrode potential was usually a function of the magnetic stirrer speed. The electrode resistance appeared to be about the same order of magnitude as that of the standard glass electrode.

$K^{\text{Pot}}_{\text{Li,Na}}$ was found to be 0.30 from the potentials measured in the different solutions. Since the sodium and potassium curves superimpose, $K^{\text{Pot}}_{\text{Li,K}}$ was also 0.30.

To verify that the electrode behaviour was not a function of the anion used, lithium nitrate, sulphate, and perchlorate were also studied. The chloride and nitrate curves superimposed exactly, but the sulphate curve had a slightly higher slope, 60.0 mV/decade as compared to the 57.5 mV/decade for the other two salts. This difference can probably be explained by the fact that the response varies gradually over a period of time in any case, and the experiments were not conducted with electrodes of the same age.

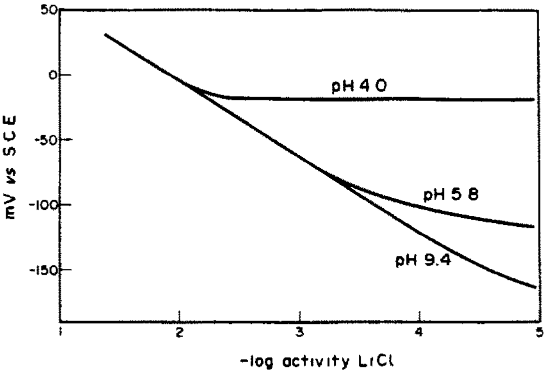

Fig. 3. Response of n-decanol electrode at 25°C to LiCl solutions at pH 4.0, 5.8, and 9.4.

As a further check on the effect of anions the other lithium halides were investigated. At concentrations $>10^{-2}M$, severe downward drifts in potential were observed on successive additions of the bromide or iodide. This drift is probably due to the transport of the halide ion through the low-dielectric membrane as an ion-pair with lithium, which occurs more readily at higher concentrations, causing mixed potentials at the internal Ag/AgCl reference electrode.

The limit of detection for this electrode is pH-dependent (Fig. 3). Solutions of pH < 4 gave very limited response to changes in lithium activity, but the electrode showed nearly linear EMF–log activity curves for hydrochloric acid solutions from 10^{-1} to $10^{-6}M$ with a 53.5 mV/decade slope. From these data and from Fig. 3, $K^{\text{Pot}}_{\text{Li,H}}$ was calculated to be ~50–100.

To study the behaviour of the electrode in strongly basic media, lithium and sodium hydroxide solutions were used. The results were almost quantitatively the same as those obtained with the chlorides (Fig. 2). Again the tailing that appeared was due to the interference from caesium hydroxide which was added to adjust the pH. From the difference in potential for $10^{-3}M$ solutions, $K^{\text{Pot}}_{\text{Li,Na}}$ was found to be 0.33, indicating that the electrode response and selectivity were affected little by strongly basic solutions.

To prove that the selectivity for lithium was not due to an ion-exchange mechanism on the "Millipore" cellulose acetate filter, a Lexan "Nucleopore" 0.4-μm filter, which should not possess ion-exchange properties, was substituted for the "Millipore". The results for pH 9.4 lithium and sodium chloride solutions are shown in Fig. 4. The

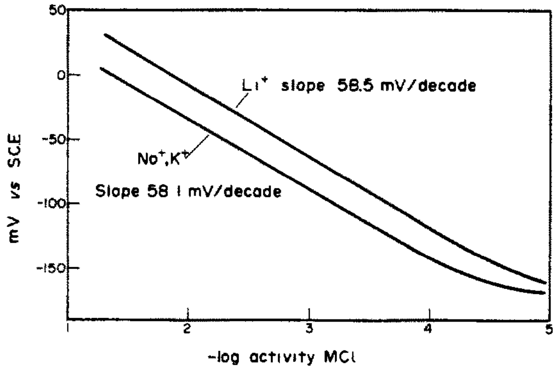

Fig. 2. Response of the n-decanol electrode to LiCl, NaCl, and KCl solutions at pH 9.4 and 25°C.

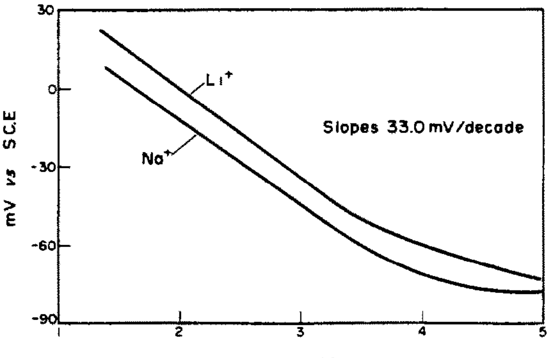

Fig. 4. Response of the n-decanol electrode to LiCl and NaCl solutions, with a "Nucleopore" filter membrane.

Table 1 Experimentally determined activities of "unknown" LiCl solutions

Actual activity of unknown solutions, *M*	Experimentally determined activity, *M*	Relative error %
1.47×10^{-2}	1.50×10^{-2}	+2.3
8.25×10^{-3}	8.21×10^{-3}	−0.5
5.23×10^{-3}	5.39×10^{-3}	+3.1
3.18×10^{-3}	3.07×10^{-3}	−3.6
2.81×10^{-3}	2.21×10^{-3}	−4.3
9.56×10^{-4}	9.29×10^{-4}	−2.8

curves were obtained after soaking the electrode for 24 hr in 0.1*M* lithium chloride (as for the "Millipore" electrodes). The response to both ions was linear over only a short range, and the slopes for both ions were 33 mV/decade. From this slope and the difference in potentials at a given activity, $K^{\mathrm{Pot}}_{\mathrm{Li,Na}}$ was calculated to be ~0.4, close to that obtained with the "Millipore" filter, indicating that the selectivity is due only to the n-decanol. The reduced slopes obtained with the "Nucleopore" membrane are probably attributable to insufficient pre-equilibration times.

A suitable pH buffer–ionic strength adjustment medium could not be found for use with the electrode. All those tried—various amine salts and organic bases—gave rise to such a potential that low activities could not be investigated, and the electrode showed little selectivity between univalent ions. Organic bases often inhibited or altered the electrode response by apparently dissolving in the n-decanol.

Table 1 shows the results of a number of typical lithium determinations on pure solutions. They suggest that in the 10^{-2}–$10^{-3}M$ region the errors are determined primarily by the reproducibility of the potential readings.

CONCLUSIONS

Lithium salts are known to be somewhat selectively extracted from aqueous solutions by higher alcohols. This phenomenon may be the origin of the selectivity for lithium relative to sodium observed for the n-decanol–water interface electrode.

Liquid–liquid membrane electrodes have been described before, *e.g.*, in the classic work of Haber and Klemensiewicz[5] and more recently by Liteanu and Mioscu[6] who showed that liquid–liquid interface potentials are functions of hydrogen-ion concentration in the aqueous phase.

The results of this study indicate that a long-chain alcohol such as n-decanol has the ability to complex and transport alkali metals through an organic membrane. The electrode exhibits linear near-Nernstian cationic response from 10^{-1} to approximately $5 \times 10^{-5}M$ for lithium ion, and the exhibited selectivity seems to be a property due to the solvent rather than the membrane. The response of the n-decanol system is relatively unaffected by the anions used in the test solutions. The slope of the electrode response varies slightly with the age of the electrode, but is usually within 56–58 mV/decade as long as the n-decanol is replaced at fairly frequent intervals. With suitable calibration, the electrode could be used to determine the activities of unknown lithium solutions with errors of less than 5%. The selectivity coefficients for lithium relative to sodium or potassium are ~0.30–0.33. $K^{\mathrm{Pot}}_{\mathrm{Li,Na}}$ is nearly the same as that of the LAS 15–25 glass electrode for lithium ion. $K^{\mathrm{Pot}}_{\mathrm{Li,H}}$ was found to be ~50–100. However, because of the overall lack of selectivity towards other univalent ions and the stringent pH-control needed to detect low activities, the electrode would be rather limited for practical lithium determinations in other than pure solutions of lithium salts. However it should be noted that long-chain alcohols such as n-decanol have often been used as solvents in liquid-membrane ion-exchanger electrodes[7,8] and the response of this system to alkali metal ions should be taken into consideration in ISE research where true responses of experimental systems might be altered by this effect.

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Summary—An electrode selective for lithium relative to other alkali metal ions is described. The sensor is based on n-decanol as both the liquid membrane and exchanger. The electrode exhibits more than 3 decades of linear near-Nernstian response and has selectivity comparable to the LAS 15–25 glass univalent-cation electrode.

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DETERMINATION OF LEAD IN PROPELLANT SAMPLES BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Lead salts such as the resorcylate, salicylate, stearate and 2-ethylhexoate and the red oxide (minium) are employed as modifiers of propellants. Classical techniques[1,2] for the determination of lead in powder formulations involve wet oxidation of the sample with nitric and sulphuric acids followed by determination of lead in the residue, either as the sulphate or the chromate. These are lengthy procedures and the determination as molybdate[3] is also time-consuming. Macorkindale and Lamond[4] reported the use of perchloric acid, achieving complete oxidation of the propellant sample in approximately 1 hr. The lead in the resulting solution was determined by polarography or by complexometric titration with EDTA. The U.S. MIL-STD-286B[5,6] specifies the determination of lead in propellants by an atomic-absorption technique. This method (T 311.5)[5] achieves complete oxidation of the specimen with nitric and perchloric acids, but is hazardous and requires the use of a good fume-cupboard made from non-organic materials. A second method (T 316.1)[6] specified in the American Standard, recommends incomplete digestion in nitric acid and the residual organic matter can clog the capillary inlet of the atomic-absorption spectrophotometer. This technique also suffers from matrix effects.

The present work was undertaken to improve the lead extraction procedure in the analysis of powders and 10% acetic acid was used to extract the lead from different types of propellants. The present paper compares the results so obtained with those of the gravimetric chromate method.

EXPERIMENTAL

Apparatus

Lead extractions were performed in 300-ml Erlenmeyer flasks fitted with reflux condensers (ground-glass joints).

All results were obtained with a Carl Zeiss PMQII Spectrophotometer with the FA2 flame attachment. A Servogor pen-recorder was used in conjunction with a Zeiss TE-converter. The lead resonance line at 283.3 nm was used.[7] An oxidizing non-luminous air–acetylene flame was used.

Reagents

All solutions were prepared with glass-distilled water and all chemicals used were of analytical-reagent grade. A stock solution of lead was prepared from lead nitrate and contained 5% v/v nitric acid. Stock and calibration solutions were made up to volume with 10% v/v acetic acid.

Sample preparation

Samples used in this study included cast and extruded double-base propellants and double- and single-base casting powders. Propellant samples were prepared by grinding to approximately 20-mesh in a Wiley mill,[8,9] but casting powder granules were not ground.

Procedure

The following extraction procedure is applicable to all the powder formulations mentioned. For extruded double-base propellants there is an alternative technique for lead extraction, which does not require complete dissolution of the sample. In all cases the sample should not be larger than 2.0 g.

Place an accurately weighed amount of sample containing 0.0075–0.015 g of lead in an Erlenmeyer flask containing 10 ml of 10% v/v acetic acid. Add 50 ml of acetone and reflux until dissolution is complete. (The acetone can be omitted, if desired, but 20 ml of glacial acetic acid must be used and the dissolution takes longer, 40–60 min.) While the solution is still hot add 100 ml of 10% v/v acetic acid (180 ml of distilled water if glacial acetic acid was used as solvent) with stirring, in order to obtain a fine-grained or fibrous precipitate (avoid the formation of a thick gummy precipitate). Boil gently for 5 min under reflux, then filter hot into a 500-ml volumetric flask containing 10 ml of glacial acetic acid. Add 100 ml of 10% v/v acetic acid to the residue, reflux for 5 min, into the volumetric flask then filter and repeat this step twice more, once with 100 ml of 10% v/v acetic acid and finally with 40 ml of distilled water. (If acetone was used as the solvent, use 50 ml of 10% v/v acetic acid and 90 ml of water for the last two extractions.) Make up to the mark with 10% v/v acetic acid, mix, and measure the lead by atomic-absorption spectrophotometry, adding acetone to the standards in order to obtain the same concentration as in the sample solution. The standards should contain 15–30 ppm of lead.

An alternative method applicable only to extruded double-base propellants is as follows. Transfer an accurately weighed amount of the specimen containing 0.0075–0.015 g of lead to an Erlenmeyer flask. Add 100 ml of 10% v/v acetic acid and reflux for 30 min. Transfer the hot supernatant liquid into a 500-ml volumetric flask containing 10 ml of glacial acetic acid. Add 100 ml of 10% v/v acetic acid to the residue and reflux for 15 min. Transfer to the volumetric flask and repeat the extraction one with 100 ml of 10% v/v acetic acid and finally with 90 ml of distilled water, using extraction times of 10 min. Make up to the mark with 10% v/v acetic acid. Determine the lead content by atomic-absorption spectrophotometry.

RESULTS

To establish the validity of the technique, the lead content of several samples was determined by the procedure described and also by the chromate method.[2] The results are given in Table 1. It can be seen that, in all cases, good agreement was obtained.

A study of the precision showed the relative standard deviation to be 3.1% (ten replicates), which is satisfactory.

Table 1. Comparison of propellant lead content determined by the gravimetric chromate method and the proposed procedure

Sample	Chromate method Pb, %	Acetone–10% acetic acid extraction/AAS Pb, %	10% acetic acid extraction/AAS Pb, %
Cast propellant A	1.75	1.73	
Cast propellant B	1.59	1.60	
Casting powder C	1.72	1.75	
Casting powder D	2.30	2.29	
Casting powder E	1.85	1.79	
Extruded double-base propellant F	0.97		1.00
Extruded double-base propellant G	1.15		1.13
Extruded double-base propellant H	1.39		1.41

DISCUSSION

The proposed procedure was used satisfactorily for a number of solvent-free and cast double-base propellants and double- and single-base casting powders containing lead salicylate, lead 2-ethylhexoate, lead stearate and lead resorcylate. Some variation will be needed for powder formulations containing red lead oxide (minium), such as dissolution in 20 ml· of glacial acetic acid. However, it has been established that the present extraction procedures are satisfactory for the samples studied.

It appears likely that the extraction of lead from the sample with 10% acetic acid is controlled by the complexing action of the nitrocellulose. The ability of the polymer to form a stable complex with the metal ion has a decisive effect on the extraction efficiency. Cast formulations are not completely extracted with 10% acetic acid even if finely ground material (80-mesh or finer) is used. Porous samples of casting powders obtained by prior extraction with methylene chloride did not give complete extraction of lead, even though the amount extracted was larger than that from non-porous samples. Only when the sample was completely dissolved in acetone or glacial acetic acid was total lead extraction achieved. On the other hand, with highly plasticized extruded propellants, complete extraction was achieved with 10% acetic acid from milled samples (20-mesh), without treatment with acetone or glacial acetic acid.

Important advantages of the proposed method are its safety and simplicity. It avoids sample digestion with strong acids and the use of a dilute acetic acid solution (to remove matrix materials) avoids matrix interferences (*e.g.*, effects of the nitrocellulose polymers) on the properties affecting nebulization rate. The extracted material never constituted more than 0.1% of the final solution even when acetone or glacial acetic acid was used. It is unnecessary to use the method of standard additions or to match standard and sample solutions (except for acetone content).

We have found that the proposed technique is also suitable for copper extraction, allowing simultaneous determination of lead and copper in propellants.

Acknowledgement—This work was done under the auspices of the Applied Chemistry Department of CITEFA and is published with its permission.

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Summary—A procedure is described for the determination of lead in different types of propellant samples by atomic-absorption spectrophotometry. The method is simple, rapid and avoids the use of strong acids and prior sample digestion. Complete lead extraction is achieved with 10% acetic acid. The results obtained by the proposed method are compared with those obtained by the gravimetric chromate method. The variation of the efficiency of lead extraction with sample type is discussed.

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SOLVENT EXTRACTION OF COPPER(II) WITH CHLORENDIC ACID

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Long-chain monocarboxylic acids, including versatic, naphthenic, and capric acids have been used as extractants for such metal ions as Fe(III),[1,2] Cu(II),[3–6] Ni(II),[7,8] and Co(II).[2,6,9] In many cases, these metal species have been found to be extracted as polymers into benzene as solvent. Cu(II) has been particularly noted as being capable of forming dimeric complexes with acetic acid,[10] as well as with the other monocarboxylic acids listed above. Recently, chlorendic acid, a hexachloro-substituted norbornyl 1,2-dicarboxylic acid, has been studied as an agent for extracting Fe(III) into both MIBK and benzene. In both cases only monomeric species are extracted.[11] In this work, the equilibrium between Cu(II) and chlorendic acid will be studied to compare the parameters with those for the monocarboxylates.

EXPERIMENTAL

Reagents

Copper(II) solutions were prepared from reagent grade $Cu(ClO_4)_2.6H_2O$. Chlorendic acid was obtained from Hooker Chemical Co. (Niagara Falls, N.Y.). Benzene and methyl isobutyl ketone (MIBK) were of reagent grade and used without further purification.

Apparatus

Solutions were shaken automatically. The pH was measured with a Fischer Accumet model 520 pH-meter equipped with a combination glass and calomel electrode. Absorption spectra were recorded with a Beckman DB-G spectrophotometer, and atomic-absorption measurements were made with the Jarrell-Ash model 810 atomic-absorption spectrometer.

Equilibration and analysis

Ten-ml aliquots of Cu(II) solution were shaken with equal volumes of chlorendic acid dissolved in either MIBK or benzene. The pH was adjusted by dropwise addition of either concentrated perchloric acid or 10% sodium hydroxide solution. After equilibration for designated time periods, the phases were allowed to settle, and the aqueous phase was separated, and filtered to remove any suspended drops of the organic phase. The pH of the aqueous phase was measured and then the phase was analysed by atomic-absorption spectroscopy.

RESULTS AND DISCUSSION

Equilibrium considerations

The generalized equilibrium expressions for the solvent extraction of metal ions with dibasic acids has been derived previously,[12] and given as follows,

$$\log D = \log K_{ex} + \frac{1}{x}\log x + (p + q + r)\log\overline{[H_2L]} + (2p + q)\,pH + \frac{(x - 1)}{x}\log\overline{[Cu(II)]} \quad (1)$$

The equation may be rewritten as,

$$\frac{1}{x}\log\overline{[Cu(II)]} - \log[Cu(II)] = \log K_{ex} + \frac{1}{x}\log x + (p + r + q)\log\overline{[H_2L]} + (2p + q)pH \quad (2)$$

The species in the organic phase are designated by the horizontal bar, while other parameters are defined as follows:

D = distribution coefficient
K_{ex} = overall equilibrium constant
p = number of L^{2-} species
q = number of HL^- species
r = number of H_2L species
x = degree of polymerization

The equation may be used to determine the various extraction parameters empirically, by use of a graphical slope technique.

Extractions as a function of metal concentration

Figure 1 illustrates the plot of log D *vs.* $\log\overline{[Cu(II)]}$ at different equilibrium pH ranges. Since K_{ex}, $\overline{[H_2L]}$, pH, and x remain reasonably constant in the ranges studied, the slope of the plot, $(x - 1)/x$, may be used to calculate x, the degree of polymerization, from equation (1). Curves

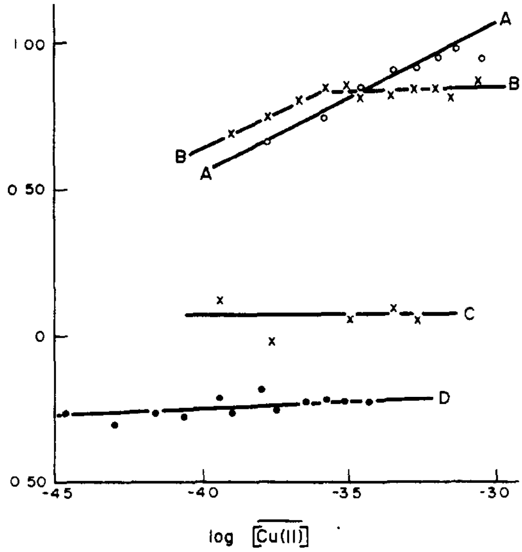

Fig. 1. A plot of log D *vs.* $\log\overline{[Cu(II)]}$. A: $[Cu(II)]_{in}$ = 0.2×10^{-3}–$1.0 \times 10^{-3}M$, $\overline{[H_2L]}_{in}$ = 0.10M, pH_{eq} = 4.7–5.0. B: $[Cu(II)]_{in}$ = 0.1×10^{-3}–$1.0 \times 10^{-3}M$, $\overline{[H_2L]}_{in}$ = 0.10M, pH_{eq} = 4.6–4.9; C: $[Cu(II)]_{in}$ = 0.2×10^{-3}–$1.0 \times 10^{-3}M$, $\overline{[H_2L]}_{in}$ = 0.10M, pH_{eq} = 3.5–3.7; D: $[Cu(II)]_{in}$ = 0.1×10^{-3}–$1.0 \times 10^{-3}M$, $\overline{[H_2L]}_{in}$ = 0.10M, pH_{eq} = 3.2–3.5

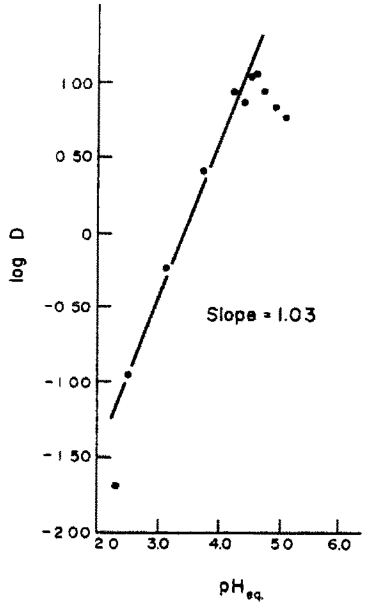

Fig. 2. A plot of log D *vs.* equilibrium pH. $[Cu(II)]_{in}$ = $1 \times 10^{-3}M$, $[\overline{H_2L}]_{in} = 1.0 \times 10^{-1}M$.

A and B, in the equilibrium pH ranges 4.7–5.0 and 4.6–4.9 respectively, show slopes equal to 0.5, which corresponds to values of $x = 2$, indicative of the extraction of dimeric species. While curve B flattens out at higher metal concentrations, it would be anomalous to infer that a monomer is being extracted, since existence of the polymer would be favoured at higher concentrations.[13] In the lower pH ranges, 3.2–3.5 and 3.5–3.7 for curves C and D, slopes equal to zero are obtained, implying that monomeric complexes are favoured.

Extraction as a function of equilibrium pH

In Fig. 2 the plot of log D *vs.* equilibrium pH is shown. Experimentally, the pH was changed by dropwise additions of either perchloric acid or sodium hydroxide solution. The slope of the line in the pH range 2.5–4.5 is equal to 1.03, which corresponds to the extraction of a metal ion with a charge of +1 from the aqueous phase. At first, one would think that the partially hydrolysed $Cu(OH)^+$ is extracted; however, equilibrium calculations for this pH range indicate that the concentration of $Cu(OH)^+$ is miniscule compared to the concentration of Cu^{2+}.[14] However, the extraction of $CuHL^+$ as the main aqueous species would explain the slope of +1.

To test this hypothesis for the extraction of a dimerized species, equation (2) would have to be used since in the case of polymerization there is a dependence of the extraction on the metal ion concentration. However, plotting (log $[\overline{Cu(II)}])/x$ − log [Cu(II)] *vs.* pH for $x = 2$, still gives a slope equal to unity, implying the extraction of $CuHL^+$ for the dimer as well as for the monomer.

At pH values greater than 4.5, the distribution coefficients begin to decrease, probably due to the formation of anionic Cu^{2+}-chlorendic acid complexes which are back-extracted into the aqueous phase. In this pH range, 4–5, chlorendic acid exists as H_2L only to the extent of 0.01–3.3% ($pK_{a1} = 2.60$, $pK_{a2} = 4.76$). At higher pH ranges, the proportion of $L^{2-}:HL^-$ increases, indicating that more highly dissociated ligands are present in the aqueous phase, increasing the likelihood of the formation of hydrophilic anionic Cu^{2+}-chlorendates. Similar phenomena were observed by Dyrssen in the extraction of metal–β-diketonates.[15]

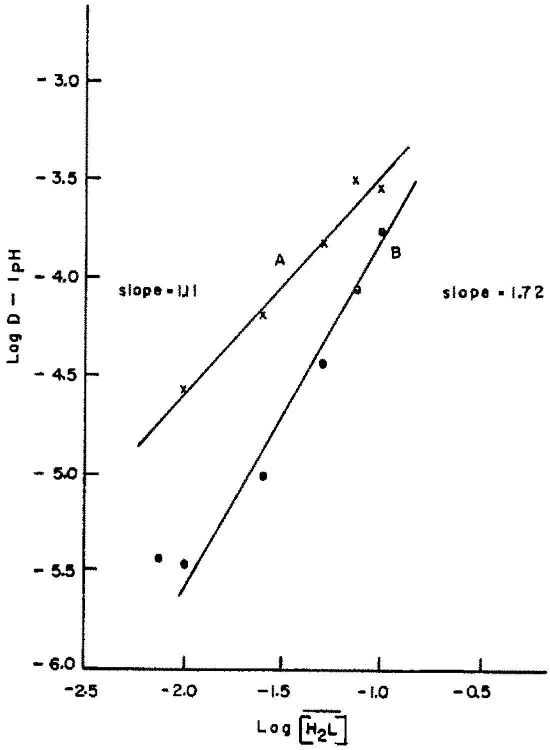

Fig. 3. Plot of log D − 1 pH *vs.* log $[\overline{H_2L}]$. Curve A: $[Cu(II)]_{in.} = 1 \times 10^{-3}M$, $[\overline{H_2L}]_{in.} = 0.1 \times 10^{-1} - 1.0 \times 10^{-1}M$, $pH_{eq.} = 3.6$–4.5. Curve B: $[Cu(II)]_{in.} = 1 \times 10^{-3}M$, $[\overline{H_2L}]_{in.} = 0.075 \times 10^{-1} - 1.0 \times 10^{-1}M$, $pH_{eq} = 4.7$–5.8.

Extraction as a function of ligand concentration

In the pH range 3.6–4.5, which was found to yield monomeric species, the slope of the plot of log $D - (2p + q)$pH *vs.* log$[\overline{H_2L}]$, for $2p + q = 1$, gives a slope equal to 1.11 for line A, Fig. 3. This is indicative of the extraction of a 1:1 chlorendic acid–Cu(II) complex, most probably $[Cu(II)(L^{2-})]$.

However, in the higher pH range 4.7–5.8, curve B, the slope of the plot of log D − pH *vs.* log $[\overline{H_2L}]$ is equal to 1.72, indicating a 2:1 complex. This would imply the extraction of $[Cu(II)(HL^-)_2]_2$ and/or $[Cu(II)(L^{2-})\cdot H_2L]_2$. Again, since a dimer is expected to be extracted in this range, the plot of (log$[\overline{Cu(II)}])/x$ − log[Cu(II)] − pH *vs.* log$[\overline{H_2L}]$ still generates a slope equal to two.

Effect of extracting solvent

In the equilibrium pH range 2.0–6.0, Cu(II) is not extracted into benzene. This is very unusual since other monocarboxylate–Cu(II) complexes are very readily extracted.[3–6] Apparently, whatever complex forms in the aqueous phase is much too polar to be extracted into the non-polar benzene. However, MIBK, being a polar solvent, would be much more likely to extract a highly polar complex. In addition, the presence of the carbonyl oxygen atom, a co-ordinating donor, would probably cause some interaction between the complex and the solvent, thus enhancing the extraction efficiency.

With MIBK, the extractions proceed quite rapidly, achieving equilibrium within 15 min.

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Summary—The solvent extraction of Cu(II) with chlorendic acid has been studied. The composition of the extracted species appears to be a function of pH. In the pH range 3.2–4.6, a monomeric species exists $[\mathrm{Cu(II)}(L^{2-})]$, while at pH values greater than 4.5, a dimer in the form of $[\mathrm{Cu(II)}(L^{2-})\cdot H_2L]_2$ and/or $[\mathrm{Cu(II)}(HL^-)_2]_2$ is extracted.

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ANALYTICAL DATA

FORMATION CONSTANTS FOR THE COBALT(II) CHLORIDE–1-NITROSO-2-NAPHTHOL SYSTEM IN ETHANOL–BENZENE MIXTURES*

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The earlier investigations on the complex species obtained from cobalt(II) chloride and 2-nitroso-1-naphthol in ethanol–benzene solvent mixtures[1,2] have been repeated for the isomeric ligand 1-nitroso-2-naphthol.

EXPERIMENTAL

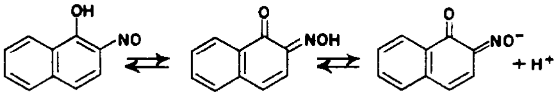
Materials, apparatus and operative conditions were the same as previously described.[1,2]

RESULTS AND DISCUSSION

The absorbance of the reaction mixtures ($C_L/C_M = 10$) increases slowly, becoming constant in about 1 hr. The spectrophotometric results at 500, 525 and 550 nm were processed by the mole-ratio[3] and Asmus (modified by Klausen and Langmhyr)[4] methods to determine the complexation ratios of the species and the conditional formation constants (Table 1). The absorption spectrum does not alter meaningfully with changing solvent medium; this is confirmed in the literature.[5]

The β' values obtained from the data for the different wavelengths were in good agreement. Increasing the ethanol content in the mixture raises the L/M complexation ratio to 4:1. The presence of such a species with a unidentate ligand is confirmed in other solvents.[6].

The same interpretations as before[1,2] can be applied to these results; 1-nitroso-2-naphthol should be present mainly in the quinonoid form (**IIa, IIb**) in all the four solvent mixtures investigated:



(I) (IIa) (IIb)

The tautomeric equilibrium for this ligand is reported to be shifted to the right (forms **IIa, IIb**) quantitatively (visible, ultraviolet, and NMR spectra),[7,8] while for the isomer 2-nitroso-1-naphthol the equilibrium seems to be strongly dependent on the solvent.[8,9] When the ethanol content is high, the donicity of the solvent mixture is relevant; the naphthol can hardly co-ordinate the cobalt by its quinonoid oxygen, the electrons of which are strongly bound in the benzene ring resonance, particularly because of the competitive action exerted by the solvent. At lower ethanol percentages, the donicity of the solvent diminishes, so the naphthol can act as a bidentate ligand. Uni- and bidentate complexation by the nitrosonaphthols is in agreement with the structural conclusions presented by Sathe and Shetty[10] about the species formed by the ligand in its quinonoid form with copper(II).

The formation constants of the cobalt(II) complexes with the two isomers are very similar (they differ by only one order of magnitude at most). This is in accordance, at least

Table 2. Absorptivities (10^3 l. mole^{-1}.cm^{-1}) for cobalt(II) chloride–1-nitroso-2-naphthol (ϵ_1) and cobalt(II) chloride–2-nitroso-1-naphthol (ϵ_2) systems calculated graphically at 525 nm, for ligand excess ($C_L/C_M = 10$)

Ethanol concn., % *v/v*	ϵ_1	ϵ_2*
100	9·6	14·2
75	10·3	14·5
50	9·8	15·0
25	9·2	15·5

* Values not reported in ref. 2.

Table 1. Values of the conditional formation constants for the cobalt(II) chloride 1-nitroso-2-naphthol system in ethanol–benzene mixtures at 25°C

Ethanol concn., % *v/v*	Species found, L/M	β'*			
		$\lambda = 550$ nm	$\lambda = 525$ nm	$\lambda = 500$ nm	Mean
100	4:1	$5{\cdot}8 \times 10^{15}$	$6{\cdot}3 \times 10^{15}$	$6{\cdot}0 \times 10^{15}$	$6{\cdot}0 \times 10^{15}$
75	4:1	5.9×10^{15}	$5{\cdot}1 \times 10^{15}$	$5{\cdot}4 \times 10^{15}$	$5{\cdot}4 \times 10^{15}$
50	3:1	$3{\cdot}9 \times 10^{11}$	$3{\cdot}2 \times 10^{11}$	$4{\cdot}9 \times 10^{11}$	$4{\cdot}0 \times 10^{11}$
25	3:1	$1{\cdot}2 \times 10^{11}$	$1{\cdot}3 \times 10^{11}$	$1{\cdot}1 \times 10^{11}$	$1{\cdot}2 \times 10^{11}$
25	2:1	$0{\cdot}9 \times 10^{6}$	$2{\cdot}6 \times 10^{6}$	$2{\cdot}1 \times 10^{6}$	$1{\cdot}9 \times 10^{6}$

* (mole/l.)$^{-i}$ for species ML_i.

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* Work supported financially by the Consiglio Nazionale delle Ricerche, Rome, Italy.

in principle, with the acidity constants of the two ligands, which were found polarographically to be different by one logarithmic unit (in aqueous solution).[11] The most striking difference is presence of the ML_2 species in the 2-nitroso-1-naphthol system in 50% ethanol medium, but not with the isomer investigated here; this is to be interpreted only through the differences in the tautomeric equilibria and the effect of the solvent. Increasing the benzene concentration shifts the equilibrium to the left for the 2-nitroso-1-naphthol isomer, favouring bidentate ligand action and an ML_2 species.

The molar absorptivities of the complexes formed with the two isomers are similar (Table 2) and not appreciably influenced by changing the medium.

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Summary—The values of conditional formation constants for the cobalt(II) chloride–1-nitroso-2-naphthol system were determined at 25° in ethanol–benzene mixtures of different compositions by spectrophotometry in the visible region. Comparisons were made with the results previously obtained with the isomeric ligand 2-nitroso-1-naphthol. In both cases the L/M complexation ratio of the species found increases with increasing ethanol content of the medium.

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GAS–LIQUID CHROMATOGRAPHIC STUDY OF MONOSUBSTITUTED BENZALDEHYDE ISOMERS

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(*Received* 4 *June* 1974. *Revised* 8 *January* 1975. *Accepted* 30 *October* 1975)

Gas–liquid chromatography has been used for the identification and separation of aromatic compounds, including aldehydes.[1,2] Procedures have been given for the detection of benzaldehyde and some of its derivatives.[3,4] Prabucki and Lenz[5] reported the separation of aromatic aldehydes on a mixture of polyethylene glycol isophthalate and polyethylene glycol 400. The selectivity of stationary liquid phases was studied by several workers[6–11] but only a few investigators have used aldehydes as test compounds.[12,13]

In the present work, general quantitative separation of monosubstituted benzaldehydes on liquid phases of various physical and chemical characteristics has been achieved and the selectivity of these liquid phases for benzaldehyde isomers investigated.

Table 1. Packing specification of the columns

Stationary phase	Density, g/cm	Loading, % w/w	Weight of liquid phase, g	Maximum operating temp. °C	Solid support	Mesh size
Silicone oil MS200/50 (SO)	0.971	20	3.40	225	Chromosorb P	60 – 80
Silicone gum rubber (SGR) (Se – 30)	–	2.5	0.527	250	Chromosorb G AW – DMCS	80 – 100
Apiezon L (APL)	–	20	3.40	325	Chromosorb P	80 – 100
Di(2-ethylhexyl) sebacate (DEHS)	0.912^{25}	20	3.40	175	Chromosorb P	60 – 80
Dinonyl phthalate (DNP)	–	10	1.031	150	Chromosorb W	80 – 100
2,4,7-Trinitrofluorenone (TNF)	–	10	0.995	200	Chromosorb W	80 – 100
Versamide 930 (VS)	–	2	0.191	250	Chromosorb W AW – DMCS	80 – 100
Polypropylene glycol (PPG) (L.B.– 550 – X)	0.984	15	1.73	150	Chromosorb W	80 – 100
Apiezon L + Bentone 34 (APL + 34)	–	10 + 10	1.814	250	Chromosorb W	80 – 100

in principle, with the acidity constants of the two ligands, which were found polarographically to be different by one logarithmic unit (in aqueous solution).[11] The most striking difference is presence of the ML_2 species in the 2-nitroso-1-naphthol system in 50% ethanol medium, but not with the isomer investigated here; this is to be interpreted only through the differences in the tautomeric equilibria and the effect of the solvent. Increasing the benzene concentration shifts the equilibrium to the left for the 2-nitroso-1-naphthol isomer, favouring bidentate ligand action and an ML_2 species.

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Table 2. Specific retention volumes V_g^0 (ml/g) for monosubstituted benzaldehydes at different column temperatures on the liquid phases studied

	Compounds	DNP			DEHS			PPG			SO			SGR			APL + 34			APL	TNF	VS	
		140°C	130°C	120°C	180°C	160°C	140°C	140°C	130°C	120°C	180°C	160°C	140°C	140°C	120°C	100°C	140°C	120°C	100°C	180°C	180°C	180°C	170°C
1	Benzaldehyde	234	302	367	77	107	175	133	166	211	30	42	63	58	92	153	20	36	57	53	53	127	143
2	*o*-	448	632	793	133	196	345	237	305	398	48	70	112	96	153	263	34	58	108	83	81	170	203
3	*m*-Tolualdehyde	448	632	793	133	196	345	237	305	398	48	70	112	96	153	263	36	63	120	83	81	170	203
4	*p*-	494	689	881	145	214	379	260	338	441	51	75	117	101	164	289	36	63	120	99	92	184	218
5	*o*-	201	268	328	67	91	150	117	151	189	28	37	57	56	82	131	20	31	49	46	45	113	128
6	*m*-Fluorobenzaldehyde	220	300	370	73	99	166	117	151	195	28	37	57	56	82	131	20	31	52	46	45	113	128
7	*p*-	239	329	400	76	105	178	127	161	205	28	37	57	56	82	131	20	31	57	53	46	113	128
8	*o*-	596	847	1074	178	259	448	313	407	540	60	89	144	121	189	363	47	82	156	108	99	211	258
9	*m*-Chlorobenzaldehyde	720	1040	1350	202	306	543	367	482	649	60	89	144	121	189	363	52	94	184	124	112	233	279
10	*p*-	720	1040	1350	202	306	543	367	482	649	60	89	144	121	189	363	49	86	164	124	112	233	279
11	*o*-	1058	1552	2002	281	447	803	550	730	985	80	138	230	176	317	623	79	150	301	195	165	325	401
12	*m*-Bromobenzaldehyde	1283	1917	2526	339	536	986	654	876	1199	80	138	230	176	317	623	86	173	367	247	192	352	472
13	*p*-	1283	1917	2526	339	536	986	654	876	1199	89	138	230	176	317	623	79	155	321	247	192	352	472
14	*o*-	1410	2037	-	351	582	1128	862	1176	1654	100	159	276	937	429	888	116	180°C 38	160°C 62	271	306	423	551
15	*m*-Methoxybenzaldehyde	1074	1536	-	286	463	876	644	868	1209	88	127	217	174	291	568	88	31	48	199	229	325	429
16	*p*-	1694	2407	-	419	701	1379	1016	1399	1983	107	173	298	237	429	888	151	47	77	349	393	480	643
17	*o*-	Not eluted		——	627	1133	-	Not	eluted	——	126	263	358	272	180°C 108	160°C 167	192	55	102	-	652	706	930
18	*m*-Nitrobenzaldehyde	Not eluted		——	911	2004	-	Not	eluted	——	155	262	426	343	128	196	256	75	135	-	1032	1058	1430
19	*p*-	Not eluted		——	834	1542	-	Not	eluted	——	144	239	380	323	123	187	272	78	144	-	869	945	1279
20	*o*-	411	572	718	123	183	320	234	307	396	45	64	97	96	180°C 47	160°C 64	31	15	22	91	87	184	229
21	*m*-Hydroxybenzaldehyde	Not eluted			Not	eluted		Not eluted			154	256	-	393	123	196	-	118	237	-	Not eluted	4520	6705
22	*p*-	Not eluted			Not	eluted		Not eluted			221	398	-	888	219	388	-	238	509	-	-	8998	13495

EXPERIMENTAL

Apparatus

A Perkin-Elmer model 451 fractometer equipped with a thermistor-type thermal-conductivity detector was used. The recorder was a 2.5-mV Honeywell Electronic unit. Nitrogen was used as the carrier gas. The average column temperature was controlled to within 0.2°. The columns (2 in. long and $\frac{1}{4}$-in. o.d.) were specially made to specification by Perkin-Elmer, U.K. They were U-shaped, made from stainless steel, and covered with asbestos sleeves to ensure uniform heating. The composition of the liquid phases and the packing specifications of the columns are shown in Table 1.

Samples

Equal weights of the isomers (Fluka, purest available) were blended in 3-ml cylindrical Pyrex cells. Sample sizes ranged from 0.1 to 4 μl for liquid isomers and from 0.2 to 8 μl of 10% w/w solution in acetone for solid isomers. Samples were injected with a 10-μl Hamilton syringe with a 1-in. fixed needle.

RESULTS AND DISCUSSION

Flow-rates were found to be optimum at 25 ml/min at NTP and this value was used throughout. Each injection for an individual isomer or mixture of isomers was repeated at least twice and the results were found to be reproducible.

The specific retention volumes, V_g^0, were calculated according to Littlewood *et al.*[14] The retention volume for the air-peak was taken as zero. Specific retention volumes for monosubstituted benzaldehydes at different column temperatures on the liquid phases examined are listed in Table 2.

The general elution order of the benzaldehyde isomers was mainly *o*-, *m*- and *p*. The *o*-isomers were resolved from *m*- and *p*-isomers and had the shortest retention volumes with the exception of *o*-methoxybenzaldehyde. This is mainly atttributed to the "*ortho*" effect, the intramolecular hydrogen-bonding that occurs between the formyl group and *o*-substituents, which minimizes the interaction of the *o*-isomers with the liquid phases. However, the fluoro, chloro and nitro groups, which possess higher inductive effects in the *o*-position, will decrease the basicity of the carbonyl groups and reduce their association with the liquid phases.

The elution order of *m*- and *p*-benzaldehydes followed the order of their dipole moments, with the exception of *m*- and *p*-nitrobenzaldehydes on APL + 34, and *m*- and *p*-fluorobenzaldehydes on DNP, DEHS, PPG and APL + 34. The reversed elution order in the first case may be attributed to the two partial negative charges on the nitro groups in the *p*-position, which may be attracted by the large positive charges on APL + 34, while the boiling point and dispersion forces have a greater influence on the elution order in the second case.

The most selective liquid phase for the separation and quantitative determination in this investigation is APL + 34, followed by DNP and DEHS, which is probably due to its special activity toward aromatic isomers. DNP and DEHS selectively resolved fluorobenzaldehydes, but only partial resolution of these isomers was obtained on PPG.

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Summary—Monosubstituted benzaldehyde isomers have been studied quantitatively on nine stationary liquid phases of various physical and chemical characteristics and at different operating temperatures. Apiezon 1 + Bentone 34, dinonyl phthalate and di(2-ethylhexyl)sebacate are found to be selective for quantitative separation of the isomers studied.

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ANNOTATION

THERMODYNAMIC EXAMINATION OF pH MEASUREMENTS

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Consider the acid–base reaction

$$A_1 + B_2 \rightarrow A_2 + B_1 \qquad (a)$$

where A_1,B_1 and A_2,B_2 are two conjugate acid–base pairs in the Brønsted–Lowry sense. If the extent of the reaction is denoted by ξ the affinity for the reaction can be expressed by

$$-\left(\frac{\delta G}{\delta \xi}\right)_{T,P} = -\Delta\mu^\circ + RT\ln\frac{a_{A_1}}{a_{B_1}} - RT\ln\frac{a_{A_2}}{a_{B_2}} \qquad (b)$$

μ being the chemical potential and a the activity of a component at temperature T. If now both acid–base pairs refer to the same aqueous solution, the affinity is zero; if, further, A_2,B_2 represents the pair H_3O^+, H_2O, equation (*b*) can be rearranged to

$$p = \log\frac{a_{H_2O}}{a_{H_3O^+}} = \frac{\Delta\mu^0}{RT\ln 10} + \log\frac{a_B}{a_A} = -\log K + \log\frac{a_B}{a_A} \qquad (c)$$

which gives the thermodynamic definition of p, its relation to pH, and its relation to the well-known Henderson–Hasselbach equation, K being the equilibrium constant.

Electromotive force, p, *and pH*

Consider now the electrochemical reaction

$$A + e^- \rightarrow B + \tfrac{1}{2}H_2 \qquad (d)$$

where A,B is an acid–base pair. The electromotive force, E, of this half-reaction is given by

$$E = E^0 - \frac{RT}{F}\ln\frac{a_B}{a_A} - \frac{RT}{F}\ln a_{H_2}^{\frac{1}{2}} \qquad (e)$$

If the acid–base pair is H_3O^+, H_2O then, as known, the value zero is given to E^0. When E refers to this acid–base pair it will be denoted by E_w in what follows; further, it is assumed that the activity of hydrogen is always the same for any two expressions which give a difference ΔE. When this is the case the difference

$$E_1 - E_2 = E_1^0 - \frac{RT}{F}\ln\frac{a_{B_1}}{a_{A_1}} - \left(E_2^0 - \frac{RT}{F}\ln\frac{a_{B_2}}{a_{A_2}}\right) \qquad (f)$$

expresses the thermodynamic affinity of reaction (*a*). If the pair A_2,B_2 represents H_3O^+, H_2O, then

$$E - E_w = E^0 - \frac{RT}{F}\ln\frac{a_B}{a_A} + \frac{RT}{F}\ln\frac{a_{H_2O}}{a_{H_3O^+}} \qquad (g)$$

All half-reactions (*d*), referring to the same solution, have the same electromotive force. Therefore, if E and E_w refer to the same solution, (*g*) may be rearranged to

$$p = \log\frac{a_{H_2O}}{a_{H_3O^+}} = \frac{-E^0 F}{RT\ln 10} + \log\frac{a_B}{a_A} = -\log K + \log\frac{a_B}{a_A} \qquad (h)$$

However, if two acid–base pairs, A_1,B_1 and A_2,B_2, do not refer to the same solution but to the solutions X and S, respectively, then equation (*h*) is valid for each solution and

$$p_X - p_S = \log\left(\frac{a_{H_2O}}{a_{H_3O^+}}\right)_X - \log\left(\frac{a_{H_2O}}{a_{H_3O^+}}\right)_S = \frac{-(E_1 - E_2)F}{RT\ln 10} = \frac{-(E_X - E_S)F}{RT\ln 10} \qquad (i)$$

which shows that an electrometric determination of p_X in comparison with p_S—if p_S is selected as a standard—results in a pH determination if, and only if, the activity of water is the same in both solutions. A consistent electrometric determination of pH involves this extra restriction which is not necessary when p is measured.

The present operational definition of pH should, strictly speaking, be modified by adding this restriction.[1] However, this will hardly be generally accepted, and this problem can probably be solved most easily by accepting the present definition as prescribing the measurement of the quantity p. When desired, the activity of water may be kept constant, whereby Δp will give ΔpH.

By assigning a value to one of the solutions, *viz.* solution S, a value can be found for the other. For this purpose it is more meaningful and useful to assign p values instead of pH values to solutions prepared from buffer substances, *e.g.*, as prescribed by the National Bureau of Standards.[2] It is often pointed out that a pH scale—*e.g.*, the NBS scale—only has significance for dilute solutions where the activity of the water is practically the same as for pure water.[3,4] One notices that the results of these considerations are not conditioned by such an assumption about the composition of the systems involved.

The thermodynamic basis of the operational definition may be elucidated further by means of the following expression derived from (*b*) and (*h*).

$$p_X - p_S = \log\frac{Q_{1,2}}{K_{1,2}} = \left(\frac{\delta G}{\delta \xi}\right)/RT\ln 10$$

where $Q_{1,2}$ is a mass-action expression of the same form as the equilibrium constant $K_{1,2}$; both are associated with reaction (*a*). Thus the present operational definition can be said to prescribe an evaluation of the instantaneous rate of change of G (at constant T and P) with respect to the extent of the Brønsted–Lowry acid–base reaction (*a*) in which any two acid–base pairs may participate as long as the one pair belongs to solution X and the other to solution S.

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Summary—The electrometric determination of pH is essentially an evaluation of the thermodynamic quantity $-\log a_{H_3O^+}$ from a measurement of an electrical potential difference between two electrodes. It is accordingly necessary to examine the electrometric method in light of thermodynamic concepts in order to disclose the meaning of experimental pH values and their limitations. In this paper it is shown by thermodynamic considerations that the evaluation of $-\log a_{H_3O^+}$ is actually a special case of the evaluation of the thermodynamic quantity

$$\log \frac{a_{H_2O}}{a_{H_3O^+}}$$

The operational definition of pH prescribes a general method to evaluate this quantity, but not $-\log a_{H_3O^+}$ as commonly believed.

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PRELIMINARY COMMUNICATIONS

MANGANESE(IV) AS AN OXIDIMETRIC REAGENT IN SULPHURIC ACID SOLUTIONS

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During studies on the behaviour of oxidizing agents on a tetrachlorohydroquinone (TCHQ) column,[1] we observed difficulty in reducing potassium permanganate in acidic medium. Preliminary experiments showed that permanganate solution prepared in sulphuric acid of high concentration (*ca.* 9*M*) changes its colour from pink to yellow in about 24 hr. This reaction is initially very vigorous and takes place with evolution of oxygen. The solution, when passed through a TCHQ column, is reduced quantitatively to manganese(II). Addition of a measured and excessive amount of iron(II) and back-titration with a standard dichromate solution shows that a 2-electron reaction occurs. We therefore suggest that manganese(IV) is formed from permanganate at high sulphuric acid concentration.

Manganese(IV) salts are strong oxidizing agents. The standard potential[2] of the redox system $Mn^{4+} + 2\underline{e} \rightarrow Mn^{2+}$ is 1.577 V (*cf.* $Mn^{4+} + \underline{e} \rightarrow Mn^{3+}$, 1.62 V; $Mn^{3+} + \underline{e} \rightarrow Mn^{2+}$, 1.511 V; $MnO_4^- + 8H^+ + 5\underline{e} \rightarrow Mn^{2+}$, 1.52 V). The older literature cited by Mellor[3] reported the reduction of permanganate in concentrated sulphuric acid, but there was little evidence for formation of manganese(IV).[4-6] Some authors[7-10] have reported the formation of manganese(IV) by reduction of permanganate with alkaline tellurite or by oxidation of manganese(II) with alkaline hydrogen peroxide in the presence of excess of tellurate, which stabilizes the manganese(IV). Desideri[11] studied the mechanism of permanganate reduction at a platinum electrode and presented evidence for the existence of manganese(III) and MnO^{2+} as intermediates in presence of manganese(II) and sulphuric acid. Kharabadze[12] reported the production of sulphates of manganese(III) and (IV) by the anodic dissolution of manganese metal in concentrated sulphuric acid.

This preliminary investigation reports the conditions under which manganese(IV) can be obtained in sulphuric acid solution and its use as an oxidimetric reagent. Potassium permanganate solutions in 9*M* sulphuric acid were found to be reduced within 12 hr. The choice of sulphuric acid concentration was somewhat arbitrary. At lower acidities conversion of permanganate into manganese(IV) was slow, but for purposes of titrimetry it is not desirable to go above this acidity. The solution is yellow in dilute and dark-brown in concentrated solutions.

Spectrophotometric studies

The absorption spectrum of a dilute solution of potassium permanganate (8×10^{-5}*M*) in sulphuric acid was scanned from 200 to 600 nm at various time intervals. There is a gradual decrease in the permanganate concentration and after about 7 - 8 hr there is no permanganate left. The absorption spectrum of a 12-hr old 2×10^{-4}*M* manganese(IV) solution in 9*M* sulphuric acid is shown in Fig. 1. There is a shoulder at 265 - 285 nm, but no maximum was observed for manganese(IV) in the visible region although permanganate and manganese(III) show maxima at 546 and 500 nm respectively. Manganese(III), which is stable in pyrophosphate medium, does not absorb in the ultraviolet region.[13]

Preparation of standard manganese(IV) solution

To prepare a 0.05M solution, dissolve about 7.9 g of potassium permanganate in 9M sulphuric acid with vigorous stirring, preferably by magnetic stirrer, over a period of 6 - 8 hr. Leave the solution overnight, then make it up to 1 litre with 9M sulphuric acid and then standardize it as follows:

(i) With iron(II) sulphate solution. Make 25 ml of iron(II) solution (previously standardized with permanganate or dichromate) 1 - 5M in sulphuric acid, and titrate it with the manganese(IV) solution in the presence of a drop of ferroin indicator.

(ii) With sodium oxalate solution. Heat 25 ml of sodium oxalate solution (in 1 - 5M sulphuric acid) to 70°, and titrate it with the manganese(IV) solution. The end-point is indicated by a light pink colour, presumably due to manganese(III).

The titre deteriorates by 0.1 - 0.2% per day and solutions need to be standardized daily.

Manganese(IV) as an oxidimetric reagent

Our initial studies have shown that manganese(IV) can act as an oxidizing agent for almost all the conventional reductants, e.g., Fe^{2+}, VO^{2+}, As^{3+}, $C_2O_4^{2-}$, I^- etc. It is also observed that it oxidizes cerium(III) to cerium(IV). Potentiometric titrations of manganese(IV) (platinum electrode) with Fe^{2+}, VO^{2+}, and Ce^{3+} all give two potential breaks, presumably due to the reduction of manganese(IV) first to manganese(III) and then to manganese(II). However, the first break is very small (slope 2.5 mV/0.05 ml) and only the second is useful (slope about 270 mV/0.05 ml). Equilibration of the electrode potentials takes about 3 min in the end-point region). The reverse titrations are also possible but show only the change from manganese(IV) to manganese(II) (slope about 270 mV/0.05 ml at the end-point for iron, less for the others). Manganese(IV) can be used as an oxidimetric reagent for the quantitative estimation of a variety of reductants. Detailed analytical studies and kinetics of the reduction of permanganate to manganese(IV) are now in progress and will be published later.

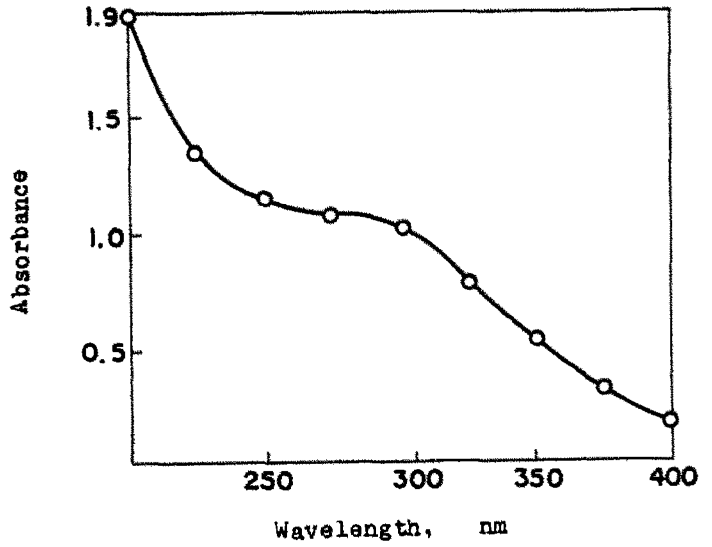

Fig. 1. Absorption spectra of 2×10^{-4}M manganese(IV) solution

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A NEW CHELATE-FORMING RESIN WITH DITHIZONE FUNCTIONAL GROUP PREPARED BY THE CONVERSION OF AN ANION-EXCHANGE RESIN

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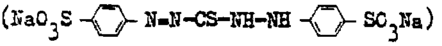
For the concentration and collection of heavy metal ions by a chelating resin, the presence of the thiol group as the chelating group on the resin is desirable because of its selectivity and ability to form stable chelates. Some effective thiol-containing chelating resins for the adsorption of heavy metal ions have been synthesized.[1–4] However, the introduction of the thiol group into the resin matrix is not easy. Further, the resin is not easily recoverable after adsorption of metal ions. Some chelate-forming granules have been introduced for the same purpose.[5–7] They are easily prepared, but their exchange capacity is not as high as that of the chelating resin.

We have prepared a chelate-forming resin of a new type, by the simple procedure described below, namely by the treatment of common strongly basic anion-exchange resin with a sulphur-containing chelating agent which involves the functional group for the anion-exchange together with the chelating group. We selected a sulphonic acid derivative of dithizone  (**I**), as chelating agent. **I** was synthesized from p-hydrazinobenzenesulphonic acid and carbon disulphide as follows. Carbon disulphide (1.5 ml) and ethanol (60 ml) were added to about 40 ml of an aqueous solution of p-hydrazinebenzenesulphonic acid (6 g) and sodium hydroxide (1.3 g) and the solution was refluxed for several hours. After the solution was cooled, addition of 200 ml of ethanol gave a white precipitate. The precipitate (1 g), dissolved in a small amount of water, was added to 25 ml of ethanol containing 0.2 g of sodium hydroxide. The solution immediately turned red. The red precipitate deposited by the addition of acetone (200 ml) was collected by filtration. Thin-layer chromatography of the product (solvent; methanol) gave one spot. **I** is stable as its sodium salt both in aqueous solution and the dry state, but is very unstable as the free acid. The spectral properties of **I** (Fig. 1) are similar to those of dithizone.

The chelate-forming resin was obtained when 1 g of the anion-exchange resin (Amberlite IRA 400 in the chloride form, 100 – 200 mesh) was stirred with 50 ml of aqueous solution of various amounts of **I**.

The exchange capacity for **I**, examined by the batchwise method, was 1.9 mmole per g of dry resin. The time required for the saturation of the resin with **I** was 2 – 3 hr, and only 20 min was needed for the adsorption of about a third of this amount, and this is enough for practical use of the resin. The resin thus prepared, if stored in a refrigerator, is stable for at least three weeks.

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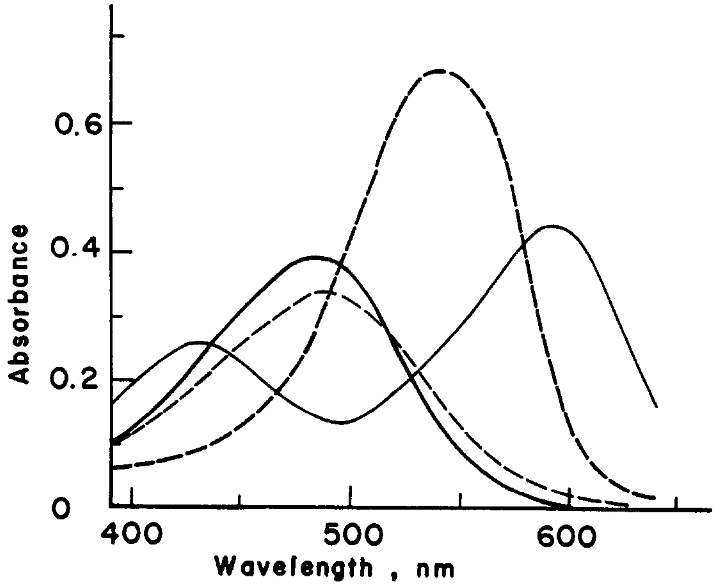

Fig. 1. Absorption spectra of 2.5 x 10^{-5}M sulphonic acid derivative of dithizone, I. (——)pH 1.2, (- -) pH 12.0, (——) pH 1.2 with 1.25 x 10^{-5}M Hg^{2+}, (- -) pH 12.0 with 2.5 x 10^{-5}M Hg^{2+}.

The occurrence of ion-exchange between the resin and I was confirmed by the release of an equal number of moles of chloride ion (determined by Mohr's method). I is, however, not eluted from the resin even with 2M sodium hydroxide. The strong adsorption of I on the resin matrix may be explained in terms of both ion-exchange and some physical adsorption. In fact, dithizone is considerably adsorbed on the resin matrix, but without release of chloride.

The behaviour of the resin towards mercury(II) is shown in Fig. 2. The binding ratio of Hg(II) to I on the resin was found to be about 1:2 from Fig. 2, and the composition of the mercury(II) chelate with I in the pH range 1.0 - 5.4 was also 1:2 (mole-ratio method). This means that the I on the resin was utilized completely for the effective adsorption of mercury(II).

The mercury(II) adsorbed could not be released by 20% mineral acid solution, but it was released almost completely by concentrated hydrochloric acid, as shown in Table 1, and the original resin was recovered. The eluate was violet after the treatment with concentrated hydrochloric acid and the absorption spectrum of the eluate was found to be similar to that of isomerized dehydrodithizone.[8] The resin recovered could be used repeatedly for the adsorption of mercury(II) by the same procedure.

Recently the preparation and properties of a similar type of resin, loaded with 8-quinolinol-5-sulphonic acid, which is useful for the collection of various kinds of metal ions, were reported briefly.[9] Resins with a sulphur-donor group may be significant for the selective collection of heavy metal ions. This new type of resin may be particularly useful because it is very easily prepared and the original resin can be recovered.

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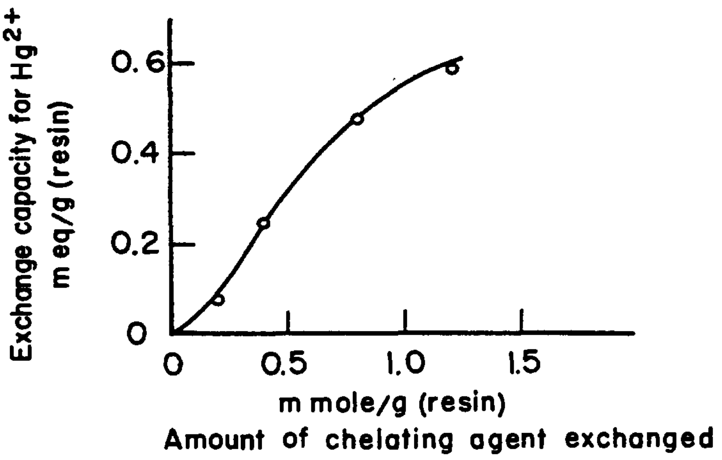

Fig. 2. Ion-exchange capacity of anion-exchange resin treated with sulphonic acid derivative of dithizone, for mercury(II).

Table 1. Recovery of mercury(II) from chelate-forming resin on which **I** (200 mg) and Hg^{2+} (44 mg) were adsorbed per g of dry anion-exchange resin

Eluent	Recovery, %*
8.7*M* HCl, 160 ml	96
11*M* HCl, 100 ml	94

*Mercury in the eluate was determined by the dithizone method

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THE INFLUENCE OF HALIDES ON AMPEROMETRIC COMPLEX-FORMATION TITRATIONS WITH THE ROTATING MERCURY ELECTRODE

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Summary—The interference of halides with complexometric titrations, indicated by means of the anodic wave of the ligand at a rotating mercury electrode, has been studied theoretically. The effect of halides strongly depends on the pH of the solution. In alkaline solutions there appears to be no interference by chloride at all. A critical value for the halide concentration can easily be found for any medium. The theoretical predictions have been verified experimentally.

Amperometric complex-formation titrations using a rotating mercury electrode as indicator electrode have been described.[1,2,3] The method enables micromolar concentrations of metal ions to be determined. In order to maintain constant values of the conditional stability constants of the metal complexes formed, the titration solution has to be buffered. Proper choice of the pH can improve the selectivity of the titrations. Low pH values further the selectivity for the determination of metal ions forming very stable complexes with the titrant,[1,3] whereas high pH values are favourable for the selective titrations of metal ions that complex only negligibly with hydroxyl ions and ions of the alkaline buffer systems.[2] The first group contains such metal ions as copper(II), thorium(IV) and gallium(III), whereas the alkaline earths ions belong to the latter group.

As the concentration of the ligand during the titration is monitored by means of the anodic dissolution of the electrode, the possible interference of halide ions has to be considered. The half-wave potential of the anodic ligand wave becomes more negative with increasing pH. Hence the interference by halides will be less serious in alkaline solutions.

In a previous paper[1] a few scattered results were given for the influence of chloride and bromide on the titration of copper(II) with TRIEN. In the present communication the problem will be treated more systematically.

THEORETICAL

The theoretical treatment will be given for the influence of halides on determinations at a dropping mercury electrode. The electrode reactions are supposed to be reversible, which is correct for d.c. polarography.[4,5]

The current–voltage curve for the anodic dissolution of mercury in a medium containing a ligand L that forms 1:1 complexes with mercury(II), is given[1] by (25°, SCE)

$$E = 0.608 + 0.0295 \log \alpha_{\mathrm{L(H)}} - 0.0295 \log K_{\mathrm{HgL}} + 0.0295 \log (i/i_{\mathrm{d}} - i) \quad (1)$$

It has been assumed that the species involved in the electrode reaction have the same diffusion constant and that the only side-reaction is that of L with protons.

Taking the value of K_{HgL} as 10^{22} and tabulated values of $\alpha_{\mathrm{L(H)}}$, the half-wave potential $E_{\frac{1}{2}(\mathrm{L})}$ can be given as a function of pH. For the anodic dissolution of mercury in a medium containing halides two possibilities arise, *i.e.*, the formation of the insoluble mercury(I) halide or the formation of a mixture of mercury(II) halide complexes. The two cases will be treated separately. When an insoluble mercury(I) halide is formed the current–voltage curve is given by

$$E = 0.543 + 0.0295 \log S_{\mathrm{Hg_2X_2}} - 0.059 \log \frac{i_{\mathrm{d}} - i}{k_{\mathrm{X}}} \quad (2)$$

as derived by Kolthoff and Miller.[6] Assuming a limiting current of 10 μA for a $10^{-3}M$ halide solution, k_{X} will have a value of 10^4 μA. 1. mole^{-1}.

For the current–voltage curve in the case of complex-formation of mercury(II) with halides, we also start with the Nernst equation,

$$E = 0.608 + 0.0295 \log [\mathrm{Hg}^{2+}]_{\mathrm{s}} \quad (3)$$

in which $[\mathrm{Hg}^{2+}]_{\mathrm{s}}$ is the concentration of mercury(II) at the electrode surface. The reaction at the electrode surface is

$$\mathrm{Hg} + \bar{n}_{\mathrm{s}}\mathrm{X}^- \rightleftharpoons \mathrm{HgX}_{\bar{n}_{\mathrm{s}}}^{2-\bar{n}_{\mathrm{s}}} + 2\mathrm{e}$$

Charges for X and the complexes will be omitted in the rest of the paper; $\bar{n}_{\mathrm{s}}$ represents the average ligand number at the surface of the electrode. The average ligand number $\bar{n}$ is defined by Bjerrum as

$$\bar{n} = \frac{\sum_{1}^{n} n\beta_n[\mathrm{X}]^n}{\sum_{0}^{n} \beta_n[\mathrm{X}]^n} \qquad (4)$$

Thus $\mathrm{HgX}_{\bar{n}_s}$ stands for a mixture of complexes of Hg(II) with X, the composition of which is fixed by $[\mathrm{X}]_s$, the concentration of the free halide at the electrode surface.

For the problem under study, simplifications can be made, leading to an explicit relationship between potential and current, but this is not so in general. As the general case may be of interest for other applications as well, it seems useful to give the full derivation here.

In equation (3) $[\mathrm{Hg}^{2+}]_s$ has to be replaced by an expression taking into account the reaction between Hg(II) and X at the electrode surface. The extent to which Hg(II) reacts with X can adequately be described by means of the side-reaction coefficient $\alpha_{\mathrm{Hg(X)}}$.

$$\alpha_{\mathrm{Hg(X)}} = \frac{\sum_{0}^{n} [\mathrm{HgX}_n]}{[\mathrm{Hg}^{2+}]}$$

Hence

$$E = 0.608 + 0.0295 \log \frac{\sum_{0}^{n} [\mathrm{HgX}_n]_s}{\alpha_{\mathrm{Hg(X)}_s}}$$

or

$$E = 0.608 - 0.0295 \log \alpha_{\mathrm{Hg(X)}_s} + 0.0295 \log \sum_{0}^{n} [\mathrm{HgX}_n]_s \qquad (5)$$

The current–potential relation can be derived by assuming a steady state at the electrode surface.[7] This means for the halide ion X that the supply of X to the electrode surface by diffusion, which is proportional to $\{[\mathrm{X}]_{\mathrm{bulk}} - [\mathrm{X}]_s\}$, is just compensated by the amount of X consumed per unit of time by Hg(II) produced at the electrode surface, which is $\bar{n}_s i/2F$.

Hence

$$i = i_a + i_c = \frac{k_\mathrm{X}}{\bar{n}_s} \{[\mathrm{X}]_{\mathrm{bulk}} - [\mathrm{X}]_s\} \qquad (6)$$

where i_a and i_c represent the anodic and the cathodic current respectively.

The supply of Hg(II) in any form per unit of time is $i/2F$, which in the steady state is compensated by the diffusion of mercury(II) and its halide complexes into the bulk of the solution, which is proportional to

$$\sum_{0}^{n} [\mathrm{HgX}_n]_s$$

if Hg(II) and its halide complexes have the same diffusion coefficient.

Hence

$$i = i_a + i_c = k_{\mathrm{Hg(II)}} \sum_{0}^{n} [\mathrm{HgX}_n]_s \qquad (7)$$

Substitution of (7) into (5) leads to

$$E = 0.608 - 0.0295 \log \alpha_{\mathrm{Hg(X)}_s} + 0.0295 \log \frac{i}{k_{\mathrm{Hg(II)}}} \qquad (8)$$

The current–potential curve can now be drawn by means of equations (6) and (8) starting with $[\mathrm{X}]_s$ as a parameter. For every value of $[\mathrm{X}]_s$ a value for $\alpha_{\mathrm{Hg(X)}_s}$ and for $\bar{n}_s$ can be calculated. Then the corresponding values of E and i can be obtained. The equations (6) and (8) reflect the continuous change in the average ligand number of the mercury(II) halide complexes formed at the electrode surface, down to $\bar{n}_s = 0$ at the final rise of the current–voltage curve. It can also be seen from equation (6) that a limiting current

$$i_d = \frac{1}{\bar{n}_s} k_\mathrm{X} \{[\mathrm{X}]_{\mathrm{bulk}} - [\mathrm{X}]_s\}$$

may occur when two conditions are fulfilled: (*a*) $[\mathrm{X}]_s$ must be negligible with respect to $[\mathrm{X}]_{\mathrm{bulk}}$, (*b*) $\bar{n}_s$ must remain constant over a certain concentration range $\Delta\log[\mathrm{X}]$ of the halide.

From equations (6) and (8) it can be seen that this limiting current will develop over a potential range

$$\Delta E = 0.0295\, \bar{n}_s \Delta\log[\mathrm{X}]$$

In practice, halides will not interfere when present in concentrations of the same order of magnitude as the compounds involved in the titration reaction, as under these circumstances the anodic ligand wave can always be seen in the polarogram even when the anodic halide wave occurs at the same potential. Therefore the interference of halides only has to be considered for concentrations large with respect to the concentration of the species to be determined. Whether the interference will be serious or not, will—from a polarographic point of view—depend on the potential at the point of intersection of the halide wave and the ligand wave, relative to the half-wave potential of the ligand wave. The current value at the point of intersection will always be low in comparison with the limiting current of the halide wave. We may assume that at these relatively low currents the halide concentration at the electrode surface will not differ much from that in the bulk of the solution. This means that for our present purpose $\alpha_{\mathrm{Hg(X)}_s}$ in equation (8) may be replaced by the constant value $\alpha_{\mathrm{Hg(X)}_{\mathrm{bulk}}}$, which results in

$$E = 0.608 - 0.0295 \log \alpha_{\mathrm{Hg(X)}_{\mathrm{bulk}}} + 0.0295 \log \frac{i}{k_{\mathrm{Hg(II)}}} \qquad (8a)$$

from which the initial rise of the current–potential curve can be drawn directly.

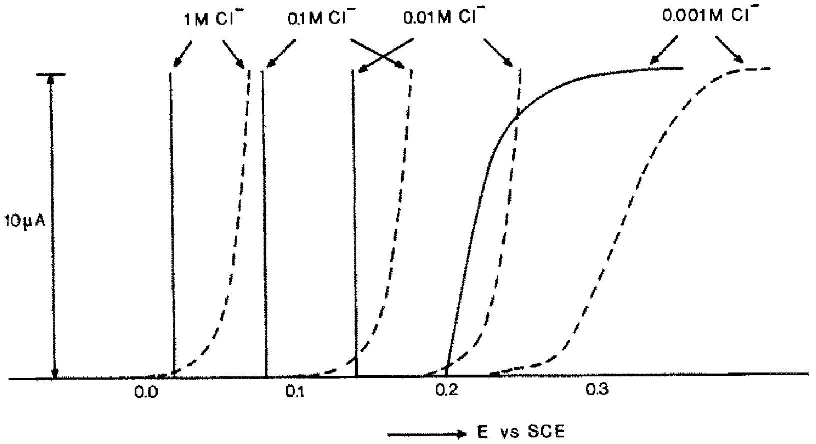

Fig. 1. Current–voltage curves, calculated for the anodic oxidation of mercury at a DME in solutions of different concentrations of chloride. Solid lines: $2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e$; Dotted lines: $Hg + nCl^- \rightarrow HgCl_n^{(2-n)+} + 2e$.

Figure 1 presents some polarograms according to equations (2), (6), (8) and (8a) for chloride concentrations 1, 10^{-1}, 10^{-2} and $10^{-3}M$. Both k_X and $k_{Hg(II)}$ have been taken as 10^4 μA. 1. mole^{-1}. Values for log $\alpha_{Hg(Cl)}$ and $\bar{n}$, given in Table 1, have been calculated with log $\beta_1 = 6.7$; log $\beta_2 = 13.2$; log $\beta_3 = 14.1$ and log $\beta_4 = 15.1$. $S_{Hg_2Cl_2}$ has been taken as $10^{-17.7}$. It can be seen from Fig. 1 that under all circumstances there is interference due to the formation of Hg_2Cl_2. The same holds for bromide. For iodide however, complex formation begins to predominate in about $5 \times 10^{-2}M$ solutions, but this is of no practical significance, as iodide interferes already in lower concentrations. So in the following only the interference by the formation of Hg_2X_2 will be considered. Furthermore the discussion will be restricted to complexometric titrations with EDTA as the ligand.

Table 1. Values of $\alpha_{Hg(Cl)}$ and $\bar{n}$ for various values of [Cl⁻]

[Cl⁻], *M*	log $\alpha_{Hg(Cl)}$	$\bar{n}$
1	15.15	3.89
10^{-1}	11.61	2.92
10^{-2}	9.24	2.09
10^{-3}	7.20	2.01

Figure 2 presents polarograms at different pH values according to equation (1) for a concentration of EDTA of about $10^{-3}M$ ($i_d = 10$ μA and log $K_{HgL} = 22$) and polarograms according to equation (2) for different concentrations of chloride. Serious interference is assumed to start when the concentration of chloride reaches a critical value at which the interfering current–voltage curve and the current–voltage curve of the ligand intersect at the half-wave potential of the ligand wave. The values of the interfering concentrations of chloride calculated in this way have been compared with experimentally obtained values.

EXPERIMENTAL

Polarograms with the dropping mercury electrode were taken with a Metrohm E polarograph. The buffers[3] and titration equipment[1-3] were the same as used before. Half-wave potentials of the ligand wave were determined by

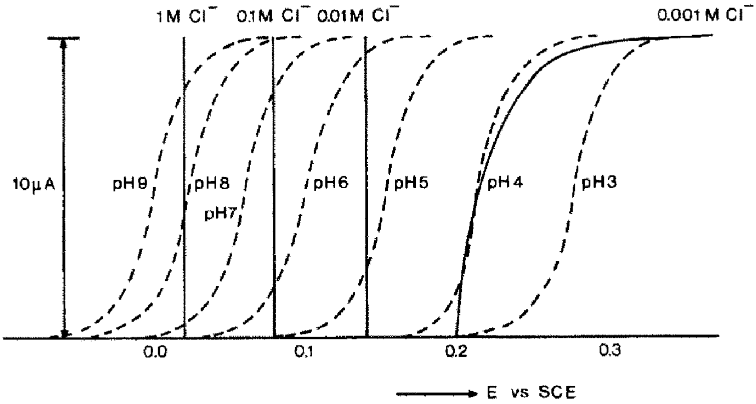

Fig. 2. Current–voltage curves, calculated according to equation (1) ($i_d = 10$ μA, dotted lines) for different pH values, and according to equation (2) (solid lines) for different concentrations of chloride.

Table 2. Critical values for [Cl$^-$] in the case of $10^{-3}M$ EDTA at a DME

pH	Buffer	[Cl$^-$], M
3.50	phthalate	0.001
4.55	phthalate	0.005
4.50	acetate	0.005
5.00	acetate	0.01

derivative polarography. Interference was assumed to occur when the peak at the half-wave potential vanished owing to the presence of the halide.

Table 2 gives the values of the chloride concentration at which the half-wave peak disappears for different pH values in the case of an EDTA concentration of $10^{-3}M$. There is good agreement between the results in Table 1 and the theoretical conclusions from Fig. 2. Table 3 gives similar results for $10^{-4}M$ EDTA. Table 4 gives some results for measurements of half-wave potentials of $10^{-4}M$ EDTA in the presence of bromide. The agreement between the experimental results and the theoretical predictions, which are not given for bromide here, is also very good.

So far, theoretical considerations and experimental results have been compared for the anodic wave at the dropping mercury electrode. It can be expected that the situation will not alter much when a rotating mercury electrode is used, indicating lower concentrations of the ligand at higher sensitivity in the presence of the same concentrations of halide.

In equation (1) the values of i and i_d will not alter much, as the possible increase of the current due to the fact that a rotating electrode is used is nearly compensated by the decrease of the current due to the smaller concentrations of the compounds involved in the titration reaction. Moreover the half-wave potential will remain the same. Hence the overall change in the wave will be small.

The curve of equation (2) will remain the same at the initial rise of the current–potential curve, where $i \ll i_d$, because the last term in equation (2) originates from $0.059 \log[X]_s$, which for $i \ll i_d$ may be written as $0.059 \log[X]_{bulk}$. Hence the lower part of the curve of equation (2) at a certain value of $[X]_{bulk}$ will be the same for the rotating and the dropping electrode.

As the halide wave [from equation (2)] and ligand wave [from equation (1)] remain nearly unaltered, the conclusions obtained from Tables 2–4 for the interference of halides with the ligand wave for concentrations of the ligand of 10^{-4} or $10^{-3}M$ at the dropping electrode will remain the same for the interference of halides with titrations involving ligand concentrations of $10^{-5}M$ at the rotating electrode.

Table 3. Critical values for [Cl$^-$] in the case of $10^{-4}M$ EDTA at a DME

pH	Buffer	[Cl$^-$], M
5.05	acetate	0.001
5.55	acetate	0.005
6.0	phosphate	0.05
7.0	phosphate	0.1
7.5	phosphate	0.5

Table 4. Critical values for [Br$^-$] in the case of $10^{-4}M$ EDTA at a DME

pH	Buffer	[Br$^-$], M
6.0	phosphate	5×10^{-4}
7.0	phosphate	5×10^{-4}
8.0	tris	0.01
9.0	borate	0.1

Table 5. Critical values for [Cl$^-$] and [Br$^-$] in the titration of $10^{-5}M$ copper(II) with EDTA at a rotating mercury electrode

pH	Buffer ($10^{-2}M$)	[Halide], M
5.0	acetate	$[Cl^-] = 10^{-3}$
5.0	acetate	$[Br^-] = 10^{-5}$
7.0	maleate	$[Cl^-] = 10^{-2}$
7.0	maleate	$[Br^-] = 10^{-4}$
9.0	tris	$[Cl^-] = 10^{-1}$
9.0	tris	$[Br^-] = 10^{-2}$

Table 6. Critical values for [Cl$^-$] in the titration of $10^{-5}M$ copper(II) with TRIEN and DTPA at a rotating mercury electrode

pH	Buffer ($10^{-2}M$)	Titrant	[Cl$^-$], M
5.0	acetate	TRIEN	0.001
5.0	acetate	DTPA	0.005
7.0	maleate	TRIEN	0.01
9.0	tris	TRIEN	0.1
9.0	tris	DTPA	0.5

If, however, the interfering process would be the formation of mercury(II) halide complexes the electrode would take a more negative potential and the interference would become more serious. As we have already seen, mercury(II) halide formation will in general not be the interfering process.

All these considerations neglect the differences between current–voltage curves obtained with a dropping and a rotating electrode. Nevertheless, the experimental results, obtained for titrations at a rotating electrode in the presence of chloride and bromide, appear to be in agreement with the theoretical considerations given for the dropping electrode.

Table 5 gives the values of the chloride and bromide concentrations which do not interfere with the determination of $10^{-5}M$ copper(II) with EDTA at different pH values. As DTPA and TRIEN have slight advantages over EDTA as a titrant for copper(II) a number of determinations with these ligands have been carried out in the presence of chloride. Some typical results are given in Table 6. When DTPA is used as the titrant, slightly larger amounts of halides can be tolerated. When TRIEN is used, the titration curves show sharper end-points.

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L'ESTIMATION DE L'ERREUR, INTRODUITE DANS LE DOSAGE DES ELEMENTS A L'ETAT DE TRACES DANS LES ROCHES, LIEE AUX CARACTERISTIQUES STATISTIQUES DE LEUR REPARTITION

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Résumé—L'analyse des éléments à l'état de traces dans les roches peut être soumise à de nombreuses causes d'erreur. On peut en distinguer deux grandes catégories: les erreurs liées à l'échantillon analysé, c'est-à-dire à la méthode d'échantillonnage, à la préparation de l'échantillon (broyage et homogénéisation), à la répartition des éléments dans cet échantillon, et, les erreurs dues à la technique d'analyse utilisée. Dans cet article, nous nous intéressons plus particulièrement à l'erreur due à la répartition des éléments dans la poudre de roche à analyser. Une méthode expérimentale relativement rapide et simple est utilisée pour évaluer l'importance de ce genre d'erreur dans quelques échantillons types. Cette méthode est fondée sur l'analyse par activation neutronique. La variance d'échantillonnage a été aussi déterminée en fonction de la masse de la prise d'essai. Les résultats montrent que des analyses faites sur des prélèvements de petite quantité de poudre peuvent entraîner des erreurs importantes sur le résultat final (erreur d'un facteur deux ou plus dans la détermination du hafnium dans un granite au niveau d'une prise d'essai de 10 mg). Un modèle théorique simplifié nous permet d'expliquer les résultats expérimentaux tout au moins qualitativement.

Le développement relativement récent de la géochimie est une conséquence directe des progrès réalisés en chimie analytique. En particulier, les méthodes physiques ou instrumentales rapides, fondées sur la comparaison d'un signal émis par un étalon et l'échantillon à analyser, soumis à une excitation (action sur le cortège électronique ou sur le noyau des atomes) sont maintenant communément utilisées pour le dosage des éléments majeurs et des éléments à l'état de traces dans les roches et les minéraux.

La quantité et la qualité des résultats disponibles s'en trouvent considérablement accrues.

Les problèmes analytiques ne sont pas tous pour autant résolus. Il suffit pour s'en convaincre, de se référer aux nombreuses compilations publiées dans la littérature, concernant les étalons de roches aussi bien américains que français. En voici quelques exemples.

Pour les éléments majeurs:

Roche	Elément	Coefficient de variation, %	Référence
G_2	Al_2O_3	3	1
G_2	SiO_2	1,5	1
DRN	Al_2O_3	3,7	2
DRN	SiO_2	1,6	2

Pour les éléments à l'état de traces:

Roche	Elément	Etendue (range) *ppm*	Référence
G_2	Zr	250–400	1
G_2	Rb	108–503	1
DRN	Co	20–70	2
DRN	Rb	52–82	2

Nous avons pris ces exemples au hasard à titre indicatif. Mais, ceux-ci montrent bien que, si pour les éléments majeurs la concordance est bonne entre différentes méthodes et différents laboratoires, la situation est assez inquiétante en ce qui concerne les éléments à l'état de traces.

Il s'agit là d'une constatation d'ordre général. L'examen critique des principales causes d'erreurs qui peuvent affecter les données géochimiques est d'une importance primordiale, puisque la vérification des théories géochimiques en dépend.

Parmi les causes possibles, Shaw[3] en distingue trois principales:

—une hétérogénéité possible au niveau de l'ensemble géologique étudié

—une erreur due à l'échantillonnage sur le terrain (celle-ci découlant de la première)

—une erreur due à l'analyse chimique.

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On peut en ajouter une, due au prélèvement d'une partie de l'échantillon en vue de l'analyse (cette erreur étant également liée à l'hétérogénéité éventuelle de l'échantillon).

Les troisième et quatrième points concernent directement l'analyste. Nous nous proposons dans ce qui suit d'étudier l'incidence de la taille des prélèvements sur le dosage des éléments à l'état de traces.

MODELES D'ECHANTILLONS

L'échantillon de roche qui parvient au laboratoire d'analyse, se présente sous la forme d'une poudre dont la taille moyenne des grains est d'environ 80 μm. Au niveau du grain cette poudre est hétérogène, et cela d'autant plus que la roche d'origine est composée de plusieurs espèces minérales. Le soin apporté à la préparation de l'échantillon broyé peut également jouer un rôle important.

Wilson[4] dans une étude théorique partant de l'hypothèse d'une distribution binomiale des grains montre que l'erreur relative introduite de ce fait dans le dosage d'un élément est inversement proportionnelle à la racine carrée du nombre de grains n contenu dans l'échantillon analysé. Soit:

$$S_R = \sqrt{\frac{K'}{n}} \quad \text{ou} \quad S_R = \sqrt{\frac{K}{m}}$$

où m est la masse de la prise d'essai, K et K' sont des constantes qui dépendent des proportions relatives des différentes espèces minérales et de leur densité. Ingamells *et al.*[5,6] dans une série d'articles consacrés au même problème proposent d'utiliser la constante K comme "constante d'échantillonnage". K a en effet la dimension d'une masse. C'est la masse de la prise d'essai telle que "le coefficient de variation dû à l'échantillonnage", soit de 1%. Cette constante est alors caractéristique d'un élément dans une poudre de roche déterminée. Une telle donnée serait précieuse pour l'utilisation des étalons de roche. Elle permet de choisir la taille du prélèvement convenable pour l'analyse.

Malheureusement, ce modèle qui a pour origine la distribution binomiale n'a pas un caractère général. Un effet de ségrégation éventuel n'apparaît pas.

Une "théorie générale de l'échantillonnage" développée de manière semi empirique par Visman[7,8] en s'appuyant sur des "modèles *à priori*" de population conduit à donner à la fonction $S_R = f(m)$ la forme:

$$S_R = \sqrt{\frac{A}{m}} + B$$

où A et B sont des constantes. A s'identifie à la constante K précédemment définie, B est la composante de la variance due à un effet de ségrégation. Duncan[9] dans une critique de la théorie de Visman donne des justifications théoriques à cette formulation et met en garde contre le fait qu'il s'agit là aussi d'une approximation. En particulier B ne peut évidemment pas être un terme constant lorsque la taille du prélèvement augmente. C'est un terme approximativement constant dans un certain domaine de taille d'échantillon.

Ces quelques rappels faits, nous nous proposons d'étudier le comportement des éléments en traces dans cette optique, c'est-à-dire de déterminer expérimentalement la fonction $S_R = f(m)$ dans des cas concrets (S_R sera exprimé en % de la teneur de l'élément).

PRINCIPE DE LA METHODE

Nous avons utilisé l'activation neutronique comme technique analytique. Il n'est pas nécessaire pour résoudre notre problème de déterminer les teneurs des éléments. Nous utilisons simplement le fait que la radioactivité mesurée pour un élément donné est proportionnelle à la masse de cet élément, ou, en ramenant à l'unité de masse de l'échantillon, à la teneur en cet élément.

Soit:

$$t_i = k_i A_i$$

ou t_i est la teneur en un élément i, A_i le résultat de la mesure de radioactivité en nombre de désintégrations par unité de temps, et k_i une constante qui dépend des caractéristiques nucléaires de l'élément et de l'intensité du flux de neutrons utilisé.

Si on irradie simultanément n échantillons, k_i est identique pour tous. Dans ces conditions, nous pouvons écrire:

$$\sigma(\log t_i) = \sigma(\log A_i) \qquad (1)$$

$\sigma(\log k_i)$ étant nul puisque k_i est une constante (le flux de neutrons étant constant comme nous l'indiquons plus loin). Si les erreurs sont faibles, elles sont assimilables à des différentielles. L'expression:

$$\frac{\sigma(t_i)}{\bar{t}_i} = \frac{\sigma(A_i)}{\bar{A}_i} = 10^{-2} S_{R_i}$$

est équivalente à (1) ($\bar{t}_i$ est la teneur moyenne dans les n échantillons; $\bar{A}_i$ est la moyenne des mesures de radioactivité pour les n échantillons irradiés simultanément).

Dans la pratique nous avons travaillé sur les séries de prélèvements de 150, 100, 50 et 10 mg. Chaque série comportait $n = 12$ à 25 prélèvements. La technique d'irradiation a été décrite par ailleurs.[10] Les mesures de radioactivité ont été faites au moyen d'un détecteur solide (germanium dopé au lithium) et nous avons estimé la variance pour chaque série j et chaque élément i par:

$$S_i^2 = \frac{\sum_{j=1}^{n} (A_{ij} - \bar{A}_i)^2}{n-1}$$

d'où

$$S_{R_i} = \frac{100 S_i}{\bar{A}_i}$$

A ce stade se pose le problème de savoir si S^2 est bien une estimation de la "variance d'échantillonnage". En effet des contributions importantes pourraient intervenir à divers niveaux:

—erreur due à des variations du flux de neutrons,

—erreur due à la pesée de l'échantillon,

—erreur due à la variation de géométrie des échantillons par rapport au détecteur,

—erreur due à la mesure de la radioactivité.

En ce qui concerne les trois premiers points, nous avons constaté que les erreurs sont négligeables par rapport à la quatrième. Cette dernière cause est prédominante et peut seule entrer en considération.

Il est possible de l'estimer. En effet: les phénomènes de désintégration sont décrits par la loi de Poisson[11] pour laquelle la moyenne est égale à la variance. Le nombre de désintégrations N mesuré étant très élevé, on admet que ce nombre appartient à une distribution de Gauss de moyenne N et d'écart type $\sqrt{N}$.

D'où

$$S_d = \frac{100\sqrt{N_i + B_i}}{A_i}\% \text{ (avec } N_i - B_i = A_i)$$

où S_d est l'écart type sur la mesure de radioactivité, N_i le nombre de désintégrations mesuré dans la zone d'énergie qui concerne l'élément i, et B_i le bruit de fond dans cette zone.

Dans bien des cas, un test de comparaison entre S_R et S_d n'est pas nécessaire.

Voici quelques valeurs caractéristiques:

Elément	S_R, %	S_d %
Th	5	0,2
Co	2,3	0,4
Ta	2,3	0,7
Rb	1,5	1,2
Ni	3,7	3,7

Nous avons éliminé les cas litigieux, c'est à dire ceux pour lesquels le test de comparaison $S_R^2 = S_d^2$ contre $S_R^2 > S_d^2$ (test de χ^2) n'était pas significatif ou tout juste significatif, soit en pratique $S_R > 2S_d$ (exemple de Rb dans le tableau précédent).

RESULTATS

Les résultats obtenus pour deux étalons du C.R.P.G. (Nancy, France) GA et GSN, qui sont des granites et pour une obsidienne (verre naturel) sont reportés en coordonnées log–log sur les figures. La masse du prélèvement est portée en abscisse et en ordonnée, les valeurs de S_R en pour cent.

Cette représentation est commode en particulier dans le cas où la fonction $S_R = f(m)$ est de la forme $S_R = \sqrt{K/m}$. La courbe représentative est alors une droite de pente $(-\frac{1}{2})$ et le point d'intersection de cette droite avec la droite $S_R = 1$ donne la valeur de K.

Cas de GSN (*Fig.* 1)

Il apparaît que le modèle le plus simple est compatible avec nos résultats pour tous les éléments étudiés dans GSN. Dans le tableau suivant, nous donnons quelques valeurs de K pour différents éléments dans cet étalon.

Elément	*K, mg*
Cs	60
Co	100
Sc	40
Ta	60
Th	400
Hf	1000

Ce résultat montre que si on veut doser le hafnium dans le granite GSN en utilisant des prises d'essai de 10 mg, il faudra faire 100 dosages pour espérer avoir une précision de 1% sur la teneur en hafnium.

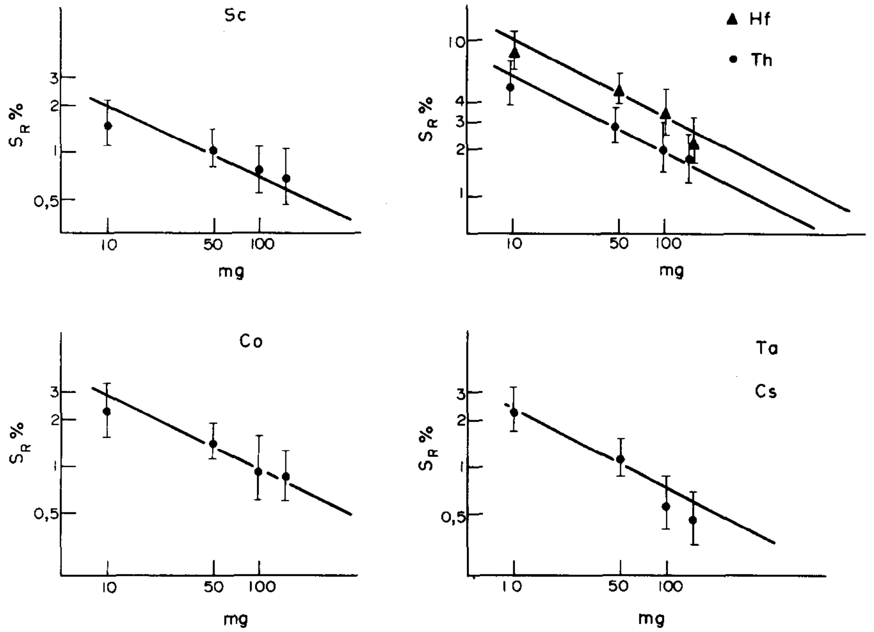

Fig. 1. Granite GSN. Evolution du coefficient de variation en fonction de la masse des prélèvements.

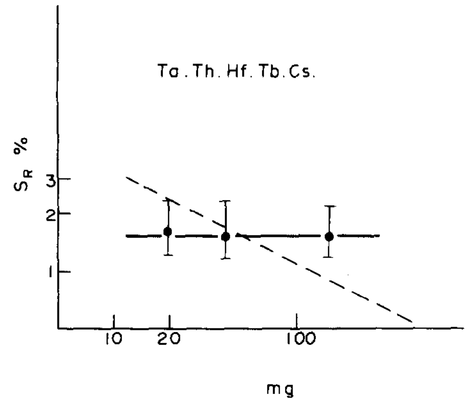

Fig. 2. Obsidienne. Evolution du coefficient de variation en fonction de la masse des prélèvements. La droite de pente $(-\frac{1}{2})$ en pointillés représente l'homogénéisation parfaite.

On ne peut évidemment pas extrapoler ces droites jusqu'à des masses voisines de 1 mg ou inférieures, mais il est à craindre qu'un dosage n'ait plus de sens à ce niveau.

Il faut remarquer aussi que pour des éléments tels que Cs, Co, Sc qui sont normalement associés à des éléments majeurs, les valeurs de K sont loin d'être faibles.

Cas de l'obsidienne (*Fig.* 2)

L'obsidienne est un verre. Tous les éléments doivent y être particulièrement bien répartis de manière uniforme. Nous constatons que tous les éléments se comportent de la même manière et que dans la gamme de 10 à 150 mg "le coefficient de variation dû à l'échantillonnage" est faible 1,5% mais constant. Cela ne peut s'expliquer que par la présence d'une phase qui n'est pas de l'obsidienne (ce qui est exact, l'obsidienne représente 95% environ de l'ensemble) et surtout que la poudre n'a pas été correctement homogénéisée après le broyage. Seule la composante de ségrégation intervient.

Le modèle

$$S_R = \sqrt{\frac{A}{m} + B}$$

convient dans ce domaine de 10 à 150 mg avec $A/m \ll B$.

Cas du granite GA (*Fig.* 3)

La situation est beaucoup plus complexe pour GA. Le hafnium et le zirconium se trouvent sous forme de zircons ($SiZrO_4$) qui sont des grains bien individualisés et répartis régulièrement dans la poudre de roche. Le modèle simple $S_R = \sqrt{K/m}$ s'applique parfaitement à ces deux éléments. Constatons seulement que la valeur de K pour le hafnium est particulièrement élevée ($K = 5000$ mg) cinq fois plus forte que celle annoncée pour GSN.

Pour des éléments tels que Th, Ta, Ce, Tb (lanthanides d'une manière générale), qui ne sont pas associés à des éléments majeurs, on observe des courbes comportant un plateau (ou tout au moins une variation très faible de S_R). Si m augmente, S_R tend vers 0. Pour les masses inférieures à 10 mg on doit s'attendre à une augmentation de la valeur de S_R.

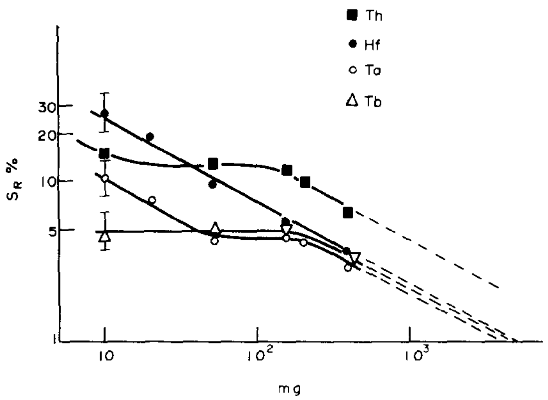

Fig. 3. Granite GA. Evolution du coefficient de variation en fonction de la masse des prélèvements.

Ce type de variation a d'ailleurs été décrit par Duncan[9] comme une "possibilité".

Ces formes de courbes traduisent un défaut d'homogénéisation. Aucun des deux modèles proposés ne permet de les décrire totalement. Nous avons déjà dit plus haut que le terme B de la formule $S_R = \sqrt{(A/m) + B}$ n'était qu'approximativement constant et ceci dans un domaine limité.

MODELE PROPOSE

Supposons que la poudre soit décomposée en n zones fictives, la proportion de zone i étant f_i ($i = 1,2\ldots$ et $\Sigma f_i = 1$).

Pour établir l'expression de la variance, nous admettons les hypothèses suivantes:

—la taille des prélèvements est petite devant la taille de chaque zone; dans ce cas, le nombre de prélèvements qui pourrait se faire sur une "frontière" entre deux zones est négligeable;

—un grain de poudre peut contenir ou ne pas contenir l'élément à doser et dans les grains qui contiennent cet élément, sa concentration y est constante;

—tous les grains ont la même dimension et dans une zone donnée, ils sont répartis uniformément.

Dans une zone i, la probabilité de rencontrer un grain contenant l'élément à doser est f_i. Pour un prélèvement de taille n grains, l'espérance du nombre de grains X_i contenant l'élément est $EX_i = np_i$.

La variance de X_i est $\sigma^2(X_i) = EX_i^2 - (EX_i)^2$ avec $\sigma^2(X_i) = np_i(1 - p_i)$.

Pour l'ensemble des zones, c'est à dire pour la totalité de la poudre, la variance est:

$$\sigma^2 = EX^2 - (EX)^2$$

avec $EX = \Sigma_i f_i EX_i$ et $EX^2 = \Sigma_i f_i EX_i^2$. Soit en exprimant EX_i et EX_i^2 en fonction de n, p_i et f_i:

$$\sigma^2 = \Sigma f_i np_i(1 - p_i) + \Sigma f_i(np_i)^2 - (\Sigma f_i np_i)^2$$

ou une valeur relative:

$$\sigma_R^2 = \frac{\Sigma f_i p_i(1 - p_i)}{n(\Sigma f_i p_i)^2} + \frac{\Sigma f_i p_i^2 - (\Sigma f_i p_i)^2}{(\Sigma f_i p_i)^2} \qquad (2)$$

Remarques

1. Dans cette expression, si $f_i = 1$ (ce qui entraîne $f_2 = f_3 \ldots f_i \ldots = 0$) le second terme est nul et

$$\sigma_R^2 = \frac{(1 - p)}{np} \qquad (3)$$

où p est une constante caractéristique de la poudre et n est proportionnel à la masse m du prélèvement. La formule (3) s'écrit: $\sigma_R^2 = A/m$ (A = constante).

2. Tant que la taille des prélèvements reste très inférieure à la taille des zones, le second terme de l'expression (2) est constant et σ_R est de la forme:

$$\sigma_R^2 = \frac{A}{m} + B$$

Ces deux formules sont celles proposées au paragraphe "modèles d'échantillons".

Il est évident que si la taille des prélèvements croît, le nombre de zones distinctes diminue. L'écart entre les f_i diminue également et σ_R^2 tend vers zéro.

EXEMPLE NUMERIQUE

Supposons que i puisse prendre deux valeurs $i = 1$ et $i = 2$. Si nous nous plaçons dans une partie de la courbe $S_R = f(m)$ où S_R est constant, le premier terme de l'expression (1) est nul et σ_R s'écrit:

$$\sigma_R^2 = \frac{(k^2 - 1)f_1 + 1}{[(k - 1)f_1 + 1]^2} - 1$$

avec $k = P_1/P_2$; f_1 peut être défini comme le degré d'homogénéisation de la poudre. Il est possible d'estimer f_1 connaissant σ_R^2 (estimé expérimentalement pour S_R^2) et k (estimé par le rapport des deux valeurs extrêmes de la série de mesures).

Pour l'obsidienne nous trouvons $f_1 = 0{,}95$ (avec $k = 1{,}07$ et $S = 0{,}015$). Pour le granite GA (élément = terbium), nous trouvons $f_1 = 0{,}80$ (avec $k = 1{,}19$ et $S = 0{,}05$).

Le modèle que nous venons de décrire distingue bien les deux composantes de la variance et surtout met en évidence ce qui les caractérise: une dépendance directe vis à vis de la taille du prélèvement pour la première composante et pour la seconde, sous certaines conditions, une indépendance (en première approximation).

Nous avons là une description de l'allure des courbes expérimentales et une possibilité de déterminer certains paramètres de la poudre de roche, en particulier le degré d'homogénéisation.

CONCLUSION

Il nous paraît essentiel que pour les étalons de roche internationaux, une description la plus complète possible de leurs caractéristiques statistiques soit donnée.

Ces renseignements sur l'homogénéité des poudres sont importants pour l'utilisateur (et pour le fabricant); ils permettent de choisir la masse de prise d'essai compatible avec une certaine précision et aussi de tester efficacement une procédure analytique.

Nous avons constaté que le seul paramètre proposé par Ingamells (A = constante d'échantillonnage) est insuffisant dans bien des cas.

Nous pensons que la donnée complète de la fonction $\sigma_R = f(m)$ soit sous forme graphique, soit sous forme d'une description statistique, est indispensable pour l'utilisation correcte des étalons de roche. Cela est surtout vrai pour le dosage des éléments à l'état de traces, mais aussi pour les éléments majeurs si les prélèvements sont petits (quelques milligrammes par exemple).

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METAL OXIDE ELECTRODES AS SENSORS IN COMPLEXOMETRIC TITRATIONS

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Summary—EDTA titrations of lead and manganese, and of some other ions by using these as indicator ions, have been followed potentiometrically with PbO_2 and MnO_2 electrodes. Explanations are put forward for the anomalies observed in the titration curves. With the MnO_2 electrode, formation of an Mn(III)–EDTA complex is responsible for the diminished potential breaks. With the PbO_2 electrode the decrease in the potential break and the distortion of the curves in acid solution may be due to reaction between electrode coating and titrant. The MnO_2 electrode has been used for titrations of Ba^{2+}, Ca^{2+}, Cd^{2+} and Cu^{2+} with errors < 1%.

Ion-selective membrane electrodes have tended to replace metal and amalgam electrodes for end-point indication in potentiometric titrations. However, it seems that for several ions metal oxide electrodes may be useful either in direct potentiometry or as end-point sensors in titrations.

Oxide electrodes were originally used for the measurement of pH.[1] The potential of an electrode consisting of a metal Me and its oxide $MeO_{n/2}$ may be expressed by

$$E = E^0_{Me^{n+}/Me} + \frac{RT}{nF}\ln K_{s0} - \frac{RT}{F}\ln a_{OH^-} \qquad (1)$$

where K_{s0} represents the solubility product of the oxide. This equation can be transformed into

$$E = E^0_{MeO_{n/2}/Me} + \frac{RT}{nF}\ln a_{H^+} \qquad (2)$$

When the metal oxide electrode is in contact with a solution of the metal ions in a different oxidation state from that in the oxide, then the potential-determining reaction may be described by

$$MeO_{n/2} + nH^+ + (n-m)e \rightleftharpoons Me^{m+} + nH_2O$$

and the potential given by

$$E = E^0_{MeO_{n/2}/Me^{m+}} - \frac{RT}{(n-m)F}\ln a_{Me^{m+}} + \frac{n}{(n-m)}\cdot\frac{RT}{F}\ln a_{H^+} \qquad (3)$$

or, when the pH and the ionic strength are constant,

$$E = E^0_{pH=const.} - \frac{RT}{(n-m)F}\ln a_{Me^{m+}} \qquad (4)$$

According to this equation the oxide electrode could, in principle, be used for a direct measurement of Me^{m+}, or in a potentiometric titration of this ion, or of other ions by using the technique of an indicator ion.[2]

Polarized platinum electrodes coated with oxides of Mn(IV), Pb(IV) or Bi were used by Kraft[3] in potentiometric titrations. Nomura and Nakagawa[4] used a Pt/MnO_2 electrode as indicator for the complexometric titration of various ions. Vandael[5] used a platinum helix coated with lead or bismuth oxide for the same purpose. Wang and co-workers[6] detected titration end-points with an electrode consisting of PbO_2 in paraffin. The shapes of the titration curves were often unexplained.

In this study the application of platinum electrodes, coated electrolytically with MnO_2 or PbO_2, as indicator electrodes in chelatometric titrations has been investigated. A mechanism is put forward as an explanation of the observed irregularities in their behaviour.

EXPERIMENTAL

Potentials were measured with Radiometer pHM 26 and Wroclaw N-512 ELPO pH-meters. Radiometer K 401 calomel and G 222 B glass electrodes were used, and indicator electrodes were prepared by anodic deposition of oxides on a 0.7-cm^2 platinum foil under conditions used in electrogravimetry.[7]

All reagents were of analytical grade. Doubly distilled water was used for the preparation of solutions. The concentrations of standard solutions were established by the usual methods.

DISCUSSION AND RESULTS

Direct chelatometric titrations

The variation of the electrode potentials as a function of pH was studied for $10^{-3}M$ solutions of manganese(II) and lead(II) with and without an excess of EDTA (Fig. 1). The curve 1 for Mn^{2+} is linear up to pH 9 with slope of 120 mV/pH, in good agreement with the 118 mV/pH predicted by equation (3). The curvature at high pH is due to the formation of hydroxo-complexes. Titrations should be possible above pH 8, but it was found that stable potentials are reached only very slowly, which make the titrations rather impractical.

The potentials of the PbO_2 electrode were much less reproducible than those of the MnO_2 electrode

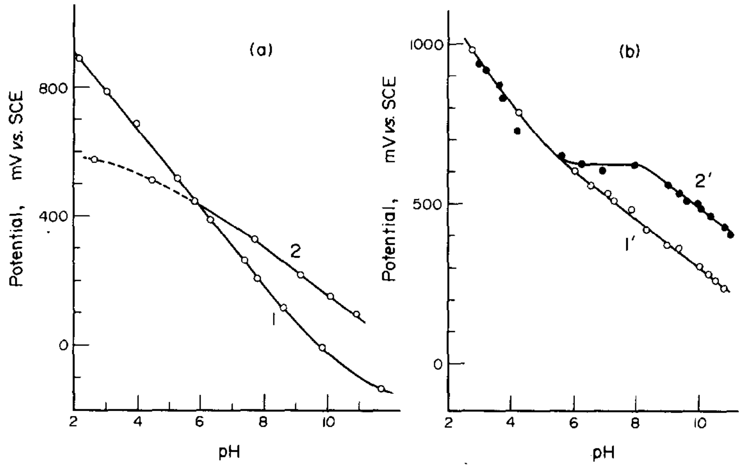

Fig. 1. Potential–pH relationship for MnO_2 (*a*) and PbO_2 (*b*) electrodes in solutions containing Mn^{2+} and Pb^{2+} ions, respectively: 1,1′—10^{-3} *M* Me^{2+}; 2,2′—10^{-3} *M* MeEDTA + 10^{-3} *M* EDTA.

and the agreement between the calculated and experimental values for a titration was poor (Fig. 2). The rate of titration significantly influences the results, which usually have a positive error (2–10% for titrations in acetate and ammonia buffers). In the first part of the titrations the potential of the PbO_2 electrode is adequately described by the equation:

$$E = E^0_{PbO_2/Pb^{2+}} - \frac{RT}{2F}\ln\frac{[Pb^{2+}]}{\alpha_{Pb}} + \frac{2RT}{F}\ln[H^+] \quad (5)$$

where α_{Pb} is the side-reaction coefficient for Pb^{2+} taking into account the presence of hydroxide and buffer. However, at pH < 6.5 for a lead concentration of about $10^{-6}M$ the system PbO_2, Pb^{2+} is thermodynamically unstable in aqueous solution. When the titrant is added in excess, the potential after the end-point should be given by the equation:

$$E = E^0_{PbO_2/Pb^{2+}} + \frac{RT}{2F}\ln\frac{[Y']K'_{PbY}}{[PbY']} + \frac{2RT}{F}\ln[H^+] \quad (6)$$

where Y represents the EDTA ligand, and K'_{PbY} the conditional stability constant of the complex. However the potential of the system PbO_2, PbY is much more positive and the reaction

$$2PbO_2 + 2H_2Y^{2-} \rightleftharpoons 2Pb(II)Y^{2-} + O_2 + 2H_2O \quad (7)$$

tends to proceed to the right. As a result of this the ratio [Y′]/[PbY′] decreases and the potential slowly decreases after the end-point. Wang found[6] that the maximum sometimes observed for this titration curve does not correspond exactly with the end-point. Reaction (7) is a source of positive error even when the titration curve has a conventional S-shape. Because of these errors, the titration does not seem likely to have any useful applications.

Chelatometric titrations with indicator ion

In this type of titration the potential of the indicator electrode[2] should be given by the equation:

$$E = E^0_{MeO_2/Me^{2+}} - \frac{RT}{2F}\ln\frac{C^0_{Me}K'_{NY}}{\alpha_{Me}\left(K'_{MeY}\dfrac{[NY']}{[N']} + K'_{NY}\right)} + \frac{RT}{F}\ln[H^+] \quad (8)$$

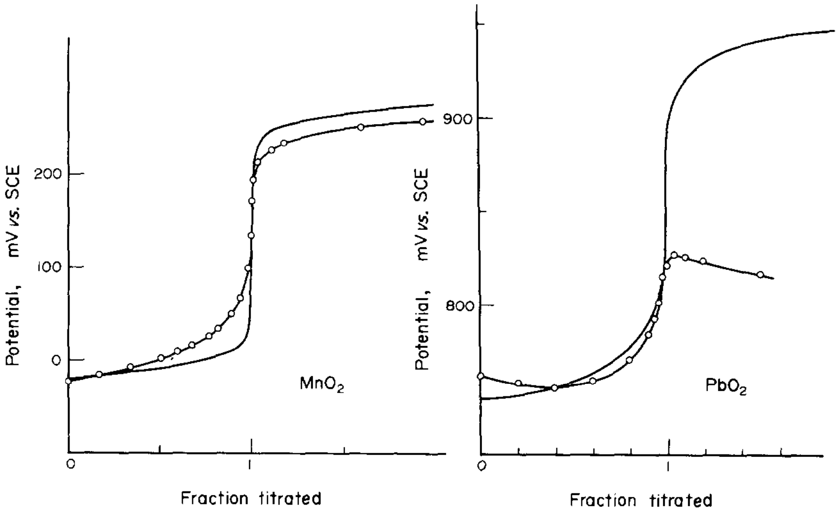

Fig. 2. Complexometric titration of 10^{-3} *M* solutions of Mn^{2+} and Pb^{2+} with MnO_2 (pH 9.3) and PbO_2 (pH 4.6) indicator electrodes: solid lines—theoretical curves; points—experimental data.

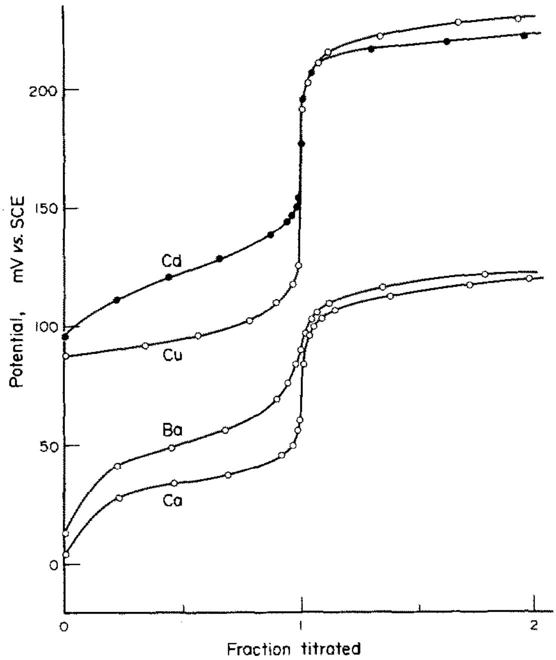

Fig. 3. Titration of $10^{-3}M$ solutions of various metal ions with MnO_2 indicator electrode in 1*M* ammonia buffer at pH 9 (Cd^{2+}, Cu^{2+}) and at pH 10 (Ba^{2+}, Ca^{2+}), $C^{\circ}_{Mn} = 10^{-5}M$.

where N represents the ion titrated, C°_{Me} the total concentration of the indicator ion and K' the conditional stability constant of the complex indicated by subscript.

In the case of the MnO_2 electrode, titrations of $Ba^{2+}, Ca^{2+}, Cd^{2+}$ and Cu^{2+} with EDTA were investigated in various buffers, in the presence and absence of dissolved oxygen (Fig. 3). The potential breaks observed are adequate for a determination of the end-point when concentrations of 10^{-3}–$10^{-4}M$ are used. As expected, the concentration of the indicator ion ($10^{-5}M$) does not affect the change in potential. The potentials observed at the beginning of the titrations ($f = 0$) are close to those predicted theoretically (Figs. 4,5) but those observed after the end-point ($f = 2$) are not, the difference being 150 or 190 mV in the presence or absence of oxygen, respectively, independent of pH and the cation being titrated. Similar discrepancies have been observed by Nomura and Nakagawa.[4]

To explain this behaviour we have considered the following reaction:

$$MnO_2 + Mn(II)Y^{2-} + H_2Y^{2-} + 2H^+ \rightarrow 2Mn(III)Y^- + 2H_2O \quad (9)$$

studied previously by Yoshino *et al.*[8] Because of formation of $Mn(III)Y^-$ the titrated solutions become yellowish after the end-point and the disproportionation of $Mn(III)Y^-$ gives a dark precipitate of MnO_2. In calculating the electrode potential the following equilibria should be considered:

$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O \quad (10)$$

$$Mn^{3+} + e \rightleftharpoons Mn^{2+} \quad (11)$$

$$Mn^{3+} + Y^{4-} \rightleftharpoons Mn(III)Y^- \quad (12)$$

Using the standard potentials, the following equation for the electrode potential can be arrived at:

$$E = 2E^0_{MnO_2/Mn^{2+}} - E^0_{Mn^{3+}/Mn^{2+}} + \frac{RT}{F}\ln\frac{[Y^{4-}]^2 K_{Mn(III)Y}[H^+]^4}{[Mn(III)Y^-]} \quad (13)$$

To compare this expression with experimental data the concentration of $Mn(III)Y^-$ should be eliminated, as it cannot be estimated directly.

From the stability constant of the complex

$$K_{Mn(III)Y} = \frac{[Mn(III)Y^-]}{[Mn^{3+}][Y^{4-}]} \quad (14)$$

and the equilibrium constant

$$K = \frac{[Mn^{3+}]^2}{[Mn^{2+}][H^+]^4} \quad (15)$$

of the redox reaction

$$MnO_2 + Mn^{2+} + 4H^+ \rightleftharpoons 2Mn^{3+} + 2H_2O \quad (16)$$

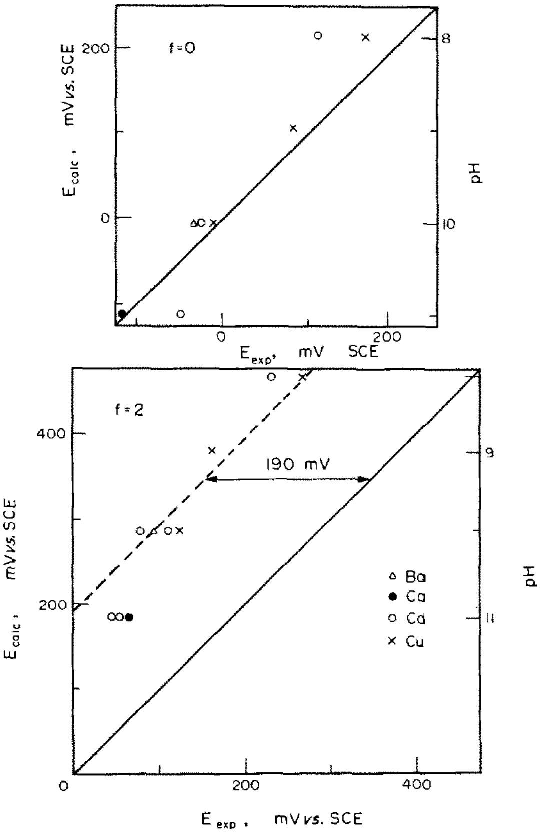

Fig. 4. Comparison of theoretical and experimental potentials of MnO_2 indicator electrodes in titrations of various metal ions in 1*M* ammonia buffer in the absence of oxygen for $C^{\circ}_{Mn} = 10^{-5}M$ at $f = 0$ and $f = 2$.

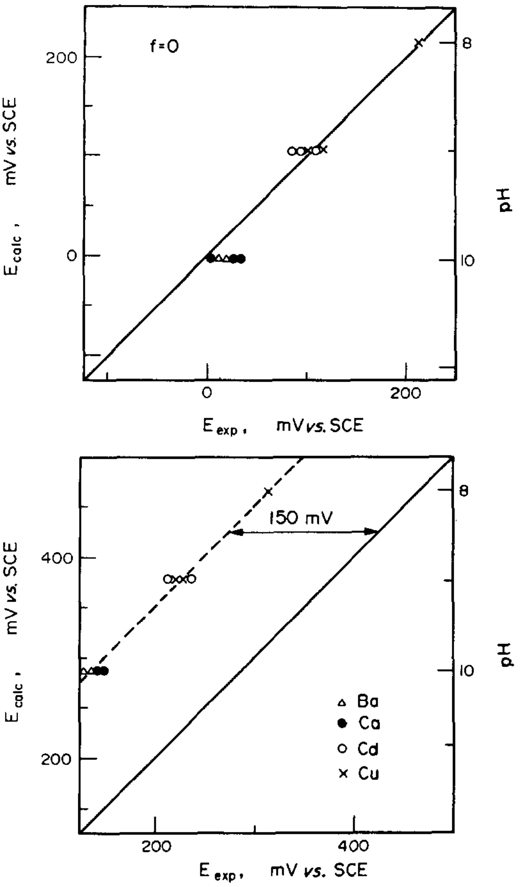

Fig. 5. Comparison of theoretical and experimental potentials of MnO_2 indicator electrodes in titrations of various metal ions in $1M$ ammonia buffer in the presence of oxygen for $C^{\circ}_{Mn} = 10^{-5}M$ at $f = 0$ and $f = 2$.

calculated from the redox potentials as equal to $10^{-8.45}$, one can obtain the following expression for the concentration of $Mn(III)Y^-$:

$$[Mn(III)Y^-] = K_{Mn(III)Y}K^{1/2}[Mn^{2+}]^{1/2}[Y^{4-}][H^+]^2 \tag{17}$$

which may be substituted in (13) to give the potential as:

$$E = 2E^0_{MnO_2/Mn^{2+}} - E^0_{Mn^{3+}/Mn^{2+}} + \frac{RT}{F}\ln\frac{[Y^{4-}][H^+]^2}{K^{1/2}[Mn^{2+}]^{1/2}} \tag{18}$$

When no $Mn(III)Y^-$ is formed, which is assumed to be the case, the potential of the electrode should be described by the equation:

$$E = E^0_{MnO_2/Mn^{2+}} - \frac{RT}{F}\ln\frac{[H^+]^2}{[Mn^{2+}]^{1/2}} \tag{19}$$

The difference between (19) and (18) is independent of both the cation titrated and the pH of the solution, and is given by

$$\Delta E = E^0_{MnO_2/Mn^{2+}} - E^0_{Mn^{3+}/Mn^{2+}} + \frac{RT}{F}\ln\frac{[Y^{4-}]}{K^{1/2}} \tag{20}$$

Table 1. Determination of various metal ions with MnO_2 indicator electrode

Metal ion	pH	Amount, *μmole* Taken	Found	Error, %
Ba^{2+}	10·0	97·1	97·4	+0·3
			96·8	−0·3
			97·5	+0·4
Ca^{2+}	10·0	95·3	95·7	+0·2
			95·5	—
			95·3	−0·2
			95·4	−0·1
			95·4	−0·1
Cd^{2+}	9·0	96·8	97·3	+0·5
			97·2	+0·4
			97·2	+0·4
			97·5	+0·7
Cu^{2+}	9·0	100·1	101·0	+0·9
			100·6	+0·5
			101·2	+1·1
			100·3	+0·2

When calculated for $C_Y = 10^{-3}M$, and using the standard potentials,[9] the value of ΔE is 177 mV, in very good agreement with the experimental values, thus lending support for the proposed reactions scheme.

Though the formation of $Mn(III)Y^-$ is not a disadvantage in a practical titration, the slowness of the electrode to give stable potentials is. However, with a 3-min wait after addition of titrant, reasonable results were obtained (Table 1).

With the PbO_2 electrode the curve of potential *vs.* pPb does not depend on the presence of other cations if no Pb^{2+} is added. From the potential *vs.*

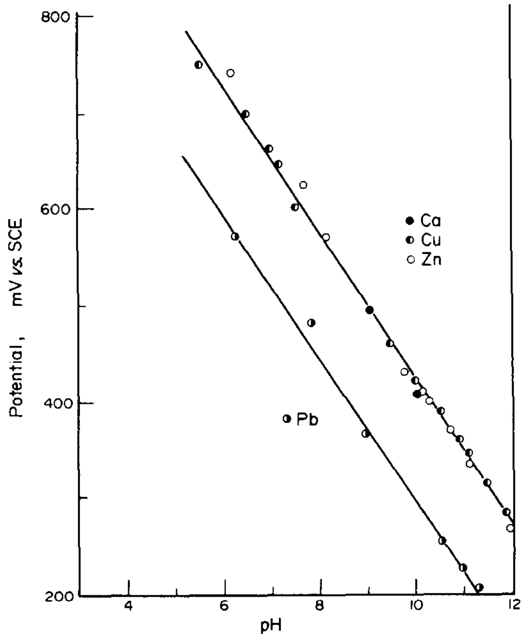

Fig. 6. Potential–pH relationship for PbO_2 electrode in 10^{-3} M solutions containing Pb^{2+}, Ca^{2+}, Cu^{2+} or Zn^{2+}.

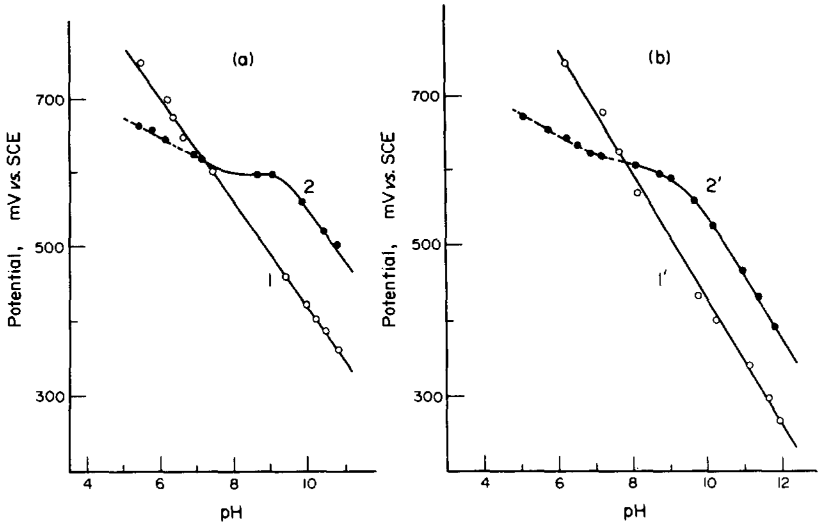

Fig. 7. Potential–pH relationship for complexometric titration of Cu^{2+} (*a*) and Zn^{2+} (*b*) with PbO_2 indicator electrode: 1,1'—10^{-3} *M* Me^{2+}; 2,2'—10^{-3} *M* MeEDTA + 10^{-3} *M* EDTA.

pH relationship (Fig. 6) it follows that in all instances the position of the equilibrium of the reaction

$$PbO_2 + 2H^+ \rightleftharpoons Pb^{2+} + 1/2\,O_2 + H_2O \quad (21)$$

depends on the lead-ion concentration, and is shifted to the right to such an extent, that in titrations of other cations it is not necessary to add Pb^{2+} as indicator ion.

As the potential–pH diagrams in the presence of Cu–EDTA and Zn–EDTA (Fig. 7) indicate that below pH 8, PbO_2 should dissolve from the electrode, titrations should only be possible at pH higher than this, which was confirmed by experimental titration curves (Fig. 8). It was found, contrary to what was stated by Wang,[6] that titrations in acetate medium were of no practical utility since the electrode reacts with the solution. Further, titrations in alkaline media are not recommended because of the large positive errors (Table 2).

Table 2. Determination of various metal ions with PbO_2 indicator electrode

Metal ion	pH	Amount, *mmole* Taken	Found	Error, %
Ca^{2+}	9·0	0·0973	0·1047	+7·6
			0·1040	+6·9
	10·1		0·1050	+7·9
Cu^{2+}	9·0	0·1050	0·1065	+1·4
			0·1090	+3·8
Zn^{2+}	8·0	0·0999	0·1035	+3·6
	9·1		0·1042	+4·3
			0·1025	+2·6
	9·4		0·1070	+7·1
	9·8		0·1040	+4·1

Both the experiments and the calculations clearly indicate that the MnO_2 and PbO_2 electrodes cannot perform reliably as sensors in titrations, because they

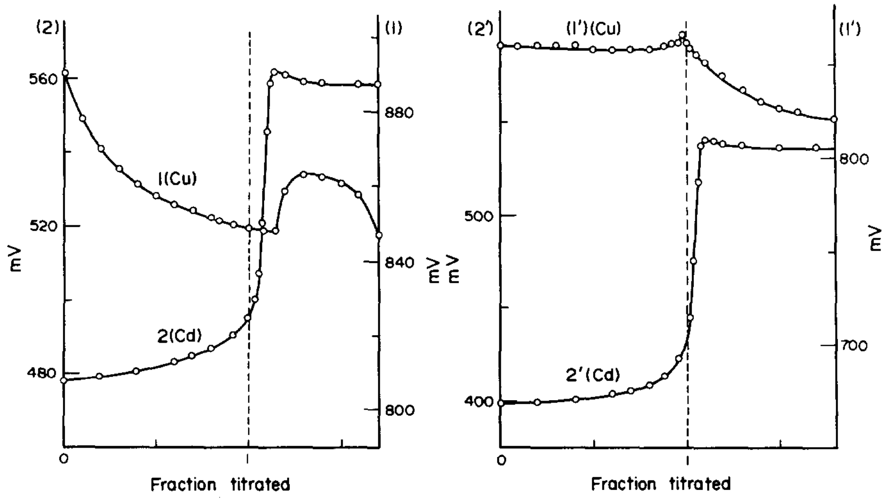

Fig. 8. Complexometric titration with PbO_2 indicator electrode in 0.1 *M* acetate buffer (1,1') and 0.1 *M* ammonia buffer (2,2'): 1,2—10^{-3} *M* Cu^{2+}; 1',2'—10^{-3} *M* Cd^{2+}.

are thermodynamically unstable under the titration conditions, although the MnO_2 electrode can be used under certain circumstances. The application of PbO_2 electrodes reported by other workers must be based only on the relative slowness of the reactions under some conditions, but stable and reproducible potentials should not be expected.

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ADDITIONAL RESULTS ON THE VALUE OF THE FARADAY

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Summary—Repetition of the authors' earlier high-precision coulometric titrations of 4-aminopyridine by the hydrazine–platinum anode and back-titration methods, at the National Bureau of Standards, has yielded a new value for the Faraday, almost identical with the earlier value but with lower uncertainty. The earlier value has been recalculated, using a new value for the density of 4-aminopyridine. The weighted average of the new and old values is 96486.57 1972 NBS coulombs per equivalent, the standard deviation of the mean being 0.48 coulombs per equivalent (4.9 ppm).

During 1975, Koch, Hoyle and Diehl[1] reported a high-precision coulometric titration of 4-aminopyridine carried out at Iowa State University (ISU) by two methods and calculated a value for the Faraday. We have now repeated both titrations at the National Bureau of Standards (NBS), where one of us (W.F.K.) was a guest worker during the spring of 1975, taking advantage of the better electrical circuitry and the national standards of electricity, time and mass there.

EXPERIMENTAL WORK

Electrical circuitry and standards

A block diagram of the basic circuitry used in the work at NBS is shown in Fig. 1. A 100-mA constant-current source, designed and built by Mr. Bruce F. Field of NBS, was used during the major portion of each titration. The current from this source was adjusted so that the potential drop across a standard resistor was exactly that of a Weston unsaturated cell. The cell and the potential drop over the resistor were arranged in opposition and the difference in potential was measured with a Leeds & Northrup Digital Linear Amplifier, Model 9829-D, capable of detecting 0.1 μV. Periodic adjustments were necessary to maintain the balance at zero, but deviations never exceeded 1 ppm/hr.

The standard resistor, nominally 10 ohms, manufactured by the Leeds & Northrup Company, was a wire-wound spool resistor without a protective canister, and was specifically adapted for coulometric work by Dr. Vincent E. Bower of NBS. The resistor was immersed in a well-stirred oil-bath kept at 26.5°. The resistance under these conditions was 9.999757 ohms (standard deviation 2×10^{-7} ohm) as calibrated against the national working standard of resistance one week before the work reported in this paper.

The Weston unsaturated cell was placed within an enclosure, the temperature of which was controlled to ±0.01°. The potential of this cell was compared, before each titration, with a set of four saturated Weston cells (Guildline Instruments, Standard Cell Enclosure Model 9152T4, Number 2300) which in turn was calibrated weekly against the national working standard. The value of the cell changed from 1.0190386 to 1.0190380 V during the three weeks of the work; the standard deviation of the mean was 2×10^{-7} V. The value obtained on the day of each titration was used in the calculations.

For the region of the equivalence-point of each titration, a constant-current source designed and built by Dr. Richard S. Davis, of NBS, was used. The output was approximately 3.35 mA, the exact value being obtained during each titration by measuring the potential drop across a standard resistor, with a well-calibrated voltmeter, Data Precision Digital Multimeter 2540A1.

Both current sources were allowed to warm up through a dummy load having a resistance comparable to that of the titration cell, about 150 ohms. A switching system of mercury-wetted relays, built by Dr. Richard S. Davis, was used to switch from the dummy load to the titration cell, simultaneously triggering the timer. No significant switching transients were observed.

Weighing

The weight-burette was weighed on a Mettler single-pan semimicro balance, Type B6. The internal weights of this balance were calibrated with a set of Ainsworth Class M stainless-steel weights, NBS Calibration Test Number 232.09/307, 15 September 1971, which had been repeatedly checked at NBS since 1971. 4-Aminopyridine was weighed on a Mettler single-pan microbalance, Type M5/SA, by the double substitution method, only the 2-g and the 5-mg weights of the Class M set being used.

All weighings were corrected to true mass, using 1.2682 g/ml for the density of 4-aminopyridine (pycnometer

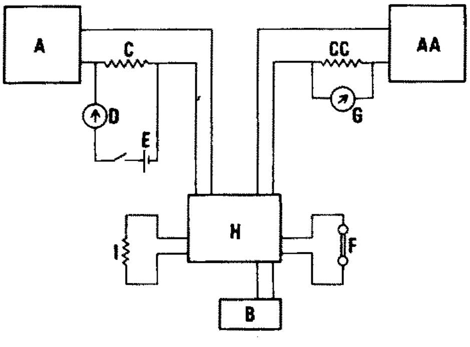

Fig. 1. Circuitry of the coulometric titration apparatus at the National Bureau of Standards. A, Constant-current source (100 mA); AA, constant-current source (3.35 mA); B, electronic timer; C, standard resistor (10 ohm); CC, standard resistor (200 ohm); D, null-point detector; E, unsaturated Weston cell; F, titration cell; G, voltmeter; H, relays and switches; I, dummy load.

method, using xylene previously saturated with 4-aminopyridine as the transfer medium and subjecting the xylene-4-aminopyridine mixture to vacuum before final filling), 1.0504 g/ml for the density of the perchloric acid (direct pycnometric measurement), 7.89 g/ml for the density of the Class M weights, 7.77 g/ml for the density of the internal weights of the semimicro balance, and for the density of air, a value obtained by weighing a Baxter's globe (the one used earlier at ISU, a recalibration at NBS agreeing with the value used earlier within 1 part per thousand). The correction to true mass was calculated by using the equation

$$\text{Weight}_{\text{vacuum}} = \frac{\text{Weight}_{\text{air}}[1 - (d_{\text{air}}/d_{\text{weights}})]}{[1 - (d_{\text{air}}/d_{\text{sample}})]}$$

rather than the usual approximation form.[2] An error of 1 part per thousand in the density of 4-aminopyridine causes an error of 0.7 ppm in the correction factor.

Timing

A General Radio Counter, Model 1192-B was tied directly to the 10-kHz NBS standard time signal and was accurate to better than 1 msec.

Titrations

These were identical to those previously described,[1] except that approximately 1 g of 4-aminopyridine was dissolved in the electrolyte before the pre-electrolysis and pretitration in all the titrations, including the standardizations of perchloric acid. This was done (1) to make the inflection-points of the pretitration and the final titration more nearly identical, and (2) to make the computer method of locating the inflection-point applicable to all titrations.

RESULTS

Data and results of the titrations are given in Tables 1 and 2. Estimated values for the systematic errors are given in Table 3. These were combined and the combined value combined with the random error as outlined in earlier papers.[1,3] The values for the Faraday thus obtained were:

By the hydrazine–platinum anode method

$F = 96486.58$ 1972 NBS coulombs per gram-equivalent weight

$\sigma_i = 0.56$ 1972 NBS coulombs per gram-equivalent weight

$\sigma_{\bar{x}} = 0.23$ 1972 NBS coulombs per gram-equivalent

By the back-titration method (platinum cathode)

$F = 96486.53$ 1972 NBS coulombs per gram-equivalent weight

$\sigma_i = 0.67$ 1972 NBS coulombs per gram-equivalent weight

$\sigma_{\bar{x}} = 0.27$ 1972 NBS coulombs per gram-equivalent weight

These values were averaged by the weighting method used in the earlier paper;[1] the weighted average is

$F = 96486.55$ 1972 NBS coulombs per gram-equivalent weight and the standard deviation of the mean is 0.57 coulombs per gram-equivalent weight or 5.9 ppm (combined random and systematic errors).

Most of the systematic errors in the work at NBS were markedly lower than those in the work at ISU;[1] see Table 3. The uncertainty in the e.m.f. of the unsaturated Weston cell used at NBS was more than one order of magnitude smaller than that of the cell used at ISU, which was estimated by Mr. Wayne A. Rhinehart to be 4 ppm. The uncertainties arising from the resistance standard, timing and null-point detection were negligible in comparison with the major errors. The timing device used at NBS was tied directly to the national standard time signals, giving an improvement of more than an order of magnitude over the timing device used at ISU. Improvement in the measurements of mass resulted largely from the use of a more sensitive balance in the weighing of the weight-burette in the back-titration method.

Because the 4-aminopyridine titrated in the work at NBS was prepared in identical fashion to that titrated at ISU, the purity was treated as before. The end-point in each titration at NBS was located by computer treatment of the data exactly as had been done at ISU;[4] hence the uncertainties remain the same. The uncertainty in the molecular weight is believed by E. Cohen and B. N. Taylor (private com-

Table 1. Coulometric titration of 4-aminopyridine with acid generated at the hydrazine–platinum anode (Performed at the National Bureau of Standards, Washington, D.C.)

Titration number	Weight of 4-aminopyridine, *g*	Quantity of electricity, *1972 NBS coulombs*	Electrical equivalent *1972 NBS coulombs/g*	Value of the faraday. *1972 NBS coulombs/equiv.*
1	2.003971	1643.55392	1025.18569	96487.42
2	2.003856	1643.44072	1025.17392	96486.31
3	1.999276	1639.68924	1025.17689	96486.59
4	1.998141	1638.74854	1025.17073	96486.01
5	2.002364	1642.22969	1025.18179	96487.06
6	1.996416	1637.33482	1025.17137	96486.07
			Average	96486.58
			Standard deviation of the individual observations	0.56
			Standard deviation of the mean	0.23

Mol. wt. 4-aminopyridine: 94.11702; purity of 4-aminopyridine: density of 4-aminopyridine: 1.2682 g/ml.

Table 2. Titration of 4-aminopyridine with perchloric acid (coulometric end-point) and standardization of perchloric acid coulometrically (Carried out at the National Bureau of Standards, Washington, D.C.)

Standardization of perchloric acid

Titration number	Weight of perchloric acid, *g*	Quantity of electricity, *1972 NBS coulombs*	Concentration of perchloric acid, *1972 NBS coulombs/g*
1	19.89932	1713.15270	86.091017
2	23.35100	2010.33282	86.091937
3	21.31479	1835.00390	86.090639
4	21.24380	1828.92525	86.092189
5	25.35871	2183.15892	86.091087
6	25.48692	2194.20708	86.091496
		Average	86.091394
		Standard deviation of the individual observation	0.000591
		Standard deviation of the mean	0.000241

A	B	C	D	E	F	G	H
1	1.994609	26.97462	2322.28264	277.46017	2044.82247	1025.17459	96486.38
2	2.000273	28.39864	2444.87850	394.23191	2050.64659	1025.18336	96487.20
3	2.005422	26.99919	2324.39790	268.50852	2055.88938	1025.16547	96485.52
4	2.006358	31.91053	2747.22201	690.33941	2056.88260	1025.18225	96487.10
5	2.006463	27.36959	2356.28616	299.31870	2056.96746	1025.17089	96486.03
6	2.004939	25.83462	2224.13845	168.71383	2055.42462	1025.18063	96486.95
						Average	96486.53
						Standard deviation of the individual observation	0.67
						Standard deviation of the mean	0.27

Headings of columns: A, titration number; B, weight of 4-aminopyridine, *g*; C, weight of perchloric acid, *g*; D, electricity delivered *via* perchloric acid, *C*; E, additional electricity to reach end-point, *C*; F, total electricity, *C*; G, electrical equivalent, *C/g*; H, value of Faraday, *C/equiv*; *C* = 1972 NBS coulomb.

Mol. wt. 4-aminopyridine: 94.11702; purity of 4-aminopyridine: 100%, density of 4-aminopyridine: 1.2682 g/ml.

munication) to be 3 ppm calculated by $\sigma^2_{\text{m.w.}} = (5\sigma_c)^2 + (6\sigma_H)^2 + (2\sigma_N)^2$; this is a more formally correct method than the weighted average method used in the earlier paper. This uncertainty reflects the maximum range of variation in all measurements reported on the isotopes of carbon and hydrogen and is not an error in the normal sense; to the extent that it can be so considered, it is used here, subject to revision after a determination of the isotope ratios in the 4-aminopyridine has been made.

The random error in the standardization of the perchloric acid was essentially the same in the work at both institutions, the same being true for the random error in the back-titrations. The reduction in the random error in the anodic titrations by a factor of three was particularly satisfying in that it added support to the validity of the hydrazine–platinum anode method[5] for titrating weak bases. It had been noticed that the current source in the 'Coulometric Analyzer" used at ISU was beginning to deteriorate

Table 3. Summary of systematic errors (ppm) affecting the titrations of 4-aminopyridine made at Iowa State University and at the National Bureau of Standards

	Anodic titrations[*]		Cathodic titrations[†]	
	ISU[‡]	NBS[§]	ISU[‡]	NBS[§]
Standard e.m.f.	4	0.2	4	0.2
Resistance standard	0.2	0.2	0.2	0.2
Time	0.2	0.01	0.2	0.01
Measurement of potential	3	[‖]	3	[‖]
Null-point detection	[‖]	0.1	[‖]	0.1
Mass	4	1.0	4	1.0
Purity	3	3	3	3
Molecular weight	3[¶]	3	3[¶]	3
End-point detection	7	7	3	3
Standardization of perchloric acid	[‖]	[‖]	3.4	2.8
Random error	6.4	2.4	2.4	2.8

[*] Coulometric titration with hydrogen ion generated at the hydrazine–platinum anode.

[†] Back-titration coulometrically after the addition of excess of perchloric acid.

[‡] Titrations made at Iowa State University (reference 1, Tables 3 and 4).

[§] Titrations made by Dr. Koch at the National Bureau of Standards and reported in this paper.

[‖] Not applicable.

[¶] Estimate revised from the value of 0.3 ppm used in earlier paper; see text.

during the later stages of the work and finally, after the titrations were completed, did require replacement of a capacitor; this could explain the larger scatter in the titrations done by the hydrazine–platinum anode method at ISU.

Combination of present and earlier values for the Faraday

The value for the Faraday reported in our earlier work, 96486.69 (8.4 ppm) 1972 NBS coulombs per gram-equivalent weight, was based on the value 1.2695 g/ml for the density of 4-aminopyridine. Recalculation with the new value for the density (obtained by vacuum treatment) and the larger value for the uncertainty in the molecular weight yields 96486.62 (8.9 ppm). The value for the Faraday obtained by averaging this value with the new value yields

$F = 96486.57$ 1972 NBS coulombs per gram-equivalent weight

$\sigma_{\bar{x}} = 0.48$ 1972 NBS coulombs per gram-equivalent weight = 4.9 ppm

Values for the Faraday obtained since 1959 are listed in Table 4. The agreement of the value reported in the present paper with that of Craig *et al.* (as recalculated) is strikingly good, the difference being only 1.5 ppm. A weighted average of the results of Craig *et al.*, Marinenko and J. Taylor (the average of their values being used), and the present work has been calculated, Table 4. The range from the low value of the present work to the high value of the Marinenko and Taylor work is 3.8 ppm, just about equal to one standard deviation of the mean (combined random and systematic errors).

Table 4. Summary of recent values for the Faraday

Author, location, year, method	Value of the Faraday (uncertainty, *ppm*) A_{BI69}, *sec. mole*$^{-1}$
1. Craig, Hoffman, Law and Hamer, NBS, 1960. Dissolution of silver. Recalculated*	96486.72 (6.8)
2. Marinenko and Taylor, NBS, 1968. Reduction of benzoic acid†. Recalculated*	96487.30 (12)
3. Marinenko and Taylor, NBS, 1968. Reduction of oxalic acid dihydrate†. Recalculated*	96486.25 (16)
4. Weighted average* of 2 and 3	96486.95 (9.6)
5. This work (weighted average of titrations at ISU and NBS)	96486.57 (4.9)
6. Weighted average of 1, 4, 5	96486.67 (3.7)
7. Cohen and Taylor‡, NBS, 1973. Indirect, calculated	96484.56 (2.8)

* As recalculated by Cohen and Taylor in 1973, ref. 6, pp. 679, 704.

† Uncertainty includes random and systematic errors and is in terms of the standard deviation of the mean, expressed in parts per million.

‡ Ref. 6, pages 704, 717.

The conclusion must be drawn that the work leading to the lower value for the Faraday as calculated by Cohen and B. N. Taylor[6] (see also ref. 1, page 727, col. 1) from other physical measurements should be re-examined. Alternatively, if the electrochemical value is incorrect, the electrode process in water must be more closely examined for some basic flaw common to such different processes as the anodic dissolution of metallic silver, the anodic generation of hydrogen ions, and the cathodic generation of hydroxyl ions. Establishing a value for the Faraday by electrochemistry in a non-aqueous solvent might contribute to the solution of this problem.

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NEW IODOMETRIC METHODS FOR THE MICRODETERMINATION OF ARSENIC IN ORGANIC COMPOUNDS

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Summary—New methods are described for the iodometric microdetermination of arsenic in organic compounds after wet digestion or oxygen flask combustion. After evaporation of the arsenic solution to dryness and dissolution of the residue in water, acetone is added and the solution is treated with iodide–iodate and the iodine liberated (by the interfering acids and the first dissociation step of arsenic acid) is reduced with thiosulphate. The KH_2AsO_4 left is then reacted with zinc sulphate in presence of excess of KI and KIO_3. Acetone is added and the liberated iodine is titrated with thiosulphate. This titration corresponds to the second and third dissociation steps of arsenic acid and is used to calculate the arsenic content of the compound. When arsenicals not containing sulphur are decomposed by the oxygen flask method, the arsenic acid solution obtained is reacted directly with zinc sulphate in presence of KI and KIO_3 and the iodine released is titrated with thiosulphate. In this case, the titration corresponds to all three dissociation steps of arsenic acid. The average recoveries obtained by the two methods are 99.5 and 99.9%, respectively.

Several methods are available for the determination of arsenic in organic compounds after wet digestion[1] or oxygen flask combustion.[2,3] Most are based on production of arsenate which is then determined gravimetrically,[1,4] potentiometrically,[5] colorimetrically,[2,3] or by atomic-absorption spectrophotometry.[6] Iodo- and iodimetric methods are familiar[1] for arsenic though both suffer from drawbacks. The reaction of arsenic acid with iodide in acidic medium has been reported[1] to be very sensitive to pH. The titration with iodine yields better results, but involves a rather lengthy and involved procedure.

In the present work, new iodometric methods are described for the microdetermination of arsenic in organic compounds, similar in principle to the methods proposed for phosphorus,[7,8] exploiting the hydrogen ions of arsenic acid. Thus, the arsenic acid, obtained after sample decomposition, is allowed to react with zinc sulphate and on addition of potassium iodide and iodate, iodine is liberated, which is titrated with standard thiosulphate.

EXPERIMENTAL

Apparatus

A 500-ml oxygen flask, the stopper of which is provided with a silica spiral (5 or 6 turns) made from a 7–8 cm length of 2-mm diameter tubing. The spiral is sealed at one end to a rod protruding from the stopper, and tapered upwards at the lower end. The tapering end of the spiral, which replaces the conventional platinum holder, is situated in the centre of the conical flask. The spiral is a slightly modified version of that advocated by Belcher *et al.*[3] for submicro work.

Reagents

All reagents were of AR or MAR grade except where otherwise mentioned, and doubly distilled water was always used.

Sodium thiosulphate solution, 0.05 and 0.01*M*, standardized against potassium iodate solutions of suitable concentrations.

Potassium iodide solution (0.1*M*), potassium iodate solution (0.02*M*), zinc sulphate solution (~0.1*M*).

Procedures

Wet digestion method. Transfer 6–8 mg of sample carefully into the bottom of a 25-ml Kjeldahl flask, add 1 ml each of concentrated sulphuric and nitric acids, and heat cautiously till the appearance of SO_3 fumes. Add a further 0.5 ml of concentrated nitric acid, heat to fuming and repeat the same step after addition of 0.5 ml of 30% hydrogen peroxide, continuing repetition until the digest becomes colourless. Continue heating till practically all the sulphuric acid has been removed. Cool and transfer the contents of the flask quantitatively into a 25-ml glass dish, with small portions of water, and evaporate to dryness on a boiling water-bath.

Dissolve the residue in *ca.* 5–7 ml of hot water and transfer the solution into a 100-ml conical flask. Add 10 ml of acetone and 2 ml each of 0.1*M* KI and 0.02*M* KIO_3 solutions. Stopper the flask and after 5 min titrate the liberated iodine, first with 0.05*M* sodium thiosulphate to a pale yellow and then with 0.01*M* thiosulphate solution till colourless. Then add 1 ml of ~0.1*M* zinc sulphate, ~100 mg of solid KI and ~50 mg of KIO_3. Stopper the flask and after 5 min again add 10 ml of acetone. Titrate the liberated iodine with 0.01*M* sodium thiosulphate till colourless. Run a blank experiment with benzoic acid as sample. Since the reaction sequence corresponds to $H_2AsO_4^- \equiv I_2 \equiv 2S_2O_3^{2-}$, then 1 ml of 0.01*M* $Na_2S_2O_3 \equiv$ 0.3746 mg of As, and the percentage of arsenic in the organic compound is

$$As = \frac{37.46\,(Y - X)M}{W} \times 100\%$$

where Y and X are the titration volumes (ml) for the sample and the blank respectively, M is the molarity of the thiosulphate solution, and W is the weight (mg) of the sample.

Oxygen flask method. For arsenicals containing no sulphur weigh enough sample to give at least 0.7 mg of arsenic. Transfer it onto a piece of ashless filter paper, and (if necessary) add 5 mg of potassium nitrate as an aid to combustion. Fold the paper twice at right angles and roll it up to fit into the quartz spiral. Burn the sample as usual in a 500-ml oxygen-filled flask containing 3 ml of conc. nitric acid. Shake the flask occasionally during the next 10 min, then rinse the stopper and walls of the flask with ~2 ml of conc. nitric acid. Place the flask on a steam-bath and evaporate the solution to dryness; repeat the evaporation step twice, adding 3 ml of water each time. Dissolve the residue in 5 ml of water and add 1 ml of 0.1M zinc sulphate solution, followed by solid KI (~100 mg) and KIO_3 (~50 mg). Stopper the flask and leave it aside for 5 min. Titrate the iodine with 0.01M sodium thiosulphate solution, using starch as indicator. Run a blank experiment with benzoic acid as sample.

Since the reaction corresponds to $2H_3AsO_4 \equiv 3I_2 \equiv 6S_2O_3^{2-}$, 1 ml of 0.01$M$ $Na_2S_2O_3 \equiv 0.2497$ mg of As, and the arsenic content of the sample is

$$\frac{24.97\,(Y-X)M}{W} \times 100$$

where Y, X, M and W have the same meanings as before.

For compounds containing sulphur as well as arsenic, proceed similarly up to the end of the evaporation steps. Then dissolve the residue in 5 ml of hot water and apply the double titration procedure described for the wet digestion method, starting with the first addition of acetone, and using the same method of calculation.

RESULTS AND DISCUSSION

The two methods are based on complete conversion of the arsenic into arsenic acid, the protons of which are used to produce an equivalent amount of iodine in the iodide–iodate reaction.

The wet digestion method

It would be desirable not to have to use an acidic digestion medium, but none was known that would decompose all the compounds tested. With the mineralization method used, the problem is to get rid of the excess of acid. This should be possible by repeated evaporations since arsenic acid dehydrates at 180–200° to As_2O_5 without loss of arsenic and As_2O_5 is stable up to 380°.[9] Only above this temperature does decomposition to As_4O_6 occur ($2As_2O_5 = As_4O_6 + 2O_2$). However, it was found that a variable amount of sulphuric acid was always left, causing high or low apparent recoveries of arsenic, depending on the relative amounts of acid left in the sample and blank solutions.

In contrast to sulphuric acid, other acids (*e.g.*, halogen acids and/or nitric acid) expected to arise from digestion of samples containing acidic elements other than arsenic, do not interfere since these are completely eliminated in the repeated evaporation steps.

However, to make the procedure generally applicable to any arsenic-containing compound, the problem of interferences was overcome completely by incorporating the two-step titration method advocated previously[7] for the analogous determination of phosphorus.

In the first step, the arsenic acid and any other acid remaining are allowed to react in aqueous acetone medium with KI and KIO_3:

$$6H_3AsO_4 + IO_3^- + 5I^- \rightarrow 6H_2AsO_4^- + 3H_2O + 3I_2$$

$$6HX + IO_3^- + 5I^- \rightarrow 6X^- + 3H_2O + 3I_2.$$

The total iodine liberated, due to arsenic(V) and any other acidity, is removed by titration, first with 0.05M thiosulphate, to avoid excessive dilution, till pale yellow, and then with 0.01M thiosulphate till colourless. This titration value is not needed, of course, in the calculation. In the second step, the dihydrogen arsenate is allowed to react with zinc sulphate whereby zinc arsenate is formed along with liberation of an equivalent amount of protons, which then react with KI and KIO_3, both added this time in solid form to avoid dilution, with quantitative liberation of iodine, which is directly titrated with 0.01M thiosulphate, to a colourless end-point. The titration value obtained in this second step is used to calculate the arsenic content of the organic sample.

$$2H_2AsO_4^- + 3Zn^{2+} \rightarrow Zn_3(AsO_4)_2 + 4H^+$$

$$6H^+ + 5I^- + IO_3^- \rightarrow 3H_2O + 3I_2$$

As in the case of phosphorus determination,[7] the acetone in the medium allows complete reaction, in the first step, of the traces of interfering acids, while making the arsenic acid function only as a monobasic acid. The presence of acetone also renders the iodine colour very bright yellow, so the iodine also acts as the indicator. To improve the end-point detection the acetone is added in two portions, one along with the iodide–iodate mixture for the first reaction, followed by titration after a 5-min waiting period, and the second only just before the second titration so that the reaction with zinc sulphate has enough time to proceed rapidly and completely.

Satisfactory results (Table 1) were obtained, showing an average absolute error of ±0.3% and an average recovery of 99.5%. Arsenazo [3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalene disulphonic acid] gave *ca.* 3.5% low arsenic recovery probably because of impurity and/or incomplete decomposition. The blank values did not exceed 0.06 ml of 0.01M thiosulphate solution which is considered reasonable for such a rather lengthy digestion procedure (up to 6 hr). It was the slowness of the decomposition that led to development of the oxygen flask method.

The oxygen flask method

Preliminary tests with the ordinary platinum sample holder and saturated bromine-water or hydro-

Table 1. Iodometric microdetermination of arsenic in organic compounds by the wet digestion method

Compound	Weight, *mg*	As, % Calc.	As, % Found	Recovery, %
Triphenylarsine	4.936	24.46	24.2	98.9
	5.805		24.2	99.0
	7.871		24.8	101.4
n-Butylarsonic acid	4.956	41.15	41.6	101.0
	6.100		40.8	99.2
Phenylarsonic acid	4.344	37.09	37.4	100.9
	7.006		36.8	99.2
Benzylarsonic acid	4.106	35.67	35.4	99.2
	5.520		36.0	100.9
4-Dimethylaminoazobenzene-4′-arsonic acid	5.986	21.46	21.2	98.9
	8.240		21.7	101.2
Triphenylarsine sulphide	5.606	22.11	22.4	101.4
	8.300		21.8	98.7
Arsenazo	6.010	13.13	12.7	96.6
	8.416		12.7	96.7

gen peroxide as absorption medium gave very low arsenic results. This was not unexpected, because arsenic has been reported[10] to alloy with platinum. Thus, a modified version of the quartz spiral stopper, introduced previously,[2,3] was used, but the arsenic values found were still low, indicating incomplete decomposition and/or incomplete oxidation of As(III) to As(V). Although it is customary to use alkaline hypobromite[3] or alkaline hydrogen peroxide[4] as absorption medium to obtain arsenic(V),[3] the use of alkaline medium was ruled out because the present method is based on the acidity of the arsenic acid.

Trials were then made with concentrated nitric acid as absorbent. In addition to oxidizing As(III) to As(V), the excess of nitric acid was easily and smoothly removed by heating on a boiling water-bath, leaving a white residue of arsenic acid which dissolved easily in hot water. Addition of zinc sulphate to this solution gave a precipitate of zinc arsenate and an equivalent amount of protons, the arsenic acid acting as a tribasic acid:

$$2H_3AsO_4 + 3Zn^{2+} \rightarrow 2Zn_3(AsO_4)_2 + 6H^+$$

The protons liberated can be determined by the iodide–iodate reaction. The volume should not exceed 6–7 ml for the precipitation reaction to proceed quantitatively within 5 min, and an equal period should be allowed for complete iodometric reaction.

The use of concentrated nitric acid as the absorbent succeeded for all the samples analysed except thorin and 4-dimethylaminoazobenzene-4′-arsonic acid, which gave results 6–9% low. About 5 mg of potassium nitrate, mixed with the sample before wrapping in the ashless filter paper flag, proved highly efficient

Table 2. Iodometric microdetermination of arsenic in organic compounds by the oxygen-flask method

Compound	Weight, *mg*	As, % Calc.	As, % Found	Recovery, %
Triphenylarsine*	4.380	24.46	24.7	101.1
	5.000		24.7	101.0
	7.531		24.2	99.1
n-Butylarsonic acid*	4.506	41.15	40.9	99.4
	5.354		41.4	100.5
Phenylarsonic acid*	4.152	37.09	37.4	100.7
	5.650		37.3	100.6
Benzylarsonic acid*	4.950	34.67	34.4	99.3
	7.017		34.5	99.5
4-Dimethylaminoazobenzene-4′-arsonic acid*	4.976	21.45	21.7	101.2
	7.401		21.2	98.9
Triphenylarsine sulphide†	5.906	22.11	22.4	101.2
	7.555		22.2	100.4
Arsenazo†	5.004	13.13	13.4	102.2
	6.826		12.8	97.8
Thorin†	5.162	18.04	17.7	97.9
	8.005		17.7	97.8

* Calculated on the basis of 3-fold amplification.

† Calculated on the basis of 2-fold amplification.

as an auxiliary oxidant during combustion. In addition to raising the arsenic recoveries to an average of *ca.* 98 and 99% for these two compounds, respectively, the potassium nitrate caused no interference, and may conveniently be added to any arsenical sample.

Satisfactory results (Table 2) were obtained. As expected, nitrogen and halogens did not interfere, because their products are readily expelled in the evaporation steps. The effect of halogens was tested by addition of micro-amounts of hydrochloric acid, bromine-water, and iodine either to the absorbed combustion products of triphenylarsine or in blank experiments.

On the other hand, sulphur-containing arsenicals could not be successfully analysed by the simple oxygen flask procedure, owing to the incomplete removal of sulphuric acid in the evaporation step, but this problem was readily solved by applying the two-step procedure developed for the wet digestion method. Arsenazo yielded better arsenic recoveries by the oxygen flask method than by wet digestion. Thorin, however, gave 2% low recovery, possibly ascribable to impurity. The results in Table 2 show an average absolute error of ±0.3% and overall average recovery of 99.9%. The blank values (0.04 ml of 0.01M thiosulphate) were smaller than those for wet digestion.

Conclusions

The oxygen flask method is superior in the following respects: (*i*) it is simpler and less tedious than the wet digestion method; it offers a 3-fold amplification (except for the sulphur arsenicals) compared with the 2-fold amplification for the wet-digestion method; (*ii*) in general it gives the better results.

Phosphorus, of course, interferes quantitatively, as expected from the previous work[7,8] but compounds containing both arsenic and phosphorus are not very common.

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NON-DESTRUCTIVE MULTI-ELEMENT PHOTON-ACTIVATION ANALYSIS OF ENVIRONMENTAL MATERIALS

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Summary—A non-destructive method of photon-activation analysis with 30-MeV bremsstrahlung followed by high-resolution gamma-spectrometry has been developed for multi-element determination in ambient air and in air-pollution emissions. The sample materials were the NBS standard reference material, Fly Ash, and atmospheric particulates collected on a Millipore filter. Simultaneous irradiation of the sample with synthetic multi-element standards containing 33 elements has shown that the technique can determine up to 21 elements in a single sample. The method is simple and gives reproducible results.

Because of increasing concern with environmental pollution problems, attempts have been made to develop methods for the elemental analysis of water, air and soil. The most immediate problem is the analysis of air-pollution samples and many laboratories are devoted to this task.[1] Any method employed must be sensitive, accurate, versatile, and if possible, capable of the simultaneous determination of many elements. Because air-pollution samples have complex, ill-defined matrices, wet methods may introduce errors by loss or contamination of trace species. Many of these difficulties are avoided by activation analysis, without chemical treatment, before irradiation. Neutron-activation analysis has been applied to the measurement of many elements in atmospheric particulate materials,[2–9] but this method is not capable of analysing for all elements of environmental significance. Lead, which has unsuitable nuclear properties, is determined by atomic-absorption spectrophotometry or X-ray fluorescence, although pulse methods[10,11] to detect the 0.8-sec ^{207m}Pb, or fast neutron,[12] photon-[13–16] and charged-particle[17–19] activation may be used. The advantage of multi-element determination is shared by activation analysis and photon- and particle-excited X-ray fluorescence,[20–23] but severe matrix effects are encountered with the last technique.

Photon activation shares with thermal neutron activation the advantages of homogeneous activation, but produces an entirely different range of nuclides by (γ,n), (γ,p) and other photonuclear processes. A number of reviews on the principles and general features of photon-activation analysis,[24–27] useful compilations or listings of the nuclear characteristics of the products,[28–31] and gamma-ray spectrum catalogues[32–34] are now available. Aras *et al.*[35] have demonstrated the multi-element capability of photon-activation analysis in air-pollution studies by presenting abundance data for 14 elements in atmospheric particulate materials. Chattopadhyay and Jervis[16] also reported an instrumental method for the simultaneous determination of 30 elements in market-garden soils, using a 45-MeV linear accelerator.

The present paper describes the multi-element analysis of the NBS standard reference material, SRM-1633 Fly Ash, and of atmospheric particulates collected on Millipore filters from the urban atmosphere.

EXPERIMENTAL

Samples and comparison standards

The NBS standard reference material 1633 Fly Ash is provided in finely powdered form. It is prepared by the U.S. National Bureau of Standards for intercomparison purposes.[36] It was used as 1-g samples packed in aluminium foil and pressed into a disc 13 mm in diameter and 5 mm thick.

A Millipore AA membrane filter (0.8 μm pore diameter) was used for atmospheric particulate collection. A piece 20 × 25 cm was cut from the original sheet and particulates were collected by pumping 1000 m^3 of air through this filter at 0.62 m^3/min. Collections were carried out on the roof of the four-storey Miyagi Prefectural Office Building in Sendai, Japan. The filter sample was cut in two and each half was placed in the cavity of a stainless-steel hydraulic press and compacted into a cylindrical pellet 13 mm in diameter and 5 mm thick. A similar piece of unused filter was treated in the same way to provide a blank.

Comparison standards used in this work were synthetic multi-element pellets containing the elements of interest distributed evenly in a matrix of boric acid. These standards were prepared by mixing 33 elements, in the form of their oxides, at appropriate concentration levels with boric acid. In preparing these standards, reagents with a chemical purity of 99.99% or better were used. A 1-g

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Table 1. Concentrations of elements in the synthetic multi-element standard

Concentration level, *ppm*	Element
10,000	Ca, Cl, Na, K
5000	Mg
200	Br, Cr, Cu, Fe, Mn, Ni, Pb, Ti, Zn
50	Ag, As, Ba, Cd, Ce, Co, Cs, I, In, Mo, Nb, Rb, Se, Sr, Sb, Te, Tl, Y, Zr

sample of this mixture was pelleted for irradiation. Table 1 gives the concentration levels of the elements in these pellets.

Irradiation

A linear electron accelerator of Tohoku University was the bremsstrahlung source. The sample and the comparison standard pellets were stacked in a silica tube so that the standards were placed at the front and back of the sample for simultaneous irradiation. The tube was placed in a water-cooled sample holder and was aligned along the beam axis with the front face of the tube 10–15 cm from the photon-producing converter (2-mm thick Pt foil). A typical irradiation was performed with a 70-μA beam of 30-MeV electrons. The precise experimental details have already been reported.[37] The irradiation time was 2 hr for Fly Ash and 6 hr for atmospheric particulates and filter blanks. No significant chemical decomposition of the organic filter material was observed.

Counting and evaluation

Gamma-rays were observed with a lithium-drifted germanium detector with a sensitive volume of 33 cm^3, ORTEC Model 8101–0525, and its output was coupled to a 4096-channel pulse-height analyser (Toshiba Electric Co. Ltd., Japan). The counting system had a resolution of 2.4 keV for the 1332-keV gamma-line of ^{60}Co. Counting was repeated for increasing intervals over a period of one month or longer. For short-lived nuclides, ^{38}K and ^{34m}Cl, the counting time was progressively increased from 4 to 16 min. During this interval, a 50-mm thick Lucite plate was placed between the sample and the detector to absorb positrons from a number of positron-emitting nuclides. For nuclides with intermediate half-lives, counting times of 30–60 min, and for long-lived nuclides, counting times of 5-20 hr, were used. After measurement of the short-lived nuclides, the aluminium wrapper for Fly Ash was rejected and the contents were again wrapped in fresh aluminium foil for further counting. The gamma-rays were characterized by comparison with the gamma-spectra obtained by irradiating the pure elements, and listed with nuclear data.[38] In obtaining full-energy peak areas, total peak counts were computed and background contributions were subtracted, assuming linear variation of background over the peak of interest. Decay curve analyses were used to check for interferences. A mean specific activity for any specified gamma-ray in terms of the peak areas from the standards on both sides was used for calculating the abundance of the element in question in a sample.

RESULTS AND DISCUSSION

Gamma-rays observed

Typical gamma-ray spectra measured at several different decay times after irradiation of the atmospheric particulate sample are shown in Figs. 1–3, together with those of the multi-element standard measured at comparable decay times. As observed in the multi-element analysis of biological materials,[39] determination of the elements giving rise to short-lived nuclides could only be achieved for those which emitted gamma-rays with high energies, because of the swamping 511-keV annihilation radiations from positron-emitters. In the case of atmospheric particulate samples, such high activity was mainly due to 20-min ^{11}C from the organic filter material. The only products used for measurement at earlier decay times were 7.71-min ^{38}K and 32-min ^{34m}Cl. After a decay time of 1 day, however, almost all products of interest could be observed in gamma-ray spectra. For quantitative measurements, consecutive counting has been required, over periods up to 10 days, to check for spectral interferences. At this stage, all of the elements in the comparison standard, except Ag, Ba and Te, could be measured. The elements identifiable in both the sample and standard have been determined quantitatively. In selecting the peaks used for quantitative measurement, the intensities, spectral interferences and peak-to-background ratios were taken into account. Table 2 gives the elements determined and the peaks selected, together with time intervals for measurements after irradiation, practical limits of detection and major competing nuclear reactions. The spectral interferences caused by overlapping gamma-rays have been studied with the aid of a list of prominent gamma-rays emitted by various products from irradiation of each pure element with 30-MeV bremsstrahlung.[30] Most of these problems could be solved by decay analyses of the counting data, when the gamma-ray peaks given in Table 2 were selected. To rule out the 808-keV peak of ^{47}Ca, measurements of cobalt by the 811-keV peak were made 30–40 days after irradiation. Similarly, long decay periods were used for cerium to eliminate the contribution by the 160-keV peak of ^{47}Sc. Zinc was measured by using the 185-keV peak of ^{67}Cu rather than the 1115-keV peak of ^{65}Zn, because of the interference by the 1121-keV peak of ^{46}Sc.

The practical detection limits were estimated from the spectral data of the atmospheric particulate (Sample 1 in Table 4). These are the amounts of the elements giving a full-energy peak area corresponding to three times the standard deviation of the area under the peak of interest, from a particulate sample collected from 500 m^3 of urban air, with 6-hr irradiation time with a 70-μA beam of 30-MeV electrons, counted with a 33-cm^3 Ge(Li) detector for periods as stated. It is difficult to define the detection limits since they depend on the experimental conditions and the nature of the matrix.

Fly ash

Lehmden *et al.*[40] mentioned that fly ash from a coal-fired heat-generation source is important for two reasons. It has a matrix similar to that of emissions

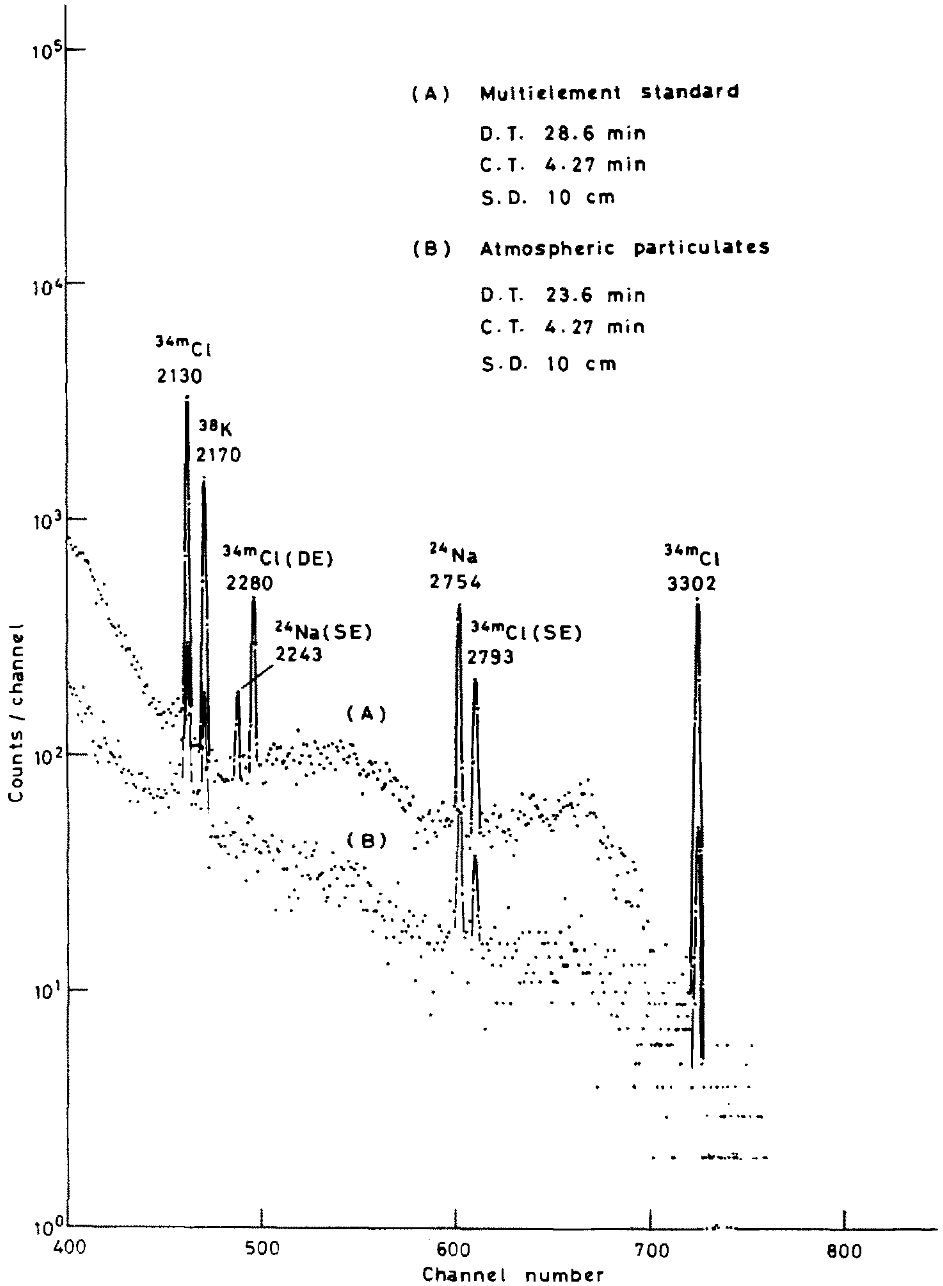

Fig. 1. Gamma-ray spectra for short-lived nuclides taken with a 33-cm^3 Ge(Li) detector after a 6-hr irradiation of an air-filter sample and a multi-element standard with 30-MeV bremsstrahlung. D.T. and C.T. designate the time interval between irradiation and counting, and the counting period, respectively; S.D. indicates source-to-detector distance; SE and DE designate single and double annihilation photon escape peaks, respectively; values on each peak are energies in keV.

to the atmosphere, but with a larger particle size, and there is interest in the removal of trace elements in coal-fired processes. Elemental abundances in Fly Ash for 17 elements have been obtained (in duplicate) and results are given in Table 3, together with literature values where available.[16,36] Error limits are based on counting statistics of sample and standards. They are the overall statistical errors associated with subtraction of the background under the full-energy peak of interest so as to obtain the net counting rates for the sample and the standards and comparison of the sample with a mean specific activity from standards on both sides of the sample. There are possibilities of contributions to the (γ,n) or (γ,p) reactions used for abundance determination from (γ,pn), (γ,α) and (γ,αn) reactions with elements adjacent in the Periodic Table (Table 2). Detailed nuclear considerations based on the experimental yields of the photo-nuclear

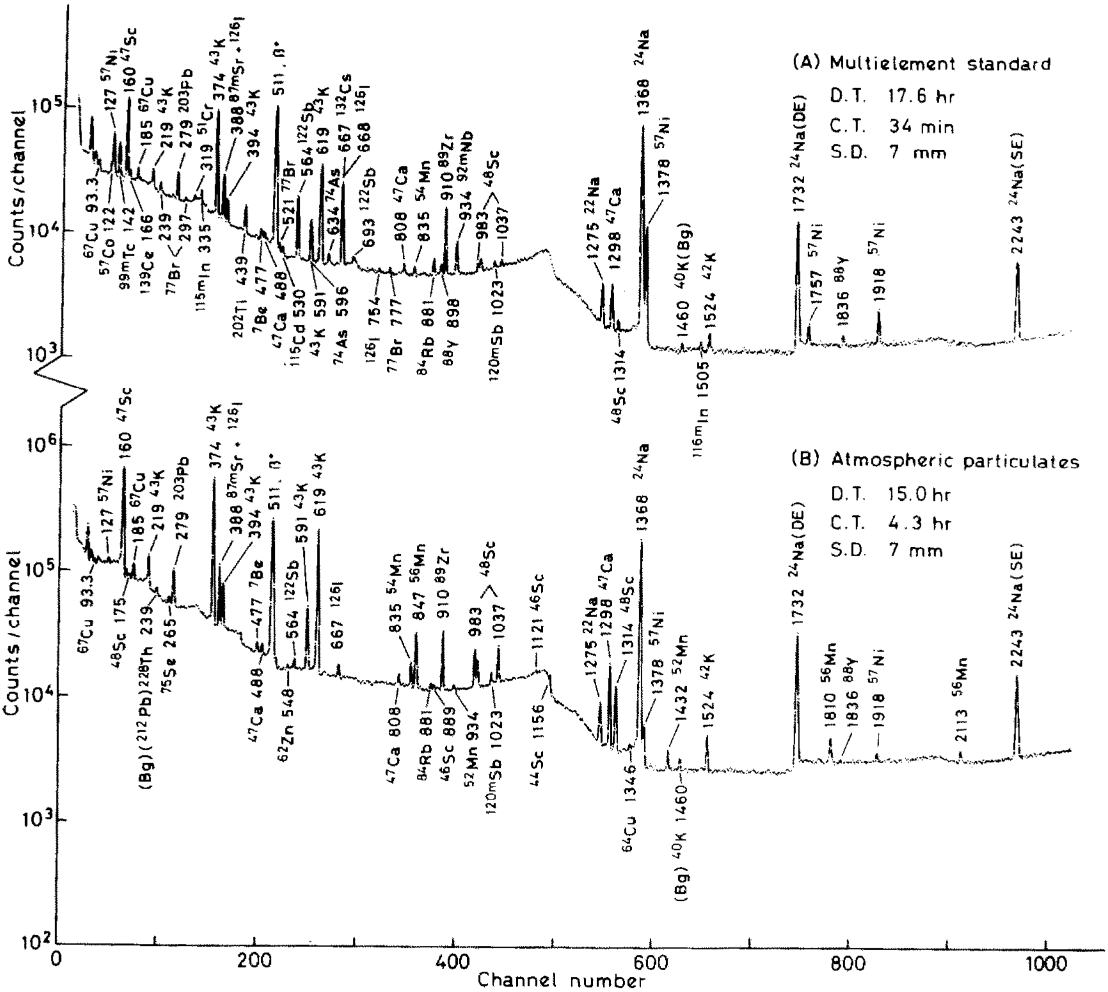

Fig. 2. Gamma-ray spectra taken at an intermediate decay time with a 33-cm^3 Ge(Li) detector after a 6-hr irradiation of an air-filter sample and a multi-element standard with 30-MeV bremsstrahlung. Bg indicates peaks occurring in natural background; see also caption for Fig. 1.

reactions of various types[28] showed that in most instances these secondary contributions did not produce serious interference problems.

Calcium was determined either by the ^{44}Ca(γ,p)^{43}K or by the ^{48}Ca(γ,n)^{47}Ca reaction. Of the peaks of ^{43}K and ^{47}Ca, the 374- and 619-keV peaks of ^{43}K and the 1298-keV peak of ^{47}Ca were found to produce precise values of calcium concentration. The values obtained from these three different peaks fell within the range $\pm 2\%$ for all samples. The calcium results given were the average of the values from these peaks (Tables 3–5).

For titanium, of the peaks of the three isotopes, ^{47}Sc, ^{48}Sc and ^{46}Sc, the 160-keV peak of ^{47}Sc gave the highest full-energy peak. Although ^{47}Sc could also be produced by the β^--decay of ^{47}Ca, interferences from its decay were not significant at earlier decay times for this material. The 1314-keV peak of ^{48}Sc was also used for determinations and the average values from these two peaks are listed (Tables 3–5).

In the determination of manganese by using the ^{55}Mn(γ,n)^{54}Mn reaction, the major source of interference is from iron by the ^{56}Fe(γ,pn)^{54}Mn reaction. When an amount of pure iron was irradiated with 30-MeV bremsstrahlung, an activity ratio of 1.03×10^{-3} was obtained as the ratio of the 835-keV full-energy peak of ^{54}Mn to the 847-keV full-energy peak of ^{56}Mn. The ^{54}Mn activity due to the ^{55}Mn(γ,n)^{54}Mn reaction for a given sample was, therefore, calculated by multiplying the count rate under the 847-keV peak by 1.03×10^{-3} and then subtracting this value from the count rate under the 835-keV peak corrected for decay to the end of irradiation. A correction of 56% was required for Fly Ash.

In the magnesium determination utilizing the ^{25}Mg(γ,p)^{24}Na reaction, aluminium interferes through the reaction ^{27}Al(n,α)^{24}Na. A separate irradiation of equal quantities of magnesium and aluminium under identical conditions resulted in a ^{24}Na production

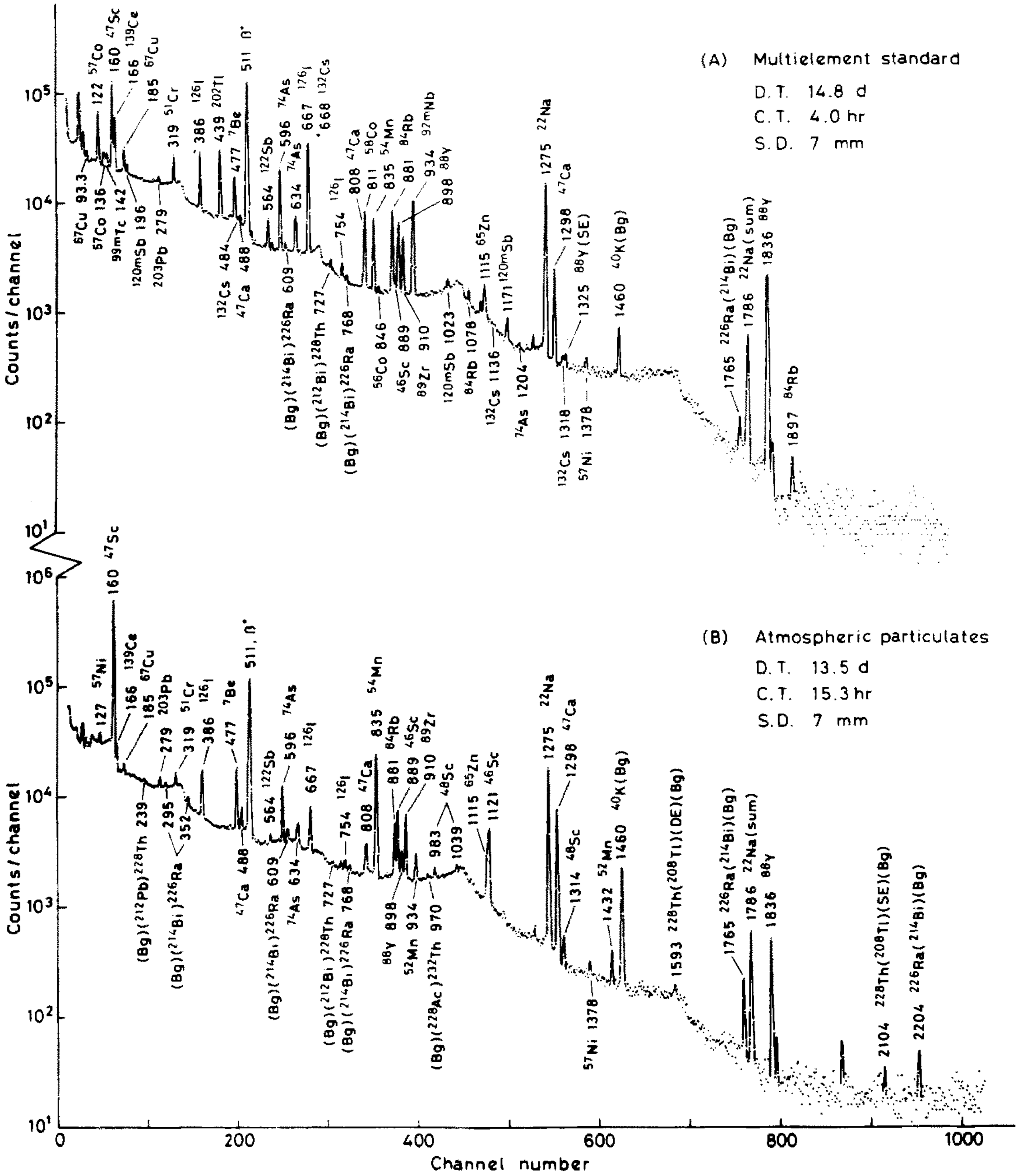

Fig. 3. Gamma-ray spectra for long-lived nuclides taken with a 33-cm^3 Ge(Li) detector after a 6-hr irradiation of an air-filter sample and a multi-element standard with 30-MeV bremsstrahlung. Bg indicates peaks occurring in natural background; see also caption for Fig. 1.

rate from aluminium which was only 0.5% of that from magnesium. By means of spectrophotometric measurement followed by solvent extraction with 8-hydroxyquinoline,[41] we obtained a value of 11.9% for aluminium in Fly Ash. From this value, the $^{27}Al(n,\alpha)^{24}Na$ contribution to the total ^{24}Na activity could be estimated to be 3.7%.

The peaks of ^{203}Pb (279 keV), ^{115}Cd (530 keV), ^{126}I (667 keV) and ^{67}Cu from zinc (185 keV) were also observed, but not used for abundance determinations for this material because of the low peak-to-background ratios. Chlorine could not be determined because of its low abundance.

As seen in Table 3, the reproducibility of the method is satisfactory. The average relative deviations for all the elements determined here, based on the duplicate samples, were within ±5%. The precision observed in our results is high because of the specific sample–multi-element standards configuration used, which would minimize the errors due to photon-flux

Table 2. Nuclides and gamma-rays used for determination and practical limits of detection for an atmospheric particulate sample

Element	Process	Product nuclide	Half-life	Gamma-ray used, *keV*	Time interval for measurement after irradiation	Practical limit of detection *ng/m*^{3}	Major competing reaction
As	(γ,n)	^{74}As	17.9 d	596	10–15 d	0.4	^{76}Se$(\gamma,pn)^{74}$As
Ca	(γ,p)	^{43}K	22.4 hr	374	1–2 d	85	^{45}Sc$(\gamma,2p)^{43}$K
Ca	(γ,p)	^{43}K	22.4 hr	619	1–2 d	110	^{46}Ti$(\gamma,3p)^{43}$K
Ca	(γ,n)	^{47}Ca	4.53 d	1298	10–15 d	140	^{49}Ti$(\gamma,2p)^{47}$Ca
Ce	(γ,n)	^{139}Ce	140 d	166	30–40 d	0.5	^{141}Pr$(\gamma,pn)^{139}$Ce
Cl	(γ,n)	^{34m}Cl	32.0 min	2130	30–60 min	90	^{39}K$(\gamma,\alpha n)^{34m}$Cl
Co	(γ,n)	^{58}Co	71.3 d	811	30–40 d	0.6	^{60}Ni$(\gamma,pn)^{58}$Co
Cr	(γ,n)	^{51}Cr	27.8 d	319	10–15 d	3.6	^{56}Fe$(\gamma,\alpha n)^{51}$Cr
Fe	(γ,p)	^{56}Mn	2.576 hr	847	2–5 hr	85	^{55}Mn$(n,\gamma)^{56}$Mn
I	(γ,n)	^{126}I	13 d	388	10–15 d	0.5	^{128}Xe$(\gamma,pn)^{126}$I
K	(γ,n)	^{38}K	7.71 min	2170	10–30 min	280	^{40}Ca$(\gamma,pn)^{38}$K
Mg	(γ,p)	^{24}Na	15.0 hr	1368	1–2 d	13	^{27}Al$(n,\alpha)^{24}$Na
Mn	(γ,n)	^{54}Mn	303 d	835	10–15 d	2.5	^{56}Fe$(\gamma,pn)^{54}$Mn
Na	(γ,n)	^{22}Na	2.60 y	1275	10–15 d	31	^{24}Mg$(\gamma,pn)^{22}$Na ^{27}Al$(\gamma,\alpha n)^{22}$Na
Ni	(γ,n)	^{57}Ni	36.0 hr	1378	1–2 d	2.9	None
Pb	(γ,n)	^{203}Pb	52 hr	279	1–2 d	12	None
Rb	(γ,n)	^{84}Rb	33.0 d	881	10–15 d	0.6	^{86}Sr$(\gamma,pn)^{84}$Rb
Sb	(γ,n)	^{122}Sb	2.80 d	564	1–2 d	1.1	^{123}Te$(\gamma,p)^{122}$Sb
Sr	(γ,n)	^{87m}Sr	2.83 hr	388	2–5 hr	0.04	^{89}Y$(\gamma,pn)^{87m}$Sr ^{92}Zr$(\gamma,\alpha n)^{87m}$Sr
Ti	(γ,p)	^{47}Sc	3.43 d	160	2–5 hr	5.6	^{51}V$(\gamma,\alpha)^{47}$Sc ^{48}Ca$(\gamma,n;\beta^-)^{47}$Sc
Ti	(γ,p)	^{48}Sc	1.83 d	1314	1–2 d	72	^{51}V$(\gamma,pd)^{48}$Sc
Y	(γ,n)	^{88}Y	108 d	1836	10–15 d	0.3	^{90}Zr$(\gamma,pn)^{88}$Y
Zn	(γ,p)	^{67}Cu	59 hr	185	2–3 d	20	^{71}Ga$(\gamma,\alpha)^{67}$Cu
Zr	(γ,n)	^{89}Zr	78.4 hr	910	1–2 d	1.4	^{94}Mo$(\gamma,\alpha n)^{89}$Zr

inhomogeneities. Although the data from NBS are not complete, the agreement, where comparable, is excellent. In comparing our results with those of Chattopadhyay and Jervis,[16] the agreement is more satisfactory for trace elements than for major elements. There is a wide range in the reported concentrations of many elements in several samples having similar matrices (prepared by the U.S. Environmental Protection Agency for intercomparison purposes,) and Lehmden *et al.*[41] have stressed the heterogeneous

Table 3. Elemental abundances of NBS Standard Reference Material 1633, Fly Ash

	Abundance, *ppm*			
	This work		Literature	
Element	Analysis 1*	Analysis 2*	NBS[36]†	Chattopadhyay and Jervis[16]
As	64 ± 1	65 ± 1	61 ± 3	60.7 ± 2.6
Ca	5.17 ± 0.05 × 10^4	5.04 ± 0.04 × 10^4	—	3.92 ± 0.28 × 10^4
Ce	156 ± 2	150 ± 2	—	—
Co	44 ± 5	40 ± 4	(38)	35.4 ± 2.8
Cr	142 ± 13	141 ± 11	125 ± 10	131 ± 6.1
Fe	4.14 ± 0.22 × 10^4	4.33 ± 0.30 × 10^4	—	6.08 ± 0.52 × 10^4
K	1.67 ± 0.05 × 10^4	1.51 ± 0.08 × 10^4	1.68 × 10^4	—
Mg	1.45 ± 0.02 × 10^4	1.43 ± 0.02 × 10^4	-	1.48 ± 0.01 × 10^4
Mn	512 ± 18	470 ± 16	495 ± 30	495 ± 25
Na	0.391 ± 0.021 × 10^4	0.380 ± 0.016 × 10^4	—	0.340 ± 0.03 × 10^4
Ni	95 ± 3	97 ± 5	98 ± 3	96.8 ± 3.2
Rb	98 ± 2	93 ± 2	(112)	—
Sb	7.2 ± 0.6	6.9 ± 1.2	—	7.14 ± 0.56
Sr	1222 ± 7	1266 ± 9	(1380)	1373 ± 95
Ti	0.786 ± 0.010 × 10^4	0.745 ± 0.009 × 10^4	—	0.723 ± 0.04 × 10^4
Y	67 ± 2	66 ± 2	—	—
Zr	289 ± 8	307 ± 10	—	301 ± 22

* Error limits are standard deviations based on counting statistics of the sample and standards.
† Probable certified values. Values in parentheses are informational values.

Table 4. Atmospheric concentrations of several elements in Sendai samples

Element	Concentration *ng/m*^{3}		
	Sample 1*	Sample 2†	
As	12	1.6	1.3
Ca	1.54×10^4	2.28 ± 10^3	2.42×10^3
Ce	8.6	1.3	1.9
Cl	570	460	490
Co	2.7	1.6	1.4
Cr	20	28	22
Fe	8.76×10^3	1.19×10^3	1.17×10^3
I	10	6.7	4.6
K	1.51×10^3	1.31×10^3	1.12×10^3
Mg	2.73×10^3	460	490
Mn	437	78	76
Na	5.27×10^3	1.82×10^3	1.79×10^3
Ni	13	4.3	5.3
Pb	220	167	165
Rb	9.5	0.5	0.7
Sb	3.4	1.6	1.9
Sr	52	4.9	5.7
Ti	1.04×10^3	158	167
Y	6.2	0.5	0.4
Zn	280	220	210
Zr	25	2.7	2.5

* Sample collected on 18–19 February 1974, 27 hr, clear weather.

† Duplicate analyses of sample collected on 2–3 September 1974, 25 hr, cloudy weather.

nature of samples of this sort. As an example, the presence of the large iron-containing particles in Fly Ash would be a contributory source of the wide variation in reported iron concentrations (5.3–25%).

Atmospheric particulates

Apart from the 17 elements determined in Fly Ash, chlorine, iodine, lead and zinc were also determined. The results obtained are shown in Table 4. The observed concentrations appear to be in the range found for other urban areas in Japan,[8,9] although the number of determinations is too limited for real comparison.

The $^{56}\mathrm{Fe}(\gamma,\mathrm{pn})^{54}\mathrm{Mn}$ contribution to the total $^{54}\mathrm{Mn}$ activity was estimated as described above, and it was found that the corrections required for the air-filter samples ranged from 11 to 14%. To check for interference from aluminium in the magnesium determination, aluminium concentrations were measured spectrophotometrically. A relatively high value of 15.5 $\mu g/m^3$ was observed for sample 1 in Table 4 and a correction of 2.6% was required in this case. When considering the Al:Mg ratios (2, or 3 at most), routinely observed in air-filter samples from industrial and urban areas,[3,6] this source of interference may not pose serious problems.

Filter blank

A critical requirement for the method is that the filter material used should have very small blanks for the elements to be determined. Table 5 gives the concentrations of the elements, determined by photon activation analysis, in the Millipore filters used, together with the literature data,[42–44] where available. Considerable variations can occur from one batch of filter material to another and also over the area of a single

Table 5. Concentrations of elements in the Millipore filter blanks

Element	Concentration *ng/cm*^{2}					
	This work AAWP304		Literature			
			Dams *et al.*[42]		Dudey *et al.*[43]	Dale *et al.*[44]
	Lot 1	Lot 2	AAWP025	AAWP047		
As	ND*	2.6	—	—	—	—
Ca	503	1000	500	370	—	—
Ce	ND*	ND*	<0.5	<0.5	—	—
Cl	2.47×10^3	2.36×10^3	1700	1000	60	—
Co	ND*	ND*	0.4	0.1	0.03	0.29
Cr	18	30	20	15	20	20
Fe	17	30	80	40	—	2060
I	12	16	—	—	—	—
K	690	410	120	100	—	—
Mg	113	660	400	200	—	—
Mn	5.3	22	2.5	2	0.25	4.72
Na	809	2.04×10^3	520	400	50	500
Ni	5.1	12	14	<20	—	—
Pb	5.2	18	—	—	—	—
Rb	0.3	4.9	—	—	—	—
Sb	ND*	0.7	0.4	1	0.013	0.20
Sr	3.2	4.9	—	—	—	—
Ti	5.5	9.6	10	<10	—	—
Y	ND*	1.6	—	—	—	—
Zn	11	20	10	7	0.16	14
Zr	ND*	0.4	—	—	—	—

* Not detected.

sheet. The blank values for all elements except chlorine were sufficiently small to require only minor blank corrections. The chlorine blanks in our filters were large, about 63% of the total amount of chlorine observed in an air sample. Large chlorine blanks have also been reported for polystyrene membrane filters.[35,42] Millipore filters are considered to be disadvantageous in neutron-activation analysis, for they tend to disintegrate during irradiation, but this filter can be used in photon-activation analysis and is easy to use, has a low blank, and a high particle retentivity.

CONCLUSION

The present method is promising for the study of air pollution and can be applied to a wide range of environmental materials as a useful complement to other analytical methods. In addition to the elements determined in atmospheric particulates by Aras *et al.*,[35] other elements such as Co, Fe, K, Mg, Mn, Rb, Sr and Y have been determined in this work. Manganese can be determined if careful correction is made for the iron contribution. Both Rb and Sr in atmospheric particulate materials can be determined much more easily than by instrumental neutron-activation analysis. For Y, as well as Pb and Zr, non-destructive analysis by thermal neutron activation is not generally attainable, because of their adverse nuclear properties. Such difficulties are not inherent in photon activation analysis. The concentrations of 20 or more elements in the same sample can be measured with reasonable sensitivity and reliability.

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USE OF ZEO-KARB 226 AND DOWEX A-1 IN THE ANALYSIS OF HIGH-PURITY ZINC AND ZINC-BASE ALLOYS FOR Tl AND In

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Summary—Utility of Zeo-Karb 226 and Dowex A-1 for the separation of Tl and In at 5-ppm level from high-purity zinc and zinc-base alloys has been investigated. With Zeo-Karb 226 (NH_4^+), Tl^+ is conveniently separated from these materials and also from many other cations, with 1.0*M* ammonium nitrate as the eluent. It is subsequently determined with Rhodamine B. This separation principle is also applied to the analysis of Pb–Tl alloys. Both Tl and In (along with Fe) are preconcentrated on Zeo-Karb 226(H^+) from a solution of the sample at pH 3.0. Suitable methods of subsequent determination of Tl and In are described. In the case of Dowex A-1(H^+), Tl^{3+}, In^{3+}, Fe^{3+} and Cu^{2+} are retained from a solution of the sample at pH 2.0. An *o*-phenanthroline solution at pH 2.0 elutes all but traces of Cu^{2+}. In^{3+} along with Fe^{3+} is eluted with 1.0*M* hydrochloric acid. Finally, Tl is eluted with 2.0*M* hydrochloric acid containing sulphurous acid.

It is necessary to control the thallium and indium contents at less than 10 and 5 ppm respectively in high-purity zinc and zinc-base alloys used in the die-casting industry.[1] Before their photometric determination, they are separated from associated elements by solvent extraction.[2,3] Use of cation- and anion-exchangers is reported for the separation of Tl and In from other cations, but not from these materials.

The ease with which Zn^{2+} forms complexes with EDTA[4] and other complexing agents[5,6] (citrate, tartrate, oxalate and pyrophosphate), unlike Tl^+, forms the basis of cation-exchange separation of thallium in zinc dusts, electrolytes *etc*. Separation of thallium from antimony in presence of zinc on a cation-exchanger by using 20% sodium hydroxide solution as the eluent is also reported.[7] Sulphuric acid (1*M*) is also used to separate thallium from zinc and other elements.[8] Thallium is separated from zinc on an anion-exchanger, on the basis of formation of the anionic chloro-complex by Zn^{2+} and not by Tl^+ in hydrochloric acid medium.[9] On an anion-exchanger in carbonate form zinc and many other cations are retained while Tl^+ passes through.[10]

Indium is separated from zinc and other elements on strong acid cation-exchangers with sulphosalicylic acid,[5,11] ethylenediammonium dihydrochloride,[12] lithium chloride,[13] ammonium sulphate or sulphuric acid[14] and hydrochloric acid.[15] Similar separations on anion-exchangers in hydrochloric acid,[16] EDTA,[17] ammonium carbonate[18,19] and ammonium sulphate[14] media are also reported.

This paper describes the use of Zeo-Karb 226 in H^+ and NH_4^+ forms and Dowex A-1 (H^+) for the separation of trace amounts of thallium and indium from high-purity zinc and zinc-base alloys and their determination at 5-ppm level.

EXPERIMENTAL

Reagents

Thallium solution. Thallous nitrate (1.30 g) was dissolved in a litre of acidified water and standardized gravimetrically by the chromate method.[20] This solution was diluted (as and when required) to give a working thallium solution of 10 μg/ml concentration.

Indium solution. The zone-refined metal (0.960 g) was dissolved in hydrochloric acid, made up to 1000 ml, and standardized by EDTA titration.[21] This solution was diluted (as and when required) to give a working solution of 10 μg/ml.

^{204}Tl and ^{114m}In were supplied by the Isotope Division of our Research Centre. All other reagents were of analytical grade.

Ion-exchangers

The preparation of Zeo-Karb 226 in the ammonium[22] and hydrogen ion[23] forms and Dowex A-1 (H^+)[24] was described earlier.

Instruments

Absorbance measurements were made with a matched pair of "Corex" cells (10-mm path-length) on a Beckman Model DU spectrophotometer. The β- and γ-counters were fabricated by the Electronics Division of this Research Centre.

Zeo-Karb 226 (NH_4^+)

Univalent alkali metal ions are separated from multivalent cations by selectively eluting with 0.1*M* ammonium solution from Zeo-Karb 226 (NH_4^+).[22] Since the exchanger has much greater affinity for Tl^+ than alkali metals ions owing to its high polarizability, K_d values of Tl^+ and some typical multivalent cations were determined as a function of ammonium nitrate concentration in the solution phase, by equilibrating 25 ml of the aqueous phase at pH 3–5 (avoiding precipitation) with 0.25 g of the exchanger for 4 hr. The results are given in Table 1. The K_d-value of Tl^+ decreases to less than 10 in presence of 1.0*M* ammonium nitrate, while those of the other ions are considerably higher.

Separation of thallium from other ions. The conditions of elution of Tl^+ were studied with 2.0 g of ion-exchanger.

Table 1. K_d values of metal ions at different concentrations of NH_4^+ on Zeo-Karb 226 (NH_4^+) (0.25 g)

Metal ion	K_d				
	—	0.5*M* NH_4^+	1.0*M* NH_4^+	1.5*M* NH_4^+	2.0*M* NH_4^+
Tl^+	6.56×10^3	25	9	7	< 5
Mg^{2+}	$> 10^4$	194	95	53	36
Ni^{2+}	$> 10^4$	910	290	181	105
Cu^{2+}	$> 10^4$	$> 10^4$	9.90×10^3	6.15×10^3	3.35×10^3
Zn^{2+}	$> 10^4$	6.56×10^3	4.90×10^3	4.03×10^3	3.53×10^3
Cd^{2+}	$> 10^4$	7.04×10^3	5.96×10^3	5.45×10^3	4.90×10^3
UO_2^{2+}	$> 10^4$	$> 10^4$	$> 10^4$	$> 10^4$	$> 10^4$
Pb^{2+}					
Al^{3+}					
Th^{4+}					

Table 2. Separation of Tl from multivalent cations (Tl taken = 1.00 mg)

Metal ion	Taken, *mg*	Found, *mg*	Tl found, *mg*
Mg^{2+}	11.3	11.3	0.99
Ni^{2+}	11.7	11.7	1.03
Zn^{2+}	11.4	11.5	1.01
Pb^{2+}	10.4	10.4	1.03
UO_2^{2+}	10.0	10.0	1.00
In^{3+}	11.6	11.5	1.01
Th^{4+}	11.0	10.9	1.00

Based on this, the following procedure was developed to separate 1.0 mg of thallium from about 10 mg each of the multivalent ions Mg^{2+}, Ni^{2+}, Zn^{2+}, UO_2^{2+}, Pb^{2+}, In^{3+} and Th^{4+}. The results, in Table 2, show quantitative separation of thallium.

Procedure. Binary mixtures of thallium(I) and a multivalent cation were prepared in 1.0*M* ammonium nitrate at a pH of 3–5 and passed through a column of Zeo-Karb 226 (1.0 × 10.0 cm) (NH_4^+ form) at a flow-rate of 1 ml/min, followed by 100 ml of 1.0*M* ammonium nitrate. Thallium in the effluent was determined by the Rhodamine B method[25] with 50 ml of aqueous phase and 10 ml of benzene phase. The other cation was then eluted with 100 ml of 2.0*M* nitric acid and determined by a suitable method.

Separation of Tl in zinc-base and Pb–Tl alloys. When 1.0 g of zinc was taken in 30 ml of 1.0*M* ammonium nitrate and passed through 12 g of exchanger (column 2.0 × 16.5 cm), followed by ammonium nitrate, zinc was found in the first 100 ml of effluent. An examination of the column revealed considerable channelling, due to the shrinkage of the exchanger on changing from the NH_4^+ to the Zn^{2+} form. This was obviated by equilibrating the zinc solution with 6.0 g of the exchanger in a beaker and then transferring this onto a column of another 6.0 g of exchanger. Under these conditions, all the Tl^+ was found in the first 200 ml of effluent, with no zinc appearing in the first 400 ml. In fact, the zinc band on the exchanger moved very little. Then synthetic samples of zinc-base alloys and high-purity zinc (zone-refined, from Chemistry Division of our Research Centre) were prepared and analysed following the procedure given below. The results are given in Table 3.

This principle is also successfully applied for the analysis of Pb–Tl alloys and the results are included in Table 3.

Procedure for zinc and zinc-base alloys. A 1.000-g sample is dissolved in 25 ml of 6*M* hydrochloric acid in a beaker. The solution is evaporated to dryness. The residue is dissolved in about 30 ml of 1.0*M* ammonium nitrate and the pH adjusted to 3.0. Then 6.0 g of the exchanger are added and stirred well. Meanwhile, a column of another 6.0 g of the exchanger (2.0 × 8 cm) is prepared. The contents of the beaker are transferred to the column, and the

Table 3. Analysis of synthetic samples of high-purity zinc, zinc-base and Pb–Tl alloys

Material	Tl taken, *µg*	Tl found, *µg*	Pb taken, *mg*	Pb found, *mg*
High-purity zinc (1.0 g)	nil	nil		
	5.0	5.0		
	10.0	10.0		
Zinc-base alloy* (1.0 g)	5.0	4.9, 5.0, 5.1 5.0, 5.0, 4.9		
Lead–thallium alloys (0.5 g)	*mg*	*mg*		
	382.4	384.8	104.6	105.2
	387.7	390.6	104.6	105.7
	193.8	194.3	205.7	207.2
	95.6	95.0	418.5	418.6

* Composition (with weight in mg in brackets): Zn (1000), Al (50), Cu (10), Mg (0.5), Fe (0.7), Pb (0.03), In (0.005), Sn (0.02), Cd (0.05).

Table 4. Analysis of synthetic samples of high-purity zinc and zinc-base alloys for thallium and indium

	Thallium, μg			Indium, μg		
		Found			Found	
Material	Taken	Zeo-Karb 226 (H$^+$) method	Dowex A-1 method	Taken	Zeo-Karb 226 (H$^+$) method	Dowex A-1 method
High-purity zinc (1.0 g)	nil	nil	nil	nil	nil	nil
	5.0	5.1	5.0	5.0	4.9	5.0
	10.0	9.8	10.6	10.0	10.2	10.7
Zinc-base alloy*	25.0	25.0, 24.0, 25.0, 23.5, 24.0, 25.0	23.6, 23.6, 24.5, 24.5, 26.6, 25.3	25.0	24.8, 26.0, 25.0, 25.0, 24.5, 25.0	25.5, 25.0, 26.5, 25.0, 25.5, 23.8

* Composition as given in Table 3.

effluent is collected. The column is washed with 250 ml of 1.0*M* ammonium nitrate. The volume of the combined effluent is reduced to 100 ml by boiling and 20 ml of concentrated hydrochloric acid are added. Tl is oxidized with 5 ml of bromine water. Excess of bromine is boiled off. After cooling, the pH is adjusted to 3.0 and the solution passed through a column of 1.0 g of Zeo-Karb 226 (NH_4^+), followed by 10–20 ml of water. The effluent is rejected. Tl^{3+} is eluted with 50 ml of 2.0*M* hydrochloric acid and determined by the Rhodamine B method (described earlier).

Procedure for Pb–Tl alloys. About 0.5 g of sample is accurately weighed and dissolved in dilute nitric acid in a beaker. The solution is evaporated to near dryness. Then 4.0 g of ammonium nitrate are added and dissolved in 50 ml of water. The pH is adjusted to 3.0. To this 2.0 g of Zeo-Karb 226 (NH_4^+) are added and stirred. Meanwhile 2.0 g of fresh exchanger are made into a column (1.5 × 6 cm). The contents of the beaker are transferred to the column quantitatively, followed by washing with 200 ml of 1.0*M* ammonium nitrate. Thallium present in the 250 ml of effluent is determined by the iodide method.[26] Lead is eluted from the column with 100 ml of 1.0*M* nitric acid and determined complexometrically with EDTA.[27]

Zeo-Karb 226 (H$^+$)

From the variation of K_d values of several cations on Zeo-Karb 226 (H$^+$) as a function of pH,[23] separation of In and Tl from high-purity zinc and zinc-base alloys appears feasible. Hence, the elution behaviour of In, Fe(III), Tl(III), Al, Sn(IV), Zn, Cu(II), Mg, Pb and Cd at pH 3.0 on a column (1.0 × 8.0 cm) of exchanger was studied, at a flow-rate of 1 ml/min. In, Tl and Fe were sorbed quantitatively, while the rest passed out readily when eluted with 200 ml of water at pH 3.0. This gives an easy method of preconcentration of Tl and In. Since the accompanying iron can be taken care of in the determination of Tl and In, the procedure given below was developed for the separation of Tl and In together from Zn and other associated elements. The two were subsequently determined in different aliquots. The results obtained are given in Table 4.

Procedure. About 5 g of zinc or alloy sample are accurately weighed into a beaker, dissolved in 50 ml of hydrochloric acid (1:1), and the solution is evaporated to dryness. The salts are dissolved in 50 ml of 2.0*M* hydrochloric acid and 5 ml of bromine water are added to oxidize Tl^+ to Tl^{3+}. Excess of bromine is boiled off. The solution is diluted to 100 ml and the pH adjusted to 3.0. This solution is passed through a preconditioned column containing 2 g of Zeo-Karb 226 (H$^+$) at a flow-rate of 1 ml/min. The column is washed with 200 ml of water at pH 3.0. The effluent is rejected. Then 50 ml of 2.0*M* hydrochloric acid are passed through the column at the same flow-rate. The effluent is collected in a 50-ml flask (up to the mark).

A 10-ml aliquot is taken in a separating funnel, 1 ml of phosphoric acid [to complex Fe(III)] is added, and the Tl content determined by the Rhodamine B method described earlier.

A 30-ml portion of the 50 ml is evaporated in a beaker. The residue is dissolved in 5 ml of 6*N* sulphuric acid, and transferred to a separating funnel with 5 ml of water. Then 10 ml of 3*M* potassium iodide are added and equilibrated with 6 ml of butyl acetate. The aqueous layer is rejected. Then 2 ml of 2% oxine solution in butyl acetate are added to the organic phase and mixed. This solution is scrubbed with 5 ml of potassium cyanide solution (10% KCN + 1*M* NH_3 in 2:3 ratio). The aqueous phase is discarded. The water droplets from the stem of the separating funnel are removed with a filter paper. The organic phase is transferred to a 10-ml volumetric flask and made up to volume with butyl acetate. The absorbance is measured at 400 nm against a corresponding reagent blank. The indium content is computed from a calibration curve.

Dowex A-1 (H$^+$)

Among the ions derived from the metals present in zinc-base alloys, Tl^{3+}, In^{3+} and Cu^{2+} exhibit high K_d values on this exchanger at pH 1.0 and 2.0.[28] Hence, their behaviour on a column (1.0 × 4.0 cm) was studied, by taking the solutions at these pH values and washing with water at the same pH. Tl^{3+} is strongly retained on the exchanger at both pH values, without elution on washing with 100 ml of acidified water. In the case of In^{3+} and Cu^{2+}, elution starts in the first 25 ml of washing at pH 1.0, but not at pH 2.0, even in 50 ml. A 0.01*M* *o*-phenanthroline solution at pH 2.0 elutes Cu^{2+} but not In^{3+} and Tl^{3+}. Experiments were then carried out on the elution of Tl and In with hydrochloric acid of different concentrations in presence and absence of sulphurous acid. Tl^{3+} is retained at any acidity between 0.4 and 2.0*N* while indium is eluted quantitatively with 50 ml of 1.0*N* acid and more than 50 ml of 0.4*N* acid. Hence, 1.0*N* acid is preferred to elute In^{3+} selectively. In presence of sulphurous acid Tl^{3+} is eluted with 2.0*N* acid. Since this acidity is convenient for its subsequent determination with Rhodamine B, other acid concentrations have not been tried.

Based on the information above, the procedure given below was found to be quite satisfactory for a sequential separation of Tl and In in zinc-base alloys and their determination at 5-ppm level.

Procedure. A 5.0-g sample is dissolved and Tl^+ oxidized to Tl^{3+} as described under *Zeo-Karb 226 (H$^+$)*. The pH of the solution is adjusted to 2.0. This solution is passed through a column (1.0 × 4.0 cm) of Dowex A-1 (H$^+$) (100–200 mesh) at a flow-rate of 1 ml/min. The column is washed with 100 ml of water at pH 2.0 to remove practically all the zinc and aluminium. Then it is washed with 100 ml of $0.01M$ *o*-phenanthroline at pH 2.0 to remove copper. Iron and indium are then eluted with 50 ml of $1.0M$ hydrochloric acid. In^{3+} is determined by the oxine method described earlier. Tl is then eluted with 50 ml of $2.0N$ hydrochloric acid containing sulphurous acid (1.2%). This solution is boiled to remove sulphur dioxide, cooled, oxidized and then analysed by the Rhodamine B method, described earlier.

DISCUSSION

The K_d value of Tl^+ on Zeo-Karb 226 (NH_4^+) is quite high (6.56×10^3). As such it is difficult to separate it from multivalent cations, which are primarily sorbed. However, in presence of $1.0M$ ammonium nitrate, the K_d value of Tl^+ decreases to a negligible value (<10), while those of multivalent ions are still considerably higher. Hence $1.0M$ ammonium nitrate is able to elute Tl^+ selectively, leaving many multivalent cations on the exchanger.

This principle is successfully applied to analyse high-purity zinc and zinc-base alloys for traces of Tl and also for the analysis of Pb–Tl alloys. When higher amounts of material are taken for analysis, the exchanger shrinks on sorption of the sample and channelling occurs. This was obviated by sorbing the sample by mixing it with the exchanger in a beaker and then transferring it to a column of the exchanger.

In the determination of Tl by the Rhodamine B method, a large excess of ammonium nitrate caused positive interference. This excess of ammonium salt is reduced by employing the same exchanger (smaller quantity) but oxidizing Tl to the tervalent state for its sorption and then eluting with acid.

Indium cannot be separated by employing the salt form of Zeo-Karb 226. However, this exchanger in H^+ form was shown to be useful to separate Tl and In together from zinc and some other associated ions, thus allowing the determination of both the elements, different aliquots being used.

The property of Dowex A-1 of functioning as a chelating as well as an anion-exchanger under suitable conditions is utilized to achieve a sequential separation of Tl and In from zinc-base alloys. At pH 2.0, ions such as Fe^{3+}, In^{3+}, Tl^{3+} and Cu^{2+} are sorbed through chelation, while Tl^{3+} in hydrochloric acid is held as an anionic chloro-complex.

It should be mentioned that elution of Cu^{2+} with 100 ml of $0.01M$ phenanthroline is not quantitative. Out of 5000 μg of Cu taken, about 150 μg remain on the column. Elution is not continued further for two reasons. The small amount of Cu coming out with indium does not interfere in the determination of the indium. Secondly, eluting the last traces of Cu may require an unduly large volume of phenanthroline solution.

Lead has a K_d value of 390 at pH 2.0. Hence it may be retained on the exchanger at the beginning, but since its K_d falls to 140 in presence of phenanthroline, it is likely to be eluted along with the copper. In view of this, its behaviour was not studied in detail. However, it was taken in the synthetic samples to ascertain whether it interferes in the present analysis.

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X-RAY PHOTOELECTRON SPECTROMETRIC AND X-RAY FLUOROMETRIC STUDIES OF SULPHUR COMPOUNDS ON THE SURFACE OF COPPER PLATES EXPOSED TO THE ATMOSPHERE

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Summary—X-Ray photoelectron spectroscopy (XPS) and XRF as techniques for monitoring air pollution are compared. Sulphide and oxides of sulphur (SO_2, SO_3 and SO_4^{2-}) have been determined on copper plates exposed for different lengths of time to an atmosphere containing hydrogen sulphide. The total amount of sulphur increases with the time of exposure but the sulphide reaches a constant value after 59 days. An interpretation of the mechanism of oxidation of hydrogen sulphide is offered.

Many studies on air pollution have been performed by using atomic absorption,[1] atomic fluorescence,[2] the ring-oven technique,[3] and X-ray fluorescence.[4] These methods are suitable for qualitative identification and quantitative determination of elements, but not for identifying their chemical form or species. Speciation, *i.e.* the determination of species, is desirable in order to understand the chemical processes in the environment and to follow the corrosion processes going on in an atmosphere containing corrosive gases. X-Ray photoelectron spectroscopy (XPS) differentiates between chemical species of an element and is a potentially useful tool for environmental studies.[5] The present investigation was undertaken to analyse the surface of a metal plate exposed for varying periods to the atmosphere. Sulphur compounds and a copper plate were selected for the study, first because the oxidation states of sulphur and copper may be correlated with XPS chemical shifts and secondly because a copper plate is easily corroded.[6–8]

EXPERIMENTAL

Commercial copper plates (JIS tough-pitch 35 × 35 × 0.35 mm) were stored in a vacuum desiccator after treatment by the following processes: soak in warm ethanol for 1 hr then wash successively with water, 1*M* hydrochloric acid and ethanol, and then dry in an air blast. The copper plates were placed under a screen (situated in various meteorological sampling stations) to avoid rainwater. Standard sulphur solutions for X-ray fluorometric determination were prepared by the procedure of Pope *et al.*[9] X-Ray fluorometric measurement was performed by using a Rigaku Gigerflex, type SXA 3, with a germanium analysing crystal and chromium target X-ray tube.

X-Ray photoelectron spectra were obtained on an AEI-ES 200 electron spectrometer, using Al $K_{\alpha 1,2}$ X-ray radiation. The photo-emission chamber was maintained at 10^{-7} mmHg. The binding energies of the photoelectrons were determined, assuming the energy of carbon 1*s* electrons to be constant at 285 eV.

RESULTS AND DISCUSSION

X-Ray fluorescence studies

Figure 1 shows a typical X-ray fluorescence spectrum of sulphur on the surface of copper. A sharp sulphur K_α line is observed at 110.7° (2θ) without any interference from other elements. A calibration curve based on this line is linear up to a concentration of 100 μg/cm² [log S (μg/cm²) = 1.090 log *C* (count/10 sec) − 4.160]. In order to test the validity of the calibration curve, known amounts of sulphur were added to the sample. A recovery of approximately 100% was obtained when the added sulphur was below

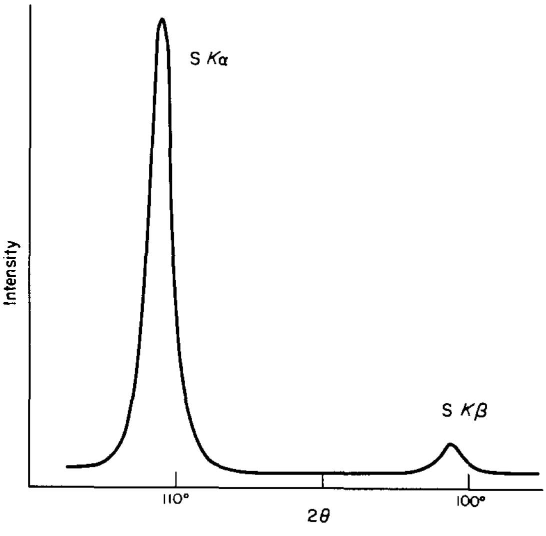

Fig. 1. X-Ray fluorescence spectrum of sulphur on the surface of a copper plate.

Table 1. Determination of the total sulphur by XRF and sulphide by XPS

Sample	Station*	Exposure, *days*	Total sulphur, *$\mu g/cm^2$*	S^{2-} species *$\mu g/cm^2$*
No. 1	desiccator (50–100 ppm H_2S)	0.5	28	28
No. 2	A	31	3.7	1.8
No. 3	A	59	15	10.5
No. 4	A	206	49	12.3
No. 5	B	12	7.7	4.4
No. 6	C	28	0.82	

* Stations A and B are in an area polluted with H_2S, A being 1.5 km from the pollution source, and B 0.3 km. Station C is in an unpolluted area.

50 μg/cm^2 though the recovery varied somewhat at the sulphur level of 100 μg/cm^2. X-Ray fluorometric (XRF) determinations of sulphur for six samples are given in Table 1. All samples produce black compounds on the surface of copper plate, indicating the formation of copper sulphides or copper (II) oxide.

At station A the total sulphur increases steadily with the number of days of exposure to the atmosphere up to 59 days when a constant value is obtained. At station B the rate of adsorption of sulphur is greater, whilst at station C it is lower. These results correspond with the position of each station.

X-Ray photoelectron spectroscopic studies

Figure 2 shows a typical photoelectron spectrum of a copper plate exposed to the atmosphere. Elements such as carbon, oxygen, sulphur, and copper are readily detectable on the surface of the plate.

Sulphur 2p *photoelectron spectra*

There is a correlation between binding energy and oxidation number in inorganic sulphur compounds,[7,10,11] sulphide [S(−II)] has the lowest binding energy (160.8 eV) and sulphate [S(VI)] the highest. Sulphite [S(IV)] and sulphur [S(0)] are also distinguishable, having binding energies of 165.8 and 164.5 eV, respectively.

Figure 3 shows typical sulphur and copper 2*p* photoelectron spectra for samples 1, 2, 4 and 6. Only the peak at 161.7 eV, corresponding to S^{2-} species, is observed on the surface of the copper plate exposed to H_2S gas in the desiccator. Since no satellite Cu 2*p* peaks, which are characteristic of Cu(II) compounds, are observed, the black compound produced on the surface is probably Cu_2S. Sulphur 2*p* peaks for samples 2 and 4 are roughly divisible into two groups having lower and higher binding energies, indicating sulphide (S^{2-}) species and sulphur oxide (SO_2, SO_4^{2-}, SO_3) species, respectively. Species such as SO_3^{2-} and S^0 are unlikely. The peak at higher binding energy is so broad that it contains components of other species. Craig *et al.*[12] reported that the peak in the vicinity of 170 eV binding energy consists of three components, SO_3, SO_4^{2-}, and SO_2, as shown in Fig. 4. The resolution of our spectrometer is not good enough to distinguish these species so we shall class SO_3, SO_4^{2-}, and SO_2 together as *sulphur oxides.* At station A the ratio of sulphur oxides to sulphide changes with the length of exposure. If no oxidation of sulphide occurred on the copper plate, the ratio would be almost constant in the course of time. Actually oxidation reactions of sulphide must proceed since the ratio changes with the exposure time. The unexpected higher ratio of sulphur oxides to sulphide as shown in Fig. 3*b* may be attributed to the prompt production of sulphur oxides from hydrogen sulphide early in the exposure. Kishi *et al.*[13] have recently investigated the mechanism of

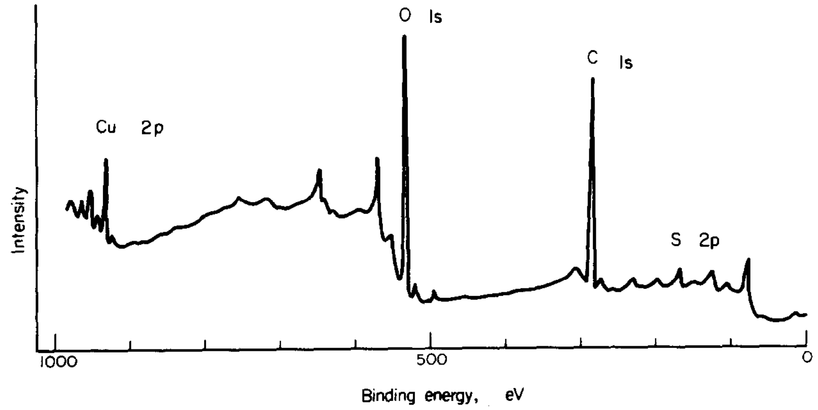

Fig. 2. X-Ray photoelectron full spectrum of a copper plate exposed to the atmosphere.

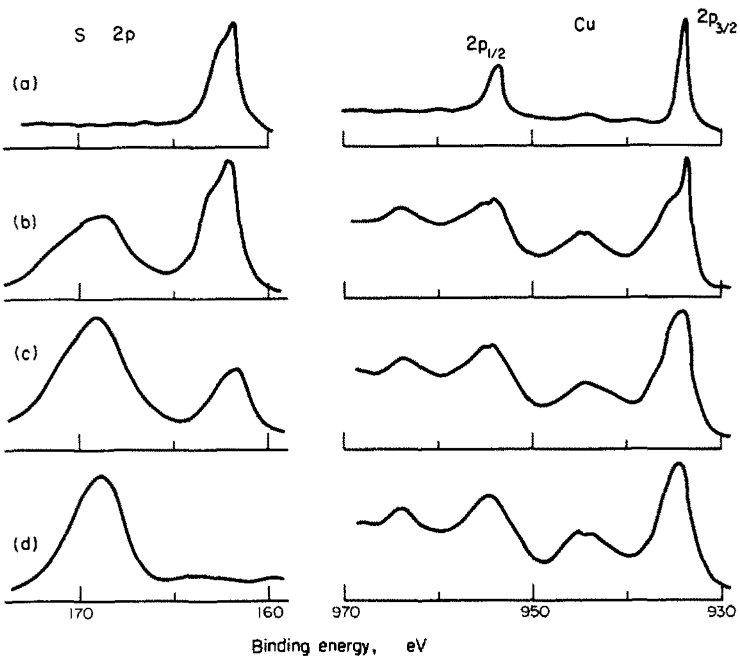

Fig. 3. Photoelectron spectra of S 2*p* and Cu 2*p*: (*a*) sample 1; (*b*) sample 2, (*c*) sample 4, (*d*) sample 6.

the interaction of hydrogen sulphide with adsorbed oxygen on lead, by XPS. According to their results, the oxygen 1*s* peak height decreased on exposure of the "oxidized" surface, which had been exposed to oxygen at 2×10^{-5} mmHg for 100 sec, to hydrogen sulphide. Accompanying the decrease in the oxygen 1*s* intensity was the emergence of the sulphur 2*p* peak: initially the sulphur 2*p* binding energy is about 163.5 eV, but later it is 160.6 eV. It would be expected from these experimental results that atmospheric hydrogen sulphide would react with the oxygen previously chemisorbed on the copper surface and with the metallic copper at the same time. Therefore nearly equivalent amounts of sulphur oxides and sulphide are produced in the early stages. In time, the oxidation of sulphur compounds takes place on the copper plate, as shown by the increase in the peak due to sulphur oxides (Fig. 3*c*). The concentrations of sulphide for samples 2–5 are given in the last column of Table 1. They were estimated from the ratio of sulphide to sulphur oxides, obtained from the sulphur 2*p* photoelectron spectra, assuming that the XPS cross-section of sulphur 2*p* and the escape depth of sulphide and sulphur oxides are approximately the same. As evident from Table 1, the sulphide concentration increases in the early stages, but during the 59–206 day period the concentration of sulphide increases only slightly, while the concentration of sulphur oxides increases considerably. The following interpretation is given for these results. The dilute hydrogen sulphide liberated in the atmosphere is adsorbed on the surface of the copper plate. The adsorbed gas immediately reacts with the previously chemisorbed oxygen and the metallic copper in the presence of oxygen and moisture, resulting[14] in the production of sulphur oxides and Cu_2S as follows:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

$$2Cu + S^{2-} + H_2O + \tfrac{1}{2}O_2 \rightarrow Cu_2S + 2OH^-$$

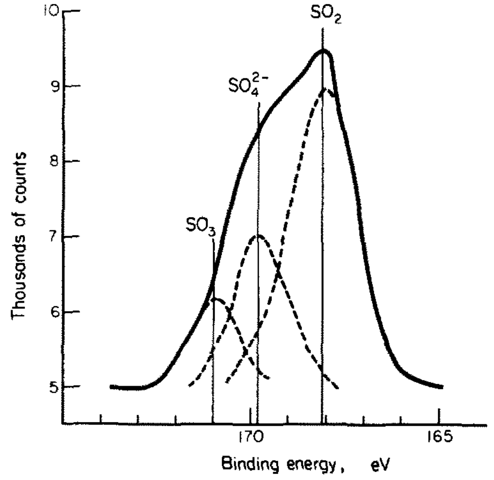

Fig. 4. Sulphur 2*p* spectrum of MgO exposed to SO_2. [Redrawn from reference 12].

Available sites on the copper surface are gradually occupied and used up by H_2S gas in the course of time. A steady state is reached with respect to sulphide in the atmospheric environment. Then the rate of copper(I) sulphide formation decreases, since the hydrogen sulphide can react with the metallic copper only after permeating the surface layers of sulphide and sulphur oxides. However, the amount of sulphur

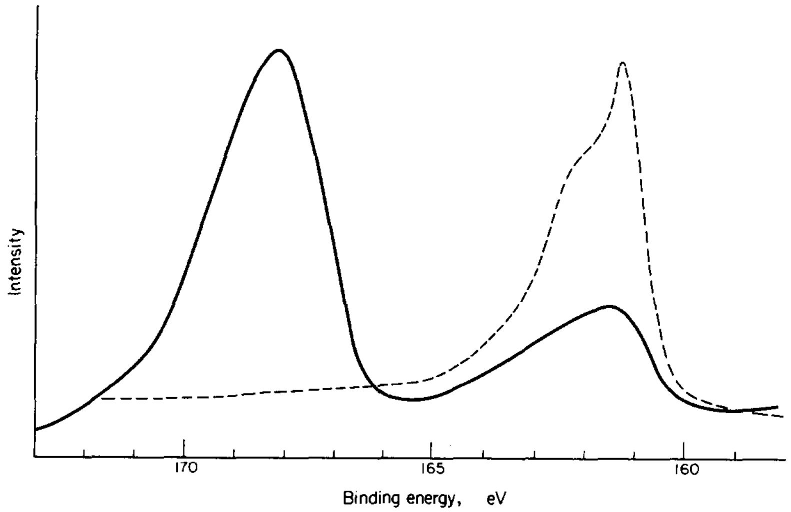

Fig. 5. S 2*p* photoelectron spectrum of a copper plate, previously treated with H_2S, then exposed to ozone. ---- Cu + H_2S; —— (Cu + H_2S) + O_3 (Intensities of the two spectra are not on the same scale).

oxides increases, by the oxidation of the surface sulphide layers, the catalytic oxidation of hydrogen sulphide on the copper plate, and the adsorption of sulphur oxides from the atmosphere.

In the laboratory experiment, hydrogen sulphide reacts immediately with the copper plate to produce black copper sulphides. At this point, sulphide species are the only sulphur compounds on the surface of the plate. When the plate is exposed to ozone ($\sim$ 1000 ppm) in the desiccator, the sulphide peak intensity decreases considerably and the intense peak of sulphur oxides appears as shown in Fig. 5. This implies that the oxidation of sulphide on the surface of the copper plate is possible during the long exposure to the atmosphere. This oxidation would start on the surface layers of sulphide. Blyholder *et al.*,[15] who studied infrared spectra of H_2S adsorbed on Fe and Ni, showed that H_2S in the atmosphere could interact dissociatively with both metallic and oxide surfaces of particles in the atmosphere. The ease with which H_2S interacts with the different kinds of surface suggests that heterogeneous reactions play a major role in the oxidation of H_2S in the atmosphere.[15] There are instances when sulphide acts as a catalyst.[16–18] Therefore the contribution from the catalytic oxidation of hydrogen sulphide on the sample plate must also be considered. It is, of course, expected that small amounts of atmospheric SO_2 and sulphuric acid mist are also adsorbed on the surface of the copper plate, as is found for sample No. 6 (Fig 3*d*).

Two reaction pathways are to be considered for the oxidation of hydrogen sulphide. One is heterogeneous oxidation of hydrogen sulphide on the surface of the copper plate as mentioned above. The other is homogeneous photo-oxidation in the atmosphere, followed by adsorption of the sulphur oxides on the copper plate. The oxidation following direct photolysis of H_2S is unlikely to occur in the atmosphere since this gas does not absorb ultraviolet radiation of wavelength longer than 260 nm.[19] It results from reaction of atoms or radicals produced by the photolysis of other species such as NO_2 and H_2O_2 in the following way:

$$NO_2 \xrightarrow{h\nu} NO\cdot + O\cdot$$

$$H_2O_2 \xrightarrow{h\nu} 2OH\cdot$$

The oxidation of hydrogen sulphide then proceeds in two steps:[20]

$$H_2S \xrightarrow{1} SO_2 \xrightarrow{2} SO_3.$$

The first step hardly occurs in the absence of the absorbing species mentioned above. However the second proceeds since SO_2 has absorption bands at 294 and 384 nm. Therefore if there are sufficiently high concentrations of oxidants such as NO_2 and O_3 in the area polluted with H_2S gas, both hydrogen sulphide and sulphur oxides produced by photo-oxidation are adsorbed on the copper plate. Photo-oxidation is most likely to occur in urban districts where the concentration of oxidants such as NO_2 is high.

Copper 2p *photoelectron spectra*

It is well known that the existence of copper 2*p* satellites is an easy guide for the determination of oxidation states of copper.[8,14] The existence of satellites is associated with paramagnetic species. Cu(II) has a paramagnetic $3d^9$ structure while Cu(I) has a filled 3*d* subshell. The copper 2*p* spectrum readily identifies Cu(II) species, but fails to destinguish between Cu(0) and Cu(I).

The surface of sample 1 shows the production of black sulphide. Since no satellites are observed in the copper 2*p* spectrum as shown in Fig. 3*a*, the reaction product should be not CuS but Cu_2S.

Samples 2–6 have satellites in the copper $2p$ spectrum, indicating the existence of Cu(II). Moreover the peaks of Cu $2p_{1/2}$ (*ca.* 954 eV) and Cu $2p_{3/2}$ (*ca.* 934 eV) are broader than those of Cu(0). This is due to the appearance of new peaks having slightly higher binding energy. The peak height of the new peaks increases with the exposure times. Therefore these new peaks would indicate the formation of Cu(I) and Cu(II), because similar peaks are observed for a sample of copper exposed for a few days to air saturated with water vapour.[21] Broadening of peaks would be due to the superimposition of the peaks of Cu(0), Cu(I), and Cu(II) with slightly different binding energy. Since CuS and Cu_2SO_4 are unstable and change into $CuSO_4$ in moist air, Cu_2S and $CuSO_4$ are expected to be the predominant copper compounds containing sulphur.

CONCLUSION

In the areas polluted with hydrogen sulphide, hydrogen sulphide liberated from the source diffuses into the atmosphere. In urban areas part of the gas is photo-oxidized in the presence of oxidants such as NO_2. However the photo-oxidation would be unlikely to occur in rural surroundings, where the concentration of oxidants is low. There most of the gas falls on the surface of the earth. Thus hydrogen sulphide is adsorbed on the copper plate. The adsorbed gas immediately reacts with metallic copper and the chemisorbed oxygen in the presence of the atmospheric moisture and oxygen, with the formation of Cu_2S species and sulphur oxides on the surface of the copper. The Cu_2S gradually changes into $CuSO_4$ as the end compound during long exposure. Additional H_2S is adsorbed on the Cu_2S layers, and a part of it permeates to react with metallic copper. This adsorbed gas is oxidized catalytically on the surface of Cu_2S to produce SO_2 and SO_3. Thus the increment of sulphide is small, while the increment of sulphur oxides is great because of additive contributions from the oxidation of Cu_2S, the catalytic oxidation of H_2S, and the atmospheric SO_2 and sulphuric acid mist.

Thus XRF and XPS are valuable techniques for monitoring air pollution and understanding of the process of corrosion of copper.

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SOLVENT EXTRACTION OF GOLD

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Summary—The separation of gold by solvent extraction is reviewed.

Liquid–liquid extraction, in favourable circumstances, combines a high degree of selectivity with the ability to concentrate minute amounts of material and to segregate the minor from the major constituents of complex mixtures. It is sometimes possible to find conditions such that a particular constituent of a mixture is removed exclusively and essentially quantitatively in a single extraction. Also it is easier than precipitation for handling large samples.

The extracted metal ion is usually incorporated in a neutral chelate molecule or an ion-association complex. Ion-association systems may be of different types, but that in which the solvent plays a specific role is particularly important. The metal ion forms an anionic complex with anions such as chloride or nitrate, which then "associates" with a protonated oxygen-containing organic solvent such as an ether. The classic example of such a system is the extraction of iron from 6*M* hydrochloric acid with ether, where the complex $HFeCl_4(C_2H_5)_2O$ is formed.[1] A similar type of behaviour is also observed for gold.[2,3] The formation of an extractable species by a suitable solvent would therefore depend on the efficiency of formation of such ion-association systems. The strength of the solute–solvent interaction will determine the extraction efficiency of the solvent used, or rather the distribution coefficient of the solute. It would be of great value to an analytical chemist to know beforehand the order of distribution coefficients of different solutes in various solvents. Some generalizations have been made by Morrison and Freiser.[4] In a homologous series, the lower members are more efficient solvents than the higher ones.[5,6] A knowledge of the dissociation constant of the solvent complex in the organic phase is important since this may also affect the distribution coefficient.[6–21] Further, the two phases must separate quickly and efficiently, and this is dependent on several factors. Thus quick separation of phases is ensured by a larger interfacial tension[22] between them, low viscosity of the organic phase, high density difference between the two solvents, and low solubility of the organic solvent in the aqueous phase.

Radiochemical, colorimetric and various spectrometric methods (such as atomic absorption and flame emission) complement solvent extraction since the organic phase may be analysed directly. Solvent extraction is particularly well suited for the purification of radioisotopes.

This review will be confined to the liquid–liquid extraction of gold, of which no comprehensive recent survey is available, though Beamish *et al.* earlier made a general review of the methods of separation and colorimetric determination of gold.[23]

Studies on the solvent extraction of gold as its chloride complex were first reported by Lenher and Kao[5] in 1926. They examined the extraction of gold into various esters, especially ethyl acetate. By this method gold can easily be separated from other elements, *e.g.*, Na, K, Mg, Ba, Fe, Al, Sr, Ca, Cr, Mn, Co, Ni, Zn, Hg, Cu, Cd, Pd, Bi, Sb, As, and Sn. Use of ethyl acetate as an extractant for gold from hydrochloric acid medium was studied by several other workers, who separated it from irradiated copper,[24] platinum,[25] refined silver,[26] fission products,[27] irradiated biological materials,[28] rocks, minerals,[29,30] sulphide ores, meteorites,[31] petrochemicals[32] and sea-water.[33] Ethyl acetate is, however, seldom used nowadays, because of its solubility in water.

Ether also finds application as a good extractant for gold.[34,35] It is particularly useful in extracting gold from nitric acid solution; the distribution coefficient is dependent on the acid concentration. The effects of temperature and salting-out agents have been studied and the complex $HAu(NO_3)_4$ has been postulated.[36,37]

Methyl isobutyl ketone (MIBK) has been found to be very useful in extracting gold from waste cyanide solution.[38] Here Au(I) is initially oxidized to Au(III) by permanganate in hydrochloric acid medium. The method is, however, not free from interferences. Along with gold, Cr(VI), Mo(VI), Ga(III), As(V), Sb(V), Sn(IV), Se(IV), Te(IV) and Ge(IV) are also partially extracted. The extraction of Au(III) by MIBK at different hydrochloric acid concentrations has been studied.[39–43] The distribution of the gold depends on the concentrations of both the gold and the hydrochloric acid, without a definite dependence on either alone. If an excess of hydrobromic acid is present, MIBK is very efficient.[44] Maeck *et al.*[45] examined the extraction of Au(III) as a quaternary ammonium salt (tetrapropylammonium) from *aqua regia* medium into MIBK. A coloured complex is formed and is the basis of a spectrophotometric determination. A complete recovery of Au(III) directly from *aqua regia* (diluted) medium with MIBK was reported[46] recently, the only interferences being due to the partial extraction of Ag, As and Sb.

Tributyl phosphate (TBP) in xylene, chloroform or iso-octane, and trioctylphosphine oxide (TOPO) in chloroform also find wide application[47] in the extraction of gold. The species that is extracted is supposed to be of the form $[H_3O^+ \cdot 3R_3PO \cdot yH_2O][AuX_4^-]$, where R is the butoxy or octyl group and X is chlorine or bromine. A solution of 50% TBP in toluene was found[48] to extract gold quantitatively from $3M$ hydrochloric acid containing lithium chloride as salting-out agent. The great potentiality of alkylphosphine oxides as analytical extractants has been utilized[49] in extracting Au(I) with tri-n-octylphosphine oxide or 2-ethyl-n-hexylphosphine oxide in cyclohexane, at different hydrochloric acid concentrations.

The extraction of gold(I) cyanide into organic solvents[50] containing tertiary amines has been studied. Au(I) is reported[51,52] to occur in the organic phase as $HAu(CN)_2$, which is solvated with one molecule of tertiary amine. The extraction is dependent on the pH of the aqueous phase. The extraction of Au(I) cyanide by a series of quaternary ammonium salts has also been examined[53,54] and a trioctylmethyl ammonium salt was observed to be the most effective extractant. Groenewald[55] described a very sensitive method for extraction of gold from its cyanide solution into a di-isobutyl ketone solution of trioctylamine (TOA) or trioctylmethylammonium chloride (TOMA). Ca and Mg ($2 \times 10^{-3}M$) and Cu, Fe, Zn and Mn (2×10^{-3}–$5 \times 10^{-5}M$) do not interfere. The solvent n-butyl acetate containing trioctylamine has also been found[56] suitable for the extraction of Au(I) cyanide directly. The aqueous phase has to be adjusted to pH 4 to ensure quantitative extraction. A highly selective method for the extraction of Au(III) from sulphuric acid into a chloroform solution of trioctylamine (TOA) has been described by Adam and Přibil.[57]

Murphy and Affsprung[58] observed that a gold chloride complex forms a precipitate with tetraphenylarsonium chloride, which can be extracted with chloroform. The extracted species is supposed to be the ion-pair $[(C_6H_5)_4As^+][AuCl_4^-]$. Interference due to iron is suppressed by means of fluoride and none of the platinum metals interferes when present in concentration one tenth that of the gold. The same reagent has been recommended [59] for the substoichiometric determination of gold after neutron activation. The presence of Sb, Te and nitrate, however, hindered the extraction. By using tetraphenylarsonium chloride Alimarin and Perezhogin[60] determined traces of gold in Pb, Bi, Cu and Zn. No interference was observed even when the primary base metals or osmium were present to the extent of ~ 1 g. The authors were able to determine 5×10^{-11} g of gold with an error of about ±5% by using the substoichiometric principle in neutron-activation analysis.

In a study by Rakovskii *et al.*[61,62] the large organic tetraphenylguadinium cation (TPG) was used for substoichiometric extraction of gold as $[Au(SCN)_4^-][TPG^+]$ into chloroform, but it was observed that the presence of Pd hindered the separation of the phases. No such problem occurred in the substoichiometric extraction of $AuCl_4^-$ with TPG in 1,2-dichloroethane.

A solution of tetrabutylammonium perchlorate in chloroform can be used as an ion-association extractant for tetrachloroaurate(III). Bravo and Iwamoto[63] showed that the distribution coefficient can be increased to 3×10^3 by variation of the $([Bu_4N^+][ClO_4^-])_{org}/[ClO_4^-]_{aq}$ ratio.

The reagent *p*-dimethylaminobenzylidenerhodanine in isoamyl acetate was found to be a selective extractant for gold from hydrochloric acid medium by Cotton and Woolf.[64] Poluektov,[65] however, preferred to use the reagent in benzene–chloroform medium for separation of gold in presence of a few drops of $1M$ nitric acid.

A method of determination of gold with Cu, Zn or Hg–diethyldithiocarbamate (DDC) in acid medium by means of radiometric titration, using tetrachloromethane as the solvent has been described.[66,67] End-points corresponding to molar Au:DDC ratios of 1:1 and 1:2 were observed on the titration curve of gold(III) when DDC was used as the titrant. The compounds formed successively are $[Cl_2Au(DDC)]$ and $[Au(DDC)_2]^+Cl^-$. The first compound is completely extracted into trichloromethane or benzene and the extractibility of the second compound increases with increasing solvent polarity. Gold(I) forms only one compound with DDC, AuDDC. For determination of gold present as impurity in beryllium metal, Negina and Zamyatnina[68] used the reagent in chloroform. Eugene[69] also used Cu–DDC solution for substoichiometric separation of gold isotopes from irradiated meteorites.

Selective extraction of gold with a solution of 0.01–$1M$ dibutyl sulphide from hydrochloric acid medium has also been reported.[70,71] Either chloroform or benzene may be used as the diluent.

Block *et al.*[72] also studied the distribution of many metal bromides, including that of gold, at various hydrobromic acid concentrations. The percentage of gold extracted into the organic solvent varies from 99.5% to 99.9% in the hydrobromic acid concentration range 1–$3M$.

The extraction properties of a number of elements with dibutyl phosphorothioic acid was studied by Handley.[73,74] The relative order of extraction was found to be Pd(II) > Au(III) > Cu(I) > Hg(II) > Ag(I) > Cu(II) > Bi(III) > Pb(II) > Cd(II) > Ni(II) > Zn(II).

The various systems referred to above are summarized in Table 1.

Table 1. Extraction systems

Aqueous phase	Organic phase	Sample studied	References
2–7*M* HCl	Diethyl ether	Rocks, meteorites	127–131
2*M* HCl	Diethyl ether	Quartz	34
8*M* HCl	Diethyl ether	Impurities	81
HCl	Diethyl ether	Platinum metals, mercury	3, 7, 8, 82
HBr	Diethyl ether	Aluminium	35
HI	Diethyl ether		88
8*M* HNO_3	Diethyl ether		36, 37
Aqua regia	Diethyl ether	Platinum	25
HCl	Isopropyl ether		95, 97
7–7.5*M* HCl	Di-isopropyl ether	Silicon	94
HI	Methyl isopropyl ether		107
1*M* HCl	Ethyl acetate	Palladium, platinum	132
HCl	Ethyl acetate	Copper	24
HCl	Ethyl acetate	Igneous rocks, meteorites and sulphide ores	29–31, 83, 85–87, 102, 103, 124
2–6*M* HCl, HNO_3	Ethyl acetate	Iridium, platinum	84
	Ethyl acetate	Sea-water	33
	Ethyl acetate	Marine organisms	104
	Ethyl acetate	Biological materials	28
	Ethyl acetate	Lead	105
	Ethyl acetate	Associated fission products	27
3*M* HCl	Isoamyl acetate	Mercury	93
H_2SO_4–KI	Toluene		100
HCl	Aliphatic esters		5
6–8*M* HCl	Benzene, carbon tetrachloride, n-heptane, chlorobenzene, *o*-dichlorobenzene, nitrobenzene		75
HCl, HNO_3, $KClO_4$–KI	Carbon tetrachloride	Silicon	92
Ph_3iso-PrPCl, NaCNS	Benzene or toluene	Gold alloys	133
HCl	Butyl acetate	Ores	135
4% HCl	Ether or ethyl acetate		140
HCl	Isoamyl alcohol	Platinum, lead	136
Aqua regia	Methyl isobutyl ketone	Ore	46
HCl	Methyl isobutyl ketone	Ore	116–121
0.5–8*M* HCl	Methyl isobutyl ketone		39–41
HBr	Methyl isobutyl ketone		44
3*M* HCl	Methyl-isobutyl ketone, methyl-n-amyl ketone, methyl-n-hexyl ketone, butyl acetate, ethyl acetate	Cyanide waste	38
HNO_3	Dibenzyl sulphoxide		98
7*M* HCl	Tribenzylamine (TBA)		123
HCl	Di-n-octyl sulphide		80
H_2SO_4	Dithizone/chloroform	Bismuth	111
H_2SO_4	Dithizone/chloroform		108, 109, 112
H_2SO_4	Dithizone/chloroform	Ores	110, 113
0.1*M* HCl	Dithizone/chloroform	Low grade ores	141
HCl, HBr	Tributyl phosphate/xylene/carbon tetrachloride/iso-octane Trioctylphosphine oxide (TOPO)/chloroform		47
0.01*M* HCl	Tetrabutylammonium perchlorate/chloroform		63
HCl	Tetraphenylarsonium chloride/chloroform	Platinum metals, iron, *etc.*	58–60, 122
0.01*M* HCl	Tetraphenylarsonium chloride/benzene		76
5.3*M* HCl	Tetraphenylguanidium salt (TPG)/1,2-dichloroethane	Natural specimens	61, 62
HSCN	Tetraphenylguanidium salt (TPG)/chloroform		79
0.1–6*M* HCl	Dibutyl sulphide/chloroform, benzene		70
0.5–1*M* HCl	Dibutyl sulphide/benzene	Rock samples	71
HCl	Crystal Violet or Methyl Violet/benzene or toluene		134

Table 1—*continued*

Aqueous phase	Organic phase	Sample studied	References
HCl	Phenyl-α-pyridyl ketoxime/ chloroform		115
HCl	Diethyldithiocarbamate/ chloroform	Beryllium	68
HCl	Diethyldithiocarbamate/ chloroform		89
H_2SO_4, HCl	Diethyldithiocarbamate/ chloroform	Biological materials, lead, silica and rocks	90, 96, 126
1*M* H_2SO_4, 0.1*M* $HClO_4$	Cu, Zn or Hg–diethyl dithiocarbamate/ chloroform or benzene	Biological materials and tin	66, 67
	Cu–diethyldithiocarbamate	Meteorites	69
Aqua regia	Trioctylamine (TOA) or trioctylmethylammonium chloride (TOMA)/di-isobutyl ketone	Geological samples	55
1–7*M* HCl	2-Ethyl-n-hexylphosphine oxide or tri-n-octyl phosphine oxide/cyclohexane		49
pH 4	Trioctylamine (TOA)/n-butyl acetate		56, 99
Aqua regia	Tetrapropylammonium/methyl isobutyl ketone		45
0.12*M* HCl	*p*-Dimethylaminebenzylidene-rhodanine/isoamyl acetate		64, 78
0.1*M* HNO_3	*p*-Dimethylaminebenzylidene-rhodanine/benzene–chloroform		65
HBr	Polyoxyethylene glycol/ dichloromethane		138
6*M* HCl	Polyoxyethylene glycol/ dichloromethane		139
HCl	Dibutyl carbitol(diethylene glycol dibutyl ether, butex)	Precious metal concentrate	144
pH 6	Phenylacetic acid (PAA)/chloroform		142
3*M* HCl	Ethyl acetate		143
HCl	Tri-n-butyl phosphate (TBP)		145, 146
HCl	Tri-n-octyl phosphine oxide/toluene		147
	Mesityl oxide (4-methyl-3-penten-2-one)		91
HCl	Primene JM-T/xylene		77
HCN	Bis(1-isobutyl-3,5-dimethyl-hexyl)amine/kerosene		101
HCl	8-Mercaptoquinoline/chloroform, benzene, *etc.*		114
HBr	Iron(II)–1,10-phenanthroline/chloroform	Elements other than platinum metals	106
	Mercaptans, RSH (R = Bu, dodecyl and *tert.*-dodecyl)		148
	O,O,S-Triethyl thiophosphate		149
8*M* HNO_3	Tributyl phosphate/carbon tetrachloride		137
H_2SO_4	Petroleum sulphoxides/C_6–C_8 alcohols	Technological waste solution	150

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SHORT COMMUNICATIONS

TITRIMETRIC DETERMINATION OF THIOCYANATE AND THIOSULPHATE IONS BY OXIDATION WITH IODINE IN ALKALINE SOLUTION

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As shown in a review,[1] one of the most well-known and useful amplification methods is the reaction in which iodide ions are oxidized to iodate ions by chlorine or bromine. After removal of excess of the oxidant, the iodate ions formed are reduced by addition of more iodide ions, in acid medium, to give three molecules of iodine for each original iodide ion. This method has often been applied indirectly to other ions which show a quantitative relationship with iodide. For example, Gawargious[2] recently applied an indirect amplification for determination of arsenic by oxidizing arsenite ions to arsenate ions with iodine. After extraction of the excess of iodine, the iodide amplification reaction was applied.

In the present work, thiocyanate and thiosulphate ions are oxidized by iodine in alkaline solution to sulphate ions. In both procedures, the excess of iodine is extracted with chloroform; the iodide ions resulting from the redox reaction are retained in the aqueous phase and then the amplification reaction is applied.

Thiocyanate

In a hydrogen carbonate medium (pH 8.2), thiocyanate ions are oxidized by an excess of iodine to sulphate ions:[3]

$$SCN^- + 4I_2 + 4H_2O \rightarrow SO_4^{2-} + ICN + 7I^- + 8H^+$$

On acidification with sulphuric acid to pH 2.5, which is necessary for the subsequent amplification reactions, the iodine cyanide reacts with iodide ions to give iodine and hydrocyanic acid:

$$ICN + I^- + H^+ \rightarrow I_2 + HCN$$

This molecule of iodine together with the excess of iodine is extracted into chloroform. Hence the overall reaction can be considered to be

$$SCN^- + 3I_2 + 4H_2O \rightarrow SO_4^{2-} + 6I^- + 7H^+ + HCN$$

Bromine water is added to this aqueous solution to oxidize iodide ions to iodate ions:

$$3Br_2 + I^- + 3H_2O \rightarrow IO_3^- + 6H^+ + 6Br^-$$

and to convert hydrocyanic acid into bromine cyanide:

$$Br_2 + HCN \rightarrow BrCN + H^+ + Br^-$$

Finally, after the destruction of the excess of bromine with formic acid, potassium iodide is added and the following reactions take place:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$
$$BrCN + 2I^- + H^+ \rightarrow I_2 + HCN + Br$$

Thus from each original thiocyanate ion, 19 molecules of iodine are obtained.

Thiosulphate

In sodium hydroxide solution (pH 12), iodine forms hypoiodite ions, which oxidize thiosulphate ions to sulphate ions:[4]

$$I_2 + 2OH^- \rightarrow OI^- + I^- + H_2O$$
$$S_2O_3^{2-} + 4OI^- + 2OH^- \rightarrow 2SO_4^{2-} + 4I^- + H_2O \quad (1)$$

On acidification, the excess of hypoiodite is converted into iodine, which is then extracted into chloroform. The amplification reaction is then applied to the iodide left in the aqueous solutions. Hence each original thiosulphate ion gives rise to 24 molecules of iodine.

Investigation of reaction conditions

Effect of pH. The oxidation reactions described are carried out in alkaline medium, and because iodine oxyanions are involved the oxidation potentials will be independent of the pH, and the reactions possible will be different from those in acidic solutions. In alkaline solutions, iodine is capable of oxidizing thiocyanate and thiosulphate ions to sulphate ions. However, the pH values required are different. For thiocyanate, a hydrogen carbonate medium (pH 8.2) is sufficiently alkaline for the oxidation. At higher pH values, for example, in sodium hydroxide solution (pH 12), inconsistent results are obtained after different reaction times, as shown in Table 1, and in acidic medium (pH 5 acetate buffer) the results are low (Table 1) because sulphate is not the end-product and a smaller consumption of iodine is to be expected.

Table 1. Effect of pH on oxidation of thiocyanate and thiosulphate ions by iodine

Solution added (10 ml)	pH	Titration volume, *ml*, for	
		SCN^-*	$S_2O_3^{2-}$†§
NaOH (1*M*)	12	6.7–9.5†	9.65
$NaHCO_3$(10% v/v)	8.2	7.40	4.00
Acetate buffer	5.0	4.5	
H_2SO_4(0.1*N*)	1		2.40

* Expected value for 22.5 μg of SCN^- is 7.39 ml of $2 \times 10^{-3}M$ $Na_2S_2O_3$.

† Oxidation period varied from 30 min to 9 hr.

§ Expected value for 44.8 μg of $S_2O_3^{2-}$ is 9.60 ml of $2 \times 10^{-3}M$ $Na_2S_2O_3$ for oxidation to SO_4^{2-} and 2.40 ml for oxidation to $S_4O_6^{2-}$.

Table 2. Range of applicability of the thiocyanate determinations

Thiocyanate taken, *μg*	2.7	4.5	9.0	22.5	45.0	90.0
No. of determinations	3	3	3	11	3	2
Mean recovery, % (titration)	103.2	100.6	99.8	99.7	99.2	98.8
Mean recovery, % (spectrophotometry)	98.8	100.1	97.4	99.9	100.1	100.4
Final volume for spectrophotometry, *ml*	50	100	100	250	500	1000

For thiosulphate oxidation, a sodium hydroxide solution (pH 12) is necessary; hydroxide ions participate in the redox reaction [reaction (1)]. Low results are obtained in a hydrogen carbonate medium, as shown in Table 1. In acidic medium (pH 1), two thiosulphate ions are oxidized by one molecule of iodine, to the tetrathionate ion (Table 1).

After complete oxidation of either anion by iodine, acidification to ≤pH 2.5 is necessary. The excess of hypoiodite is converted into iodine, which is then extracted by chloroform. The remaining aqueous solution is suitable for the amplification reaction as described above, and the iodine formed is titrated with standard thiosulphate solution or measured spectrophotometrically.[5]

The extraction of iodine was originally done by using four 10-ml aliquots of chloroform and shaking momentarily until the aqueous and organic phases were thoroughly mixed. The blank titration obtained by this procedure was 1.5–2.0 ml of $2 \times 10^{-3}M$ sodium thiosulphate. Increasing the number of extractions and the volume of chloroform gave no improvement. However, with a 1-min shaking at each extraction, four 10-ml aliquots of chloroform gave a blank of 0.5–0.6 ml of $2 \times 10^{-3}M$ thiosulphate. The use of different mineral acids for acidification, such as sulphuric or perchloric acid, led to no significant difference in the blank.

Precision and range of applicability

The coefficients of variation were calculated for eleven measurements of both ions. For 22.5 μg of thiocyanate, the coefficient of variation obtained by the titrimetric method was 0.6%, and that by spectrophotometry was 0.8%. For 44.8 μg of thiosulphate, the coefficient of variation for the titrimetric finish was 0.7%; for 33.6 μg and the spectrophotometric finish, it was 0.9%.

The determination of both anions was essentially at the trace level. The results were quantitative (>98.5% recovery) in the ranges 2.7–90 μg (>98.5% recovery) for thiocyanate and 4.5–90 μg for thiosulphate (Tables 2 and 3).

Interferences

The following cations and anions in 100-fold weight ratio to the ion being determined did not interfere in the determination of 23 μg of thiocyanate: Cd^{2+}, Pb^{2+}, Zn^{2+}, Ca^{2+}, Cr^{3+}, Co^{2+}, Na^{+}, K^{+}, Cl^{-}, Br^{-}, NO_3^{-}, SO_4^{2-}, CO_3^{2-}, ClO_4^{-}. Fe^{3+}, Cu^{2+} and Hg_2^{2+} interfered, as did anions which participated in redox reactions with iodine, such as $S_2O_3^{2-}$, SO_3^{2-}, S^{2-} and AsO_3^{3-}. These anions (and thiocyanate, but, of course, not thiosulphate) also interfered in the determination of 45 μg of thiosulphate, but of the cations tested, only Fe^{3+} and Hg_2^{2+} interfered.

EXPERIMENTAL

Reagents

Potassium thiocyanate. The analytical-reagent grade material, dried under vacuum at 80° for 24 hr, was weighed out (7.557 mg) by microbalance and dissolved in 1000 ml of distilled water. This stock solution was stable over a long period.

Sodium thiosulphate. A 0.1*M* solution prepared from standard ampoules (and stabilized with sodium carbonate), was diluted to $2 \times 10^{-3}M$. This solution is stable for two weeks when kept in the dark. A $2 \times 10^{-4}M$ solution must be prepared daily and was used as the stock solution for investigation of the determination of thiosulphate. All solutions were standardized against the potassium iodate solution.

Potassium iodate. The analytical-reagent grade material, dried at 180° was weighed out (0.2354 g) and dissolved in 1000 ml of distilled water. This stock solution is used for standardizing the thiosulphate solution and for the spectrophotometric calibration curve.

Amplification procedures

Thiocyanate (2.7–90 μg). In a 250-ml separating funnel, mix 10 ml of 10% sodium hydrogen carbonate solution and thiocyanate solution containing not more than 90 μg of thiocyanate. Add 3 drops (0.5 ml) of saturated iodine solution in chloroform and mix well by shaking. After 5 min, add 4 ml of 4*N* sulphuric acid; extract the iodine released, with four 10-ml portions of chloroform, shaking consistently for 1 min at each extraction. Completely transfer the aqueous layer to a 100-ml stoppered-flask; add 1 ml of saturated bromine water and swirl periodically during the next 5 min. Add 3 ml of 90% formic acid to destroy the excess of bromine, and add 1.5 g of potassium iodide (analytical-reagent grade). Titrate the solution with $2 \times 10^{-3}M$ thiosulphate after 5 min (1 ml of $2 \times 10^{-3}M$ $Na_2S_2O_3$ solution ≡ 3.04 μg of SCN^{-}). Alternatively, dilute to a standard volume equivalent to a thiocyanate concentration of 0.1 ppm and measure the absorbance of the solution at 350 nm in a 10-mm glass cell with distilled water in the reference cell;[5] obtain the iodine concentration (and hence

Table 3. Range of applicability of the thiosulphate determinations

Thiosulphate taken, *μg*	4.48	13.4	22.4	33.6	44.8	89.6
Mean recovery, % (titration)*	98.9 (2)	97.2 (2)	102.5 (12)	99.2 (4)	99.8 (11)	99.2 (2)
Mean recovery,† % (spectrophotometry)	97.8	97.8	98.9	99.3	101.0	102.1
Final volume for spectrophotometry, *ml*	50	100	250	250	250	500

* Number of determinations is shown in brackets.

† Mean of 3 results (11 results for 44.8 μg).

the thiocyanate concentration, $SCN^- \equiv 19I_2$) from a calibration graph, obtained as described below.

Apply the whole procedure to a blank of distilled water and subtract the reading from that obtained for the sample reading.

Thiosulphate (4.5–90 μg). Use the procedure described for thiocyanate but add 10 ml of 1*M* sodium hydroxide in place of the sodium hydrogen carbonate solution, and use 7 ml of 4*N* sulphuric acid for the acidification. (Titrimetry: 1 ml of $2 \times 10^{-3}M$ $Na_2S_2O_3 \equiv 4.66$ μg of $S_2O_3^{2-}$; spectrophotometry: $S_2O_3^{2-} \equiv 24I_2$.)

Spectrophotometric calibration procedure. Pipette exactly 2.5, 5, 8, 10, 12, and 15-ml portions of the stock potassium iodate solution into a series of 100-ml volumetric flasks. Dilute with distilled water to about 50 ml. Add 1.5 g of potassium iodide (analytical-reagent grade) to each solution followed by 5 ml of 2*N* sulphuric acid, and make up to 100 ml with distilled water. After 5 min measure the absorbance of each solution at 350 nm in a 10-mm glass cell with distilled water in the reference cell, and prepare a calibration graph of absorbance against iodine concentration (1 mole of $KIO_3 \rightarrow 3$ moles of I_2; 1 ml of standard KIO_3 solution $\equiv 3.3 \times 10^{-6}$ mole of $I_2 \equiv 100$ ml of $3.3 \times 10^{-5}M$ $I_2 \equiv 0.118$ ppm $SCN^- \equiv 0.154$ ppm $S_2O_3^{2-}$ in the final solution measured).

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SYNTHESIS AND EVALUATION OF SOME PYRIDYL-SUBSTITUTED PYRIMIDINES AS COPPER-SPECIFIC CHROMOGENIC REAGENTS

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In quest of new chromogenic reagents of the ferroin type it became of interest to consider 2,4,6-trisubstituted pyrimidines containing combinations of pyridyl, phenyl, and methyl groups. Twelve of the eighteen possible compounds in this group possess the desired ferroin chromophoric group. Nine of these, because of steric considerations, should prove chromogenic only for copper(I). To test this hypothesis, and with a view also to providing new copper-specific chromogenic reagents, the preparation of as many of these nine as possible was undertaken.

Successful synthesis of five of the desired compounds was achieved by the action of an amidine hydrochloride on an unsaturated ketone in the presence of alkali, a procedure previously demonstrated effective in synthesis of 4-phenyl-2,6-bis(2-pyridyl)pyrimidine.[1] Thus acetamidine hydrochloride with pyridylacetophenone[2] yielded 2-meth-

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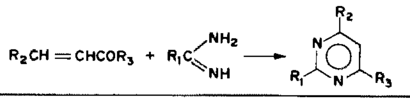

Compound	R_1	R_2	R_3	Yield, %	m.p., °C	Crystn. solvent	Formula	Calculated, %			Found, %		
								C	*H*	*N*	*C*	*H*	*N*
I	CH_3	C_6H_5	2-C_5H_4N	40	90	CH_3OH	$C_{16}H_{13}N_3$	77.7	5.30	17.0	77.5	5.2	17.1
II	CH_3	2-C_5H_4N	2-C_5H_4N	40	138	CH_3OH	$C_{15}H_{12}N_4$	72.6	4.87	22.6	72.3	5.0	22.8
III	C_6H_5	C_6H_5	2-C_5H_4N	56	217	Methyl Cellosolve	$C_{21}H_{15}N_3$	81.3	4.89	13.6	81.5	4.8	13.7
IV	C_6H_5	2-C_5H_4N	2-C_5H_4N	40	283	Methyl Cellosolve	$C_{20}H_{14}N_4$	77.4	4.55	18.1	77.4	4.7	18.3
V	2-C_5H_4N	C_6H_5	C_6H_5	22	158	CH_3OH	$C_{21}H_{15}N_3$	81.5	4.89	13.6	81.7	4.8	13.8

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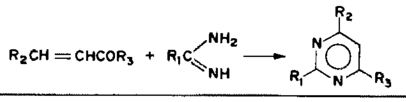

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yl-4-phenyl-6-(2-pyridyl)pyrimidine (**I**) and 2-methyl-4,6-bis(2-pyridyl)pyrimidine (**II**) with pyridalacetylpyridine.[2] From benzamidine hydrochloride and benzalacetylpyridine[2] or pyridalacetophenone, 2,4-diphenyl-6-(2-pyridyl)-pyrimidine (**III**) resulted. From benzamidine and pyridalacetylpyridine, 2-phenyl-4,6-bis(2-pyridyl)pyrimidine (**IV**) was the result. Picolinamidine hydrochloride and benzalacetophenone yielded 2-(2-pyridyl)-4,6-diphenylpyrimidine (**V**).

Attempts to use 3-pentene-2-one, benzalacetone, or crotonophenone in the same general procedure as above to prepare other compounds desired were unsuccessful. Pyridalacetone[3] was unavailable. Further attempts to condense the amidines previously mentioned with various diketones by the method of Pinner[4] or of Haley and Maitland[5] were also unavailing.

The chromogenic reactions of the successfully synthesized compounds have been evaluated with various metal ions, and the results are reported here.

EXPERIMENTAL

Preparation of trisubstituted pyrimidines

A mixture of 0.005 mole of amidine hydrochloride, 0.1 mole of unsaturated ketone, 0.01 mole of potassium hydroxide, and 25 ml of ethanol was heated for 3 hr on a steam-bath. After evaporation of half the alcohol, an equal volume of water was added. The resulting precipitate was filtered off, dried and crystallized from the solvent indicated in Table 1. **I** and **V** gave oils, which were extracted with ether; the ether was then evaporated and the residue crystallized from the solvent indicated. In the preparation of **II**, sodium ethoxide was substituted for potassium hydroxide. Elemental analyses, yields, and melting points are listed in Table 1.

Chelation studies

The procedures, reagents, and standard solutions have been described before.[6] Spectra were recorded with a Cary Model 14 spectrophotometer.

RESULTS AND DISCUSSION

All five of the new compounds yielded coloured complexes with copper(I) but not with any other ion in tests with dilute metal ion solutions. Thus the expectation that these would prove to be specific chromogens for copper(I) proved valid. Such specificity undoubtedly arises because the bulky methyl or phenyl substituents adjacent to the co-ordinating nitrogen atoms in the ligands sterically hinder complete attainment of octahedral (but not of tetrahedral) co-ordination of bidentate ligands. Copper(I) readily accommodates to tetrahedral co-ordination and is the only metal ion to be both fully complexed and to give an intense colour. This type of specificity has been observed previously for numerous examples of similarly substituted ferroin-type compounds.[7]

Compound **III** lacks sufficient solubility in aqueous media to be used as a practical colorimetric reagent. Reliable spectral data could not be obtained for its brown copper(I) chelate, because it proved insoluble in all solvents tested.

The results of studies to determine optimum formation conditions and spectral characteristics of the copper(I) chelates are summarized in Table 2. Two of the compounds, **I** and **II**, exhibit properties attractive for analytical application as copper reagents. Absorbances of their copper(I)-chelate solutions follow Beer's law and are sufficiently high to allow detection of $1.1 \times 10^{-6}M$ copper(I), with a path-length of 1 cm and an absorbance of 0.010. They compare favourably in sensitivity with previously reported copper-specific chromogens.[7,8]

The results are also of interest in providing further guidelines for synthesis of new and perhaps superior reagents. For example, the results for **III**, **IV** and **V** clearly indicate that a phenyl group *ortho* to a ferroin group will exert an adverse influence on the absorptivity of the copper(I) chelate, and reduce the solubility and stability. In the case of **IV** it is observed that its copper(I) chelate dissociates appreciably on moderate dilution with ethanol, an indication of its low stability. For the spectral study of this chelate, the alcohol content of the solutions was kept to a minimum to reduce fading but still provide sufficient solubility for the complex. Under these conditions it was necessary to filter off the excess of **IV**, which precipitated, before spectral measurement of its chelate.

Another interesting feature is that, unlike most copper(I) chelates with ferroin-type ligands, the chelates of **II** and **IV** are only partially extractable into isoamyl alcohol. Furthermore the extracts differed in colour from the aqueous phase. The low extractability and solvent-dependent spectral characteristics of these two copper(I) chelates are believed to be associated with either the unco-ordinated pyridyl or the non-utilized second ferroin group that each of their ligands possesses.

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Table 2. Properties of copper(I) chelates

Ligand	Chelate colour	pH for colour formation Range	Maximum colour	Principal absorption band* Wavelength, *nm*	ϵ, *l.mole*$^{-1}$. *cm*$^{-1}$
I	Orange-brown	3–8	5–7	484	8,700
II	Purple	3–9	3–7	495	8,800
III	Brown (ppte.)	4–8	†	†	†
IV	Violet	3–8	4–7	510	2,800
V	Orange-brown	3–12	6–7	425	5,200

* Chelate solutions prepared with pH 7 buffer and diluted to volume with 1:1 ethanol–water.
† Chelate lacks suitable solubility for reliable measurement.

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3-PHENYL-5-ISOXAZOLON-4-CARBOXYLIC ACID ETHYL ESTER AS A SELECTIVE REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(III)

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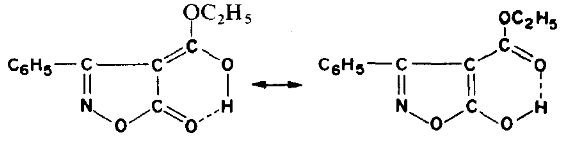
Earlier studies have shown that 3-phenyl-5-isoxazolon-4-carboxylic acid ethyl ester (HIs) (I) is a monoprotic medium strong acid which reacts as a ligand with iron(III), giving three successive complexes.[1] The uncharged species is extractable into methyl isobutyl carbinol (hexol) as a red chelate. The reaction is selective and sensitive. Under suitable conditions, the reagent can be used for the spectrophotometric determination of iron(III).



(I)

EXPERIMENTAL

Reagents

Standard iron(III) solutions. Precipitated iron(III) hydroxide was dissolved in hydrochloric or perchloric acid. The solutions obtained were then standardized gravimetrically.

3-Phenyl-5-isoxazolon-4-carboxylic acid ethyl ester. The reagent was synthesized by the method of Stagno d'Alcontres *et al.*[2] and recrystallized from diethyl ether. A stock solution (0.01*M*) was prepared by dissolving the appropriate amount of the reagent in methyl isobutyl carbinol (hexol).

Buffer solutions. Potassium hydrogen phthalate (0.1*M*) and hydrochloric acid or sodium hydroxide solutions were used to prepare buffer solutions of pH 2.2–5.0.

All other chemicals used were analytical-reagent grade.

Procedure

To a suitable aliquot containing 13.5–135.0 μg of iron, add 10.0 ml of 0.01*M* solution of HIs in hexol, keeping the pH at 2.2–5.0 with a buffer solution. Make the volumes of both phases 10 ml and shake for 5 min. Separate the organic layer and measure its absorbance at 490 nm against a hexol blank. Calculate the iron concentration from a previously prepared calibration curve.

RESULTS AND DISCUSSION

Absorption spectra and reaction conditions

The complex exhibits maximum absorbance at 490 nm where the reagent does not absorb. The colour of the complex in the organic phase is stable.

The absorbance at 490 nm is constant over the pH range 2.2–5.0 for $10^{-2}M$ HIs concentration. For general purposes, full colour development requires a total reagent concentration $\geqslant 1.4[H^+] + 0.003 + 3[Fe(III)]$, as revealed by equilibrium studies.[1] A further excess does not interfere.

The system adheres to Beer's law up to 15.0 ppm of iron. The optimum range for accurate determination, as evaluated from a Ringbom plot, is 1.35–13.5 ppm. The sensitivity of the colour reaction is 0.013 $\mu g/cm^2$ (at 490 nm), with molar absorptivity 4.2×10^3 $l.mole^{-1}.cm^{-1}$.

The precision of the method has been checked by measuring the absorbance of 10 samples, each containing a final concentration of 6.7 ppm of iron. The mean absorbance was 0.500 with standard deviation 0.007.

Composition and instability constants

The values of the partition coefficient (5.5) and dissociation constant (1.4×10^{-2}) of HIs, the formula of the extracted complex, ($FeIs_3$), its partition coefficient (10.5) and formation constant (5.6×10^9) have been obtained by partition methods.[1,3] The formation of higher complexes than the neutral species can be ignored owing to the maintenance of unvarying metal distribution at higher ligand concentration and pH.[3] This is consistent with the chelating properties of the ligand.

Effect of other ions

The effect of various ions was studied at pH 2.5. The general procedure was followed, except that the solutions of foreign ions were added before the reagent solution. The method is selective.

With 6.0 ppm of iron(III), the following ions present in the amounts (in ppm) shown in parentheses did not cause a deviation of more than ±2% in absorbance from that expected: borate (250), nitrate (3000), nitrite (2000), phosphate (1000), arsenate (4000), sulphate (5000), chloride (3000), bromide (2000), thiocyanate (2000), acetate (4000), tartrate (5000), citrate (4000), cyanide (300), fluoride (100), oxalate (200), Ag (500), Tl(I) (3000), Mg (1000), Ca (2000), Sr (4000), Pb (1500), Mn(II) (2500), Fe(II) (2500), Cd (5000),

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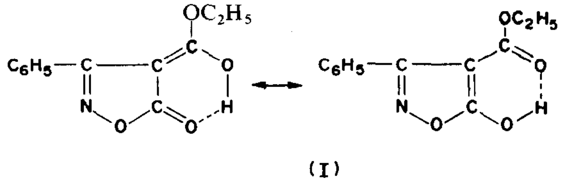

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The precision of the method has been checked by measuring the absorbance of 10 samples, each containing a final concentration of 6.7 ppm of iron. The mean absorbance was 0.500 with standard deviation 0.007.

Composition and instability constants

The values of the partition coefficient (5.5) and dissociation constant (1.4×10^{-2}) of HIs, the formula of the extracted complex, ($FeIs_3$), its partition coefficient (10.5) and formation constant (5.6×10^9) have been obtained by partition methods.[1,3] The formation of higher complexes than the neutral species can be ignored owing to the maintenance of unvarying metal distribution at higher ligand concentration and pH.[3] This is consistent with the chelating properties of the ligand.

Effect of other ions

The effect of various ions was studied at pH 2.5. The general procedure was followed, except that the solutions of foreign ions were added before the reagent solution. The method is selective.

With 6.0 ppm of iron(III), the following ions present in the amounts (in ppm) shown in parentheses did not cause a deviation of more than ±2% in absorbance from that expected: borate (250), nitrate (3000), nitrite (2000), phosphate (1000), arsenate (4000), sulphate (5000), chloride (3000), bromide (2000), thiocyanate (2000), acetate (4000), tartrate (5000), citrate (4000), cyanide (300), fluoride (100), oxalate (200), Ag (500), Tl(I) (3000), Mg (1000), Ca (2000), Sr (4000), Pb (1500), Mn(II) (2500), Fe(II) (2500), Cd (5000), Hg(II) (4000), Al (2000), As(III) (2000), Bi (200), Cr(III) (2000), La (400), Ti(IV) (50), Th (2000), V(V) (1000), Mo(VI) (200), W(VI) (300). Barium (5000), cobalt(II) (800), nickel (300), copper(II) (60) and zinc(II) (900) react with HIs, giving slightly soluble complexes, which do not give rise to any appreciable colour in the hexol phase. Palladium(II) (100) and uranium(VI) (500) give extractable yellow complexes with negligible absorption at 490 nm. Reducing agents for Fe(III) should be absent.

When required, a better selectivity can often be achieved at lower pH (1.5) and/or higher reagent concentration ($4 \times 10^{-2}M$).

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Summary—The red complex developed on interaction of iron(III) with 3-phenyl-5-isoxazolon-4-carboxylic acid ethyl ester in the pH range 2–5 can be extracted into methyl isobutyl carbinol. Based on this, a selective and rapid method for the spectrophotometric determination of traces of iron has been developed. The complex has an absorption maximum at 490 nm. Beer's law is followed up to 15.0 ppm of iron. The molar absorptivity is 4.2×10^3 l.mole^{-1}. cm^{-1}. None of the common ions interferes in the determination of iron, even though present in large excess.

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NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF PHENOLIC HORMONES

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(*Received 3 October* 1975. *Accepted 8 December* 1975)

Few methods are available for spectrophotometric determination of phenolic hormones (oestrogens and catecholamines); most of them are neither selective nor specific. Reactions with concentrated sulphuric acid alone[1] and in combination with phenolic compounds (the Kober reaction)[2] have been reported for the determination of oestrogens and many other steroid hormones having either an —OH or a $>C{=}O$ group or both. The Kober reaction, combined with the Ittrich extraction of the fluorescent colour complex, with an organic solvent containing a solution mediator, has been widely used for both spectrophotometric[3] and fluorimetric[4] estimation of oestrogens. However, the colour and fluorescence developed by these reactions depend on the acid concentration, heating time, presence of oxidant, type of solvent and excitation wavelength.

Steroids containing the $—CH_2CO—$ group are determined by reaction with *m*-dinitrobenzene (the Zimmermann reaction).[5] This reaction was satisfactorily applied to the determination of oestrone.[6] Antimony trichloride[7] and hydrazine[8] have been also used for the determination of some oestrogenic hormones containing the carbonyl function (*e.g.*, oestrone and equilenine) but progestanes and androgens react similarly. Reactions with heteropoly acids[9,10] and iodic acid[11] have been utilized for the determination of oestrogens[9] and catecholamines,[10,11] but none of these reactions is free from interferences by other non-phenolic hormones.

However, selective reactions for the determination of oestrogens and catecholamines, by virtue of their phenolic character, have been advocated. These are based on coupling reactions of oestrogens[12] and catecholamines[13] with diazotized amines or condensation of oestrogens with phthalic anhydride[14] under suitable reaction conditions. Reaction with ferric chloride in presence of air has been reported as fairly specific for adrenaline,[15] and the reaction with iodine[16] allows the estimation of noradrenaline in presence of adrenaline. The accuracy of these methods depends on critical adjustment of the experimental conditions.

The present paper reports a new simple method for the spectrophotometric determination of oestrogens and catecholamines by reaction with nitric acid followed by treatment with alkali. The effect of reaction temperature, time, solvent, and alkali concentration have been investigated and the optimum experimental conditions for successful application of this reaction to the determination of oestrone, oestradiol, ethinyloestradiol, adrenaline and noradrenaline are described. The reaction is specific and selective for phenolic oestrogens with regard to other steroid hormones of the progestane and androgen classes.

EXPERIMENTAL

Reagents

All the reagents used were of analytical-reagent grade unless otherwise specified. Stock solutions of oestrone, oestradiol, ethinyloestradiol (Nutritional Biochemical Corporation, U.S.A.), adrenaline and noradrenaline (B.D.H.) were prepared by dissolving 3 mg of each in 10 ml of ethyl alcohol. The purity of the hormone samples was not less than 99%.

Procedure

Construct a standard calibration curve for each hormone by transferring 0.20, 0.40, 0.50, 0.70, 0.90, 1.00 and 1.20 ml portions of the stock solutions to 20-ml graduated tubes. Evaporate to complete dryness on a boiling water-bath. Cool, add 1.0 ml of 16*M* nitric acid and place the tubes for 10 min in a water-bath controlled at 50 ± 5° for oestrogens (oestrone, oestradiol, ethinyloestradiol) or

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Hg(II) (4000), Al (2000), As(III) (2000), Bi (200), Cr(III) (2000), La (400), Ti(IV) (50), Th (2000), V(V) (1000), Mo(VI) (200), W(VI) (300). Barium (5000), cobalt(II) (800), nickel (300), copper(II) (60) and zinc(II) (900) react with HIs, giving slightly soluble complexes, which do not give rise to any appreciable colour in the hexol phase. Palladium(II) (100) and uranium(VI) (500) give extractable yellow complexes with negligible absorption at 490 nm. Reducing agents for Fe(III) should be absent.

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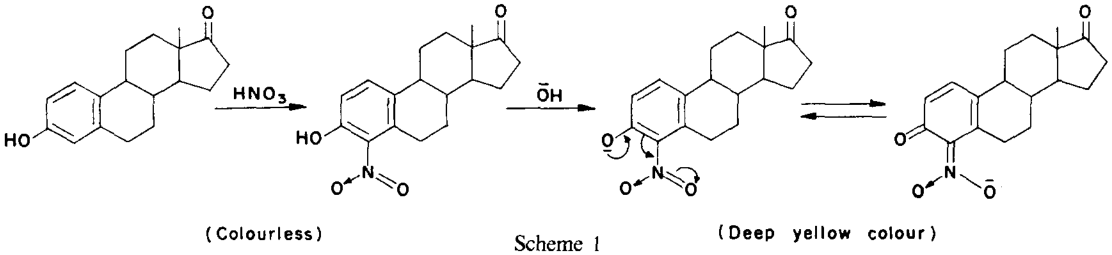
100° for catecholamines (adrenaline, noradrenaline). The heating time should be strictly adhered to. Cool, add 4 ml of 5*M* sodium hydroxide portionwise and make up to 10.0 ml with ethyl alcohol. Mix and allow to stand for 5 min at room temperature. Measure the absorbance, in 10.0-mm cuvettes, at 430, 385, 430, 380, 380 nm for oestrone, oestradiol, ethinyloestradiol, adrenaline, noradrenaline respectively, against a blank prepared under identical conditions. Draw a graph of the absorbance against hormone concentration. Follow the same procedure with samples of unknown concentrations.

RESULTS AND DISCUSSION

Nature of the reaction

To investigate the nature of the reaction, oestrone was nitrated at 50° and the reaction product was isolated, recrystallized from methanol and identified. The infrared spectrum of the product showed strong absorption peaks at 1350 and 1540 cm^{-1} due to the symmetrical and asymmetrical $—NO_2$ stretch. The absorption band observed at 810 cm^{-1} is probably due to out-of-plane deformations of two adjacent hydrogen atoms on an aromatic ring, whereas



Scheme 1

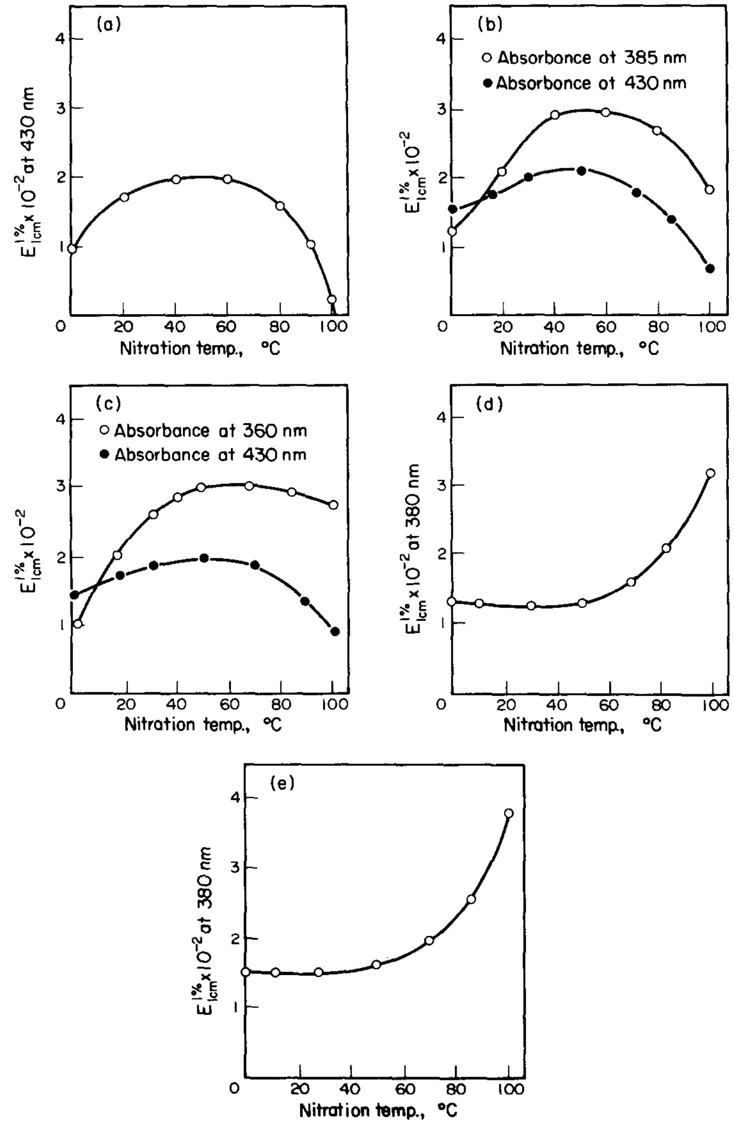


Fig. 1. Effect of nitration temperature on the absorbance of the nitration products of: (a) oestrone, (b) oestradiol, (c) ethinyloestradiol, (d) adrenaline and (e) noradrenaline, in sodium hydroxide solution.

the broad absorption band at 3100–3700 cm^{-1} belongs to the bonded —OH group.[17] Hence oestrone undergoes an electrophilic substitution reaction in position 4 under the present reaction conditions. The phenolic group, by virtue of its $+M$ effect, and the —CH_2— group, by its $+I$ effect, activate the 4-position of the aromatic nucleus. β-Naphthol is known to undergo electrophilic substitution in the α-position, which is reactive as is position 4 in oestrogens.[18] In addition, the absorption spectrum of the nitration product of oestrone, in sodium hydroxide medium, was compared with the spectra of *o*-, *m*-, and *p*-nitrophenols. *o*-Nitrophenol displays the same spectrum. Most probably, all other phenolic hormones undergo reactions of similar nature.

The formation of coloured species from the nitration products of oestrone in alkaline media is ascribed to the ability of the *o*-nitrophenate ion to tautomerize to yield the quinonoidal nitronic acid salt.[19] The formation of the aci-form is accompanied by an increase and extension of the conjugated system. Consequently, the reaction of oestrone may be represented by Scheme 1.

It is well known that the reaction of nitrophenols with alkalis is usually used for their quantitative determination.[20]

Effect of nitration temperature and time

Reaction of phenolic hormones with 16*M* nitric acid for 10 min was investigated at temperatures ranging from 0 to 100°. Oestrone, oestradiol and ethinyloestradiol show maximum and constant absorption at 430, 385 and 430 nm, respectively, on nitration at 40–60°C. With nitration at above 70°, a gradual decrease of the absorbance values is observed, which is probably due to oxidative side-reactions. However, nitration at 100° is recommended for adrenaline and noradrenaline (Fig. 1).

The effect of nitration time on the absorbance of the products was also investigated by carrying out the nitration reaction for 5, 10, 15, 20 and 30 min at 50° for oestrogens and at 100° with catecholamines. A heating time of 10 min is considered optimal for all the hormones under investigation (Fig. 2), but must be strictly adhered to.

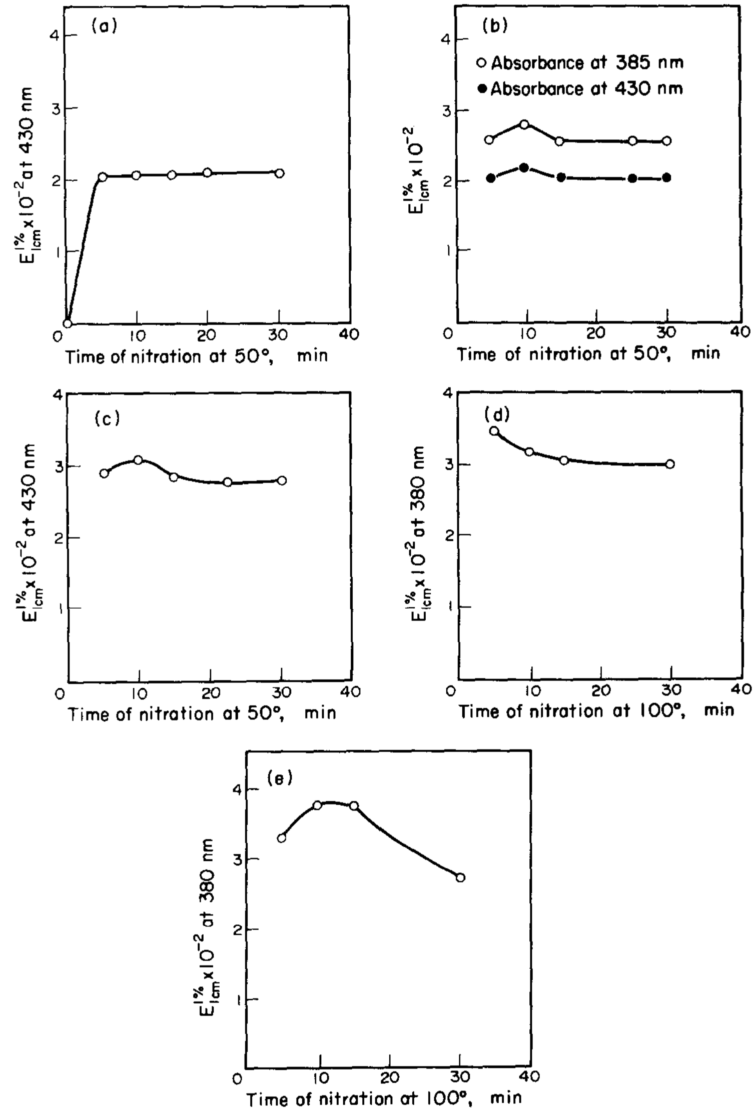


Fig. 2. Effect of nitration time on the absorbance of the nitration products of: (a) oestrone, (b) oestradiol, (c) ethinyloestradiol, (d) adrenaline and (e) noradrenaline, in sodium hydroxide solution.

Effect of solvent and alkali concentration

Since 1 ml of 16*M* nitric acid is used in the nitration reaction, 0.7 g of sodium hydroxide is needed to render the solution alkaline. Higher amounts of alkali (up to 1.2 g) do not affect the absorbance values. The intensity of the coloured nitration products after addition of sodium hydroxide was tested in various water-miscible organic solvents (*e.g.*, ethyl alcohol, acetone, dimethylformamide and dioxan). A 50% v/v concentration of ethyl alcohol proved to be the best, since there was no precipitation but maximum absorbance.

Determination of phenolic hormones

Nitration of oestrone, oestradiol, ethinyloestradiol, adrenaline and noradrenaline under the present conditions, followed by treatment with alkali gives products which display absorption maxima at 430 nm ($E^{1\%}_{1\,\mathrm{cm}}$ 187), 385 nm ($E^{1\%}_{1\,\mathrm{cm}}$ 263), 430 nm ($E^{1\%}_{1\,\mathrm{cm}}$ 183), 380 nm ($E^{1\%}_{1\,\mathrm{cm}}$ 284) and 380 nm ($E^{1\%}_{1\,\mathrm{cm}}$ 353), respectively. Beer's law is obeyed at these maxima over the range 0–500 μg of hormone in the 10-ml volume of the final solution. In a series of analyses with hormone concentrations of 10–50 μg/ml, the results obtained showed an average recovery of 98.9% and a relative standard deviation of ±0.5%.

Advantages and limitations

The present method offers two main advantages over the Kober–Ittrich reaction,[2–4] which is widely used for the analysis of oestrogens, namely simplicity and selectivity. The selectivity towards other non-phenolic steroid hormones (*e.g.*, testosterone, progesterone and androstanalone) was tested. The accuracy of the results is not affected by the presence of these steroids in up to 1000-fold molar ratio to the oestrogenic hormones, since they do not respond to the nitration reaction. On the other hand, these steroids develop intense colours in concentrated sulphuric acid solution[1] and consequently they interfere when the Kober–Ittrich reagent (hydroquinone in concentrated sulphuric acid) is used.

The present method gives results at least as accurate as those obtained by the Kober–Ittrich procedure, probably because the latter reaction is susceptible to the effect of sunlight, solvent contamination, and concentration of sulphuric acid.[2–4] These experimental variables require careful adjustment and precautions.

On the other hand, the method is less sensitive than the Kober–Ittrich reaction.[21] The least amount that can be determined by the nitration reaction with acceptable accuracy is 10 μg/ml in the final solution (*i.e.*, 100 μg of the hormone). Although a lower concentration (2 μg/ml) can be satisfactorily determined by using a 5-cm cell, the sensitivity is still below that of the Kober–Ittrich reaction.

Comparison with the methods based on the red colour developed on oxidation of catecholamines[22] shows that the present method compares favourably with many of them in both sensitivity and selectivity and is simpler than most.

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Summary—A new simple, selective and accurate spectrophotometric method is described for the determination of mono- and dihydric phenolic hormones (oestrogens and catecholamines) by nitration at 50° and 100°, respectively, for 10 min, followed by treatment with alkali. Coloured products with absorption maxima at 430, 385, 430, 380 and 380 nm, linearly proportional to the concentration of oestrone, oestradiol, ethinyloestradiol, adrenaline and noradrenaline, respectively, are obtained. Information is presented on the effect of nitration time, temperature, solvents, and alkali concentration. The method is satisfactorily applied to the determination of these hormones in the range 10–50 μg/ml in the final solution, of volume 10 ml. The relative standard deviation is ± 0.5% and no interferences are caused by non-phenolic hormones.

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EXTRACTION AND DIRECT SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH ETHYL-α-ISONITROSOACETOACETATE

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Beamish[1] has reviewed the reagents used up to 1965 for the spectrophotometric determination of ruthenium. Of these, thiourea,[2] dithio-oxamide,[3] *p*-nitrosodimethylaniline[4] and 1,10-phenanthroline[5] are the best. However, in the thiourea method Fe(III), Co(II), Cr(III), Os(IV), Ni(II), Cu(II) and Pd(II) interfere and the sensitivity is low. Dithio-oxamide is more sensitive than thiourea, but other platinum metals interfere. In the *p*-nitrosodimethylaniline method, exact adjustment of pH is required, the absorbance due to the reagent is appreciable, and the colour development is not complete even after heating for 50 min. Further, the tolerance limit for other platinum metals has not been studied. With 1,10-phenanthroline, the development of colour is not complete even after 2 hr and the precision is low. The last two methods also require distillation of ruthenium tetroxide. The present paper describes determination of ruthenium with ethyl-α-isonitrosoacetoacetate (HEINA), which has already been used for Pd(II).[6]

EXPERIMENTAL

Reagents

Ethyl-α- isonitrosoacetoacetate was prepared as reported earlier.[6] Analytical-grade chemicals and reagents were used. Stock ruthenium solution was prepared by dissolving 1 g of pure ruthenium(III) chloride in 20 ml of 10*M* hydrochloric acid by heating on a water-bath and diluting to 100 ml with water. Ruthenium in the stock solution was estimated as ruthenium metal.[1] The solution was further diluted as required. Radioisotopes were obtained from the Isotope Division, Bhabha Atomic Research Centre, Bombay, India.

Procedures

Extraction. To an aliquot of ruthenium chloride solution (containing 1 mg of ruthenium), 2.0 ml of 5% solution of HEINA in water were added and the pH was adjusted to the desired value with hydrochloric acid or sodium hydroxide solution. The mixture was heated on a boiling water-bath for 15 min, cooled and treated with 5 ml of 10*M* lithium chloride, then equilibrated for 2 min with 10 ml of benzyl alcohol. The phases were separated and ruthenium estimated in each by the rubeanic acid method.[7] The pH of the equilibrated aqueous phase was measured. The extraction coefficient was calculated. In the study of the extraction in the presence of other ions, the ion of interest was added before the reagent. Radioactive tracers, if available, were used to follow the extraction of other ions. The value for the separation factor, *S*, defined as

$$S = \frac{\text{Extraction coefficient of ruthenium}}{\text{Extraction coefficient of the element of interest}},$$

was calculated.

Spectrophotometric determination. To a solution containing 1–180 μg of ruthenium, 2 ml of 5% solution of HEINA in water were added and the pH was adjusted to 5 with sodium acetate–acetic acid buffer (total volume 5 ml). The solution was heated for 15 min, cooled, treated with 5 ml of 10*M* lithium chloride and equilibrated (2 min each time) with two 5-ml portions of benzyl alcohol. The organic extracts were collected in a 10-ml measuring flask and made up to the mark with benzyl alcohol, if necessary. The absorbance of the solution was measured at 470 nm, against benzyl alcohol. The amount of ruthenium was determined from a calibration curve prepared by the same procedure. The calibration plot was linear over the range 1–180 μg of ruthenium per 10 ml of extract.

RESULTS AND DISCUSSION

Extraction

The extraction was studied over wide range of experimental conditions. The extraction coefficient (Table 1) for ruthenium varies with the pH of the solution being maximal over the pH range 4–6. The extraction is improved considerably if the aqueous solution is heated to boiling for at least 15 min before the equilibration with benzyl alcohol (Fig. 1), and is quantitative at pH 5 from 5*M* lithium chloride (heated for 15 min). Benzyl alcohol is the most satisfactory solvent (Table 1). The extraction is not significantly affected by phosphate, pyrophosphate, chloride, bromide, iodide, chlorate, nitrate, sulphate, persulphate, sulphite, oxalate, tartrate, citrate, thiosulphate, thiocyanate and EDTA. Only cyanide, iodate and bromate suppress the extraction. The interference by iodate and bromate can be removed by adding iodide and heating on a water-bath for 15 min.

The separation factors given in Table 2 indicate that ruthenium can be efficiently separated from a number of elements, but Pd(II), Rh(III) and Pt(IV) are extracted along with the ruthenium into benzyl alcohol under the conditions used. However, ruthenium can be

Table 1. Extraction coefficients of ruthenium as a function of pH of the aqueous phase

pH	Solvent	Extraction coefficient	% Extraction
1.0	Benzyl alcohol	9.0	90.0
3.0	,,	11.0	91.7
3.5	,,	19.0	95.0
4.0	,,	101	99.0
4.2	,,	148	99.3
5.0	,,	196	99.5
6.0	,,	200	99.5
7.2	,,	24.5	96.1
9.7	,,	7.5	85.2
11.5	,,	2.6	72.2
5.0	Isobutyl methyl ketone	80	98.8
5.0	Butanol	21.0	95.3
5.0	Octanol	21.0	95.3
5.0	Isoamyl alcohol	20.0	95.2
5.0	Ethyl acetate	15.0	93.8
5.0	Amyl acetate	14.1	93.3
5.0	Ethyl methyl ketone	11.0	91.7
5.0	Chloroform	8.2	89.1
5.0	Carbon tetrachloride	5.9	84.1
5.0	Benzene	2.8	73.7

Table 2. Separation factors for different ions in the extraction of Ru–HEINA complex into benzyl alcohol from 5*M* LiCl solution at pH 5.0 Ruthenium taken, 1.0 mg; 10 ml of each phase

Separation factor	Ions
$>10^6$	Fe(III),* Sn(II),† Ni, Sb(III)†
$>10^5$	Sc, Ca, Mn(II), PO_4^{3-}, Na, Cu(II),* La,* Re(VII), Cr(III),* W(VI), Ce(III), Zn, Zr, Cs, Cd, Mo(VI), K, Pt(IV),§
$>10^4$	Tl(I), Pt(IV),‡
$>10^3$	Co(II), Ag, Ir(IV).
$>10^2$	Pt(VI).
>1	Rh(III), Pd(II).

* In the presence of citrate.
† In the presence of tartrate.
§ Solvent used CCl_4.
‡ Solvent used $CHCl_3$.

separated from rhodium and platinum by extraction into carbon tetrachloride. The recovery of ruthenium is more than 99% if the aqueous phase at pH 5 is equilibrated thrice with equal volumes of carbon tetrachloride. Separation from palladium can be achieved by extracting palladium into chloroform containing 1% HEINA, from 1*M* acetic acid medium; the loss of ruthenium from the aqueous phase is negligible.

Spectrophotometric determination

The absorption spectrum of ruthenium–HEINA in benzyl alcohol shows an intense peak at 470 nm. The absorbance due to the reagent is negligible at this wavelength (Fig. 2). Beer's law is obeyed over the range 0.1–18 µg of ruthenium per ml. The molar absorptivity is 1.05×10^4 $l.mole^{-1}.cm^{-1}$. The absorbance shows no significant change in 5 days.

An HEINA concentration corresponding to HEINA: Ru = 40 is sufficient for the extraction and colour development of 100 µg of ruthenium. However, in the presence of 10 mg of other ions which interact with HEINA, it is necessary to use 100 mg of HEINA for the extraction of 100 µg of ruthenium.

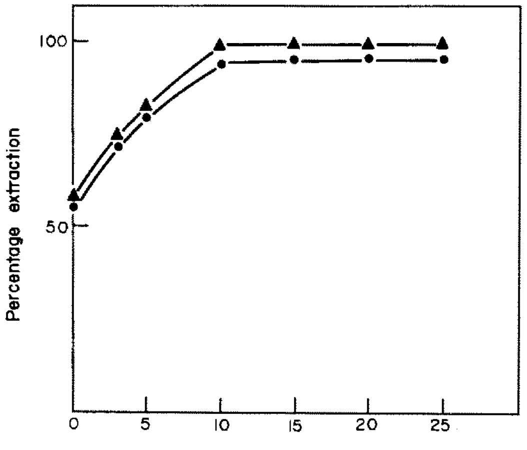

Fig. 1. Extraction of ruthenium as a function of heating time. In the absence of LiCl (●) and in the presence of 5*M* LiCl (▲).

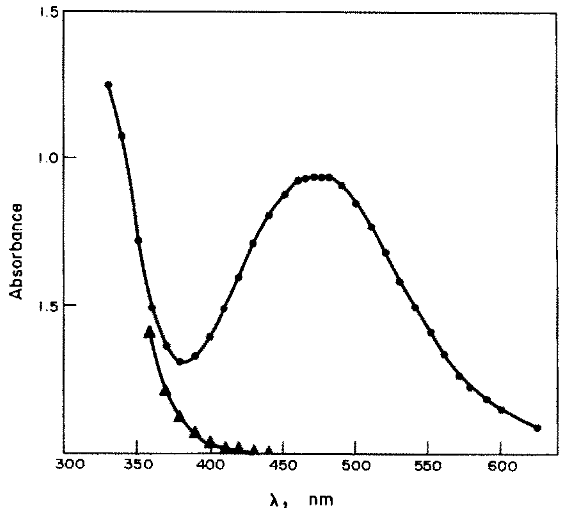

Fig. 2. Absorption spectra of Ru–HEINA complex (●) and HEINA (▲) in benzyl alcohol. Ru = $0.84 \times 10^{-4}M$, HEINA = $620 \times 10^{-4}M$.

Up to 10 mg of the following ions will not interfere in the spectrophotometric determination of ruthenium: Mn(II), Cu(II), Zn, Cd, U(VI), Mg, Ca, Ba, V(IV), Pb, Mo(VI), W(VI), Th, Be, Hg(II), Ag, Te(VI), and the anions mentioned earlier. Up to 5 mg of Os(IV), or 1 mg of each of Au(III), Se(IV) and Se(VI) will have no significant effect on the colour in the benzyl alcohol extract. The interference by the iodate and bromate can be removed as already described. Fe(II), Fe(III) and Cr(III) do not interfere in the presence of tartrate. Up to 100 µg of Pd(II), Pt(IV), Rh(III), Ir(IV) and 500 µg of Co(II) can be tolerated if the absorbance is measured at 540 nm. At this wavelength 2 µg of ruthenium in 10 ml of benzyl alcohol gives an absorbance of 0.014.

The precision and accuracy of the proposed method were tested by analysing solutions containing known amounts of ruthenium. The average of 10 determinations of 5.0 µg in 10 ml of solution is 5.0 µg and the standard deviation is 0.1 µg.

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Summary—Ruthenium is extracted by benzyl alcohol from 5*M* LiCl containing ethyl-α-isonitrosoacetoacetate at pH 4–6. The extraction is quantitative if the solution is heated to boiling for 15 min. The benzyl alcohol extract shows maximum absorbance at 470 nm and at this wavelength Beer's law is obeyed over the ruthenium concentration range 0.1–1.8 µg/ml. The error is 4% for 0.5 µg/ml.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH DIETHAZINE HYDROCHLORIDE

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There are few satisfactory methods for spectrophotometric determination of ruthenium.[1] Most use an almost neutral reaction medium and require either heating or a long time for the colour development. During investigation[2] of its reaction with palladium(II), diethazine hydrochloride (DH) was found to give a red colour with ruthenium(III) instantaneously in the presence of sulphuric or hydrochloric acid. This reaction is now utilized for rapid spectrophotometric determination of ruthenium(III).

EXPERIMENTAL

Reagents

DH solution. Prepared in doubly distilled water, stored in an amber-coloured bottle in a refrigerator, and standardized.[3]

Ruthenium solution. Ruthenium(III) chloride (~1 g) dissolved in 500 ml of doubly distilled water containing sufficient hydrochloric acid to give a concentration of 1*M*. Standardized gravimetrically[4] by precipitating the hydrous oxide, igniting in air, reducing in hydrogen, and cooling in an atmosphere of carbon dioxide. More dilute solutions were prepared as needed.

All other reagents were analytical grade and were used without further purification.

Procedure

Transfer an aliquot of sample solution, containing 25–260 μg of ruthenium, to a 25-ml volumetric flask. Add sufficient sulphuric acid for its final concentration to be 1.5*M*. Add 5 ml of 0.2% DH solution. Dilute to volume with doubly distilled water. Measure the absorbance at 515 nm *vs.* a reagent blank. Prepare a calibration curve in the same way.

RESULTS AND DISCUSSION

The complex gives maximum absorption at 515 nm, where neither the reagent nor ruthenium(III) has significant absorption. A Job plot and the molar-ratio method both indicate a 1:1 complex. Ion-exchange studies show the complex is cationic. When formed in hydrochloric acid the complex shows higher sensitivity but lower stability with time and a narrower Beer's law range than when prepared in sulphuric acid medium. Buffering does not further stabilize the complex. The absorbance is unchanged when the sulphuric acid concentration is varied between 0.1 and 2.2*M*. At least a tenfold excess of reagent is needed for completeness of reaction, so 5 ml of 0.2% solution is adequate for the range covered. The colour is stable for about 40 min in sulphuric acid medium but only 10 min in hydrochloric acid. The absorbance is not affected by temperature in the range 5–70°. The order of addition of reagents is not critical.

The complex obeys Beer's law over the range 1.0–10.4 ppm of ruthenium. The optimum range (Ringbom plot[5,6]) is 2–9 ppm. The molar absorptivity is 5.35×10^3 $\text{l.mole}^{-1}.\text{cm}^{-1}$ and the sensitivity is 0.019 $\mu g/cm^2$ for an absorbance of 0.001. The absorbance of six solutions containing 4 ppm ruthenium had a maximum relative deviation of 1.5% and an average relative deviation of 0.45%.

The following amounts (μg/ml) of foreign ions were found to give less than 2% error in the determination of 4 ppm of ruthenium: UO_2(II) 1200; Ni(II) 1000; Cu(II) 200; Co(II) 25; Ir(III) 8; Pt(IV) 6; Rh(III) 6; phosphate 2600; sulphate 2500; fluoride 2500; acetate 2400; chloride 2200; oxalate 1800; nitrate 1200; EDTA 1000; bromide 700; iodide 10. Thiosulphate, Os(VIII), Pd(II), Au(III), Ag(I), Ce(IV), Fe(III) and V(V) interfere seriously.

The sensitivity is higher than that with thiourea.[4] *p*-Nitrosodimethylaniline[7] is more sensitive than the new reagent but the permissible acidity range is narrow and heating is required. The major advantage of DH is the rapidity of the reaction at room temperature. Uranium, which is frequently associated with ruthenium, is tolerated up to 1200 ppm, which is another major advantage.

The fuel for the initial core loading of the Experimental Breeder Reactor II is an alloy of 95% uranium, 2.5% molybdenum, 2% ruthenium and smaller amounts of zirconium, palladium and rhodium. Synthetic mixtures containing the metals corresponding to this alloy were prepared and the ruthenium content was determined. The results are given in Table 1.

Table 1. Determination of ruthenium in synthetic mixtures

Composition						
Ru, *ppm*	U, *ppm*	Mo, *ppm*	Zr, *ppm*	Pd, *ppm*	Rh, *ppm*	Ru found, *ppm*
0.40	19	0.5	0.01	0.01	0.01	0.40
0.80	38	1.0	0.02	0.02	0.02	0.80
1.20	57	1.5	0.03	0.03	0.03	1.19
1.60	76	2.0	0.04	0.04	0.04	1.42
2.00	95	2.5	0.05	0.05	0.05	1.97

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Summary—Diethazine hydrochloride reacts with ruthenium(III) instantaneously at high acidity (sulphuric or hydrochloric acid) to form a red 1:1 complex with absorbance maximum at 515 nm. A tenfold molar excess of reagent is necessary for complete complexation. Beer's law is obeyed for 1.0–10.4 ppm of ruthenium(III), with optimum concentration range 2–9 ppm. The molar absorptivity is 5.35×10^3 $\text{l.mol}^{-1}.\text{cm}^{-1}$.

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HYDROGEN PEROXIDE DETERMINATION WITH LUMINOL AND A NEW CATALYST

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Luminol is 3-aminophthalic acid hydrazide or 5-amino-2,3-dihydro-1,4-phthalazinedione. This compound has been known for a long time.[1] and recommended for detection of blood and hydrogen peroxide.[2–5] In alkaline solution at about pH 12.5 it exhibits an intense blue luminescence with hydrogen peroxide, but only in the presence of a suitable catalyst. Haemoglobin and related substances, like haemin or blood, have been used, and various metal ions[6] or metal complexes.[7] Potassium ferricyanide causes strong luminescence even in the absence of peroxide. Some other compounds (hypochlorite, ozone, sulphite, chlorine, carbon dioxide) produce weak or short-lasting luminescence which must be taken into account if less than 0.0005% H_2O_2 is to be determined. Some other compounds destroy this luminescence in an unknown manner, but in water analysis only hypochlorite need be removed (by about 0.1 g of urea or ammonium chloride). Luminescence due to hypochlorite or ozone appears even in the absence of the catalyst and vanishes during one minute. Calcium and magnesium in concentration higher than 100 mg of the oxide per litre may be masked by a stoichiometric amount of EDTA (in large excess EDTA diminishes the luminescence intensity).

Hydrogen peroxide is formed from dissolved oxygen in water by various forms of radiation, *e.g.*, sound, radioactivity, ultraviolet and solar rays and by static or magnetic and bioelectric agents,[7–9] so a method for its determination in minute amounts is needed. Although haemoglobin as catalyst has been improved by mixing it with Cu-triethanolamine complex, [5,10] its use is inconvenient. It is now found that the cobalt(III)-triethanolamine complex reacts in the same way and gives the same intensity as haemoglobin.

EXPERIMENTAL

Reagents

Luminol solution, 0.05% in 5% sodium hydroxide solution. Stock 0.3% and 0.03% hydrogen peroxide solutions were prepared from 30% peroxide and standardized by permanganate titration.

A solution of the catalyst was prepared by dissolving 0.5 g of cobaltous nitrate and 2.5 ml of triethanolamine in about 50 ml of water, leaving the solution open to the air and occasionally stirring it. After 3–4 hr this solution was heated to about 80° (to destroy some traces of hydrogen peroxide formed by auto-oxidation), cooled and diluted with water to 100 ml.

Apparatus

Luminescence intensity was evaluated with a transistorized amplifier (silicon transistors) and a CdS photoresistor, according to the scheme in Fig. 1. An ammeter with two sensitivity ranges was used. Cells of 100 or 150 ml capacity can be used. Before measurement the zero is set with resistor R_1.

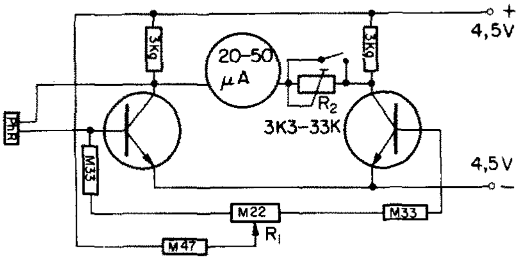

Fig. 1. Transistorized amplifier for luminosity measurement. PhR photoresistor; R_1 zero setting; R_2 sensitivity range.

Procedure

To 100–140 ml of water add 5 ml of 0.05% luminol solution and enough standard peroxide solution to give a final concentration of 0.0002–0.005% H_2O_2 and dilute accurately with water to 150 ml. Then add 5–8 drops (or 0.3 ml) of Co–TEA solution, mix well, place the cuvette in the dark chamber and measure the luminescence intensity at exactly the same time after mixing for all samples (10 or 15 sec).

The procedure for samples is the same, but with 140 ml of test water and no peroxide. A blank solution measurement is necessary. A calibration curve is shown in Fig. 2. Because the luminescence intensity decreases rapidly (by 20–30% in 30 sec), the measurement must be done at a fixed time after the solution is mixed and this time should be as short as possible. Alternatively the decay curve may be scanned (Fig. 3). For hydrogen peroxide levels below 0.0001% a photomultiplier with suitable measurement devices must be used. Freshly prepared luminol solution is not suitable, because the enol–keto equilibrium must be reached, which occurs after about 48 hr.

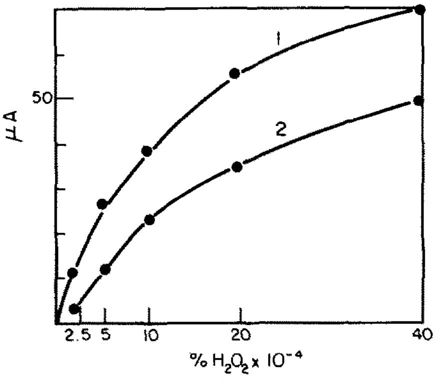

Fig. 2. Calibration curve for 0.0002–0.004% H_2O_2 in 150 ml final volume. Curve 1, luminosity after 5 secs. curve 2, luminosity after 60 sec. when catalyst has been added and mixed.

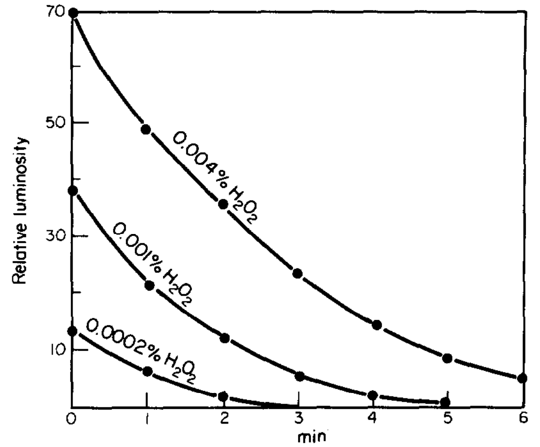

Fig. 3. Luminosity decay 10 sec after reagent mixing for three H_2O_2 concentrations, pH 12.5, temperature 18°.

RESULTS AND DISCUSSION

It was found that varying the pH between 11 and 13, the amount of luminol solution between 3 and 10 ml and of the catalyst solution between 4 and 10 drops (0.2–0.5 ml) has little or no effect on the luminescence intensity. Above pH 13 and below pH 10 the intensity decreases rapidly. The luminescence is approximately of the same intensity and duration as obtained by using haemoglobin.

Interferences and practical use

There are many positive and negative influences on luminol luminescence and further investigation is necessary. In most cases hydrogen peroxide may be detected or determined with good reproducibility, because its solution in water does not contain interfering compounds. Irradiated or activated water may also contain radicals such as $\cdot HO_2$, which can react with luminol, but our knowledge of such radicals is still poor. By use of the luminol reaction hydrogen peroxide may also easily be detected in diethyl ether.

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Summary—The Co(III)–triethanolamine complex is recommended as catalyst in the chemiluminescence determination of hydrogen peroxide with luminol.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) AND ITS APPLICATION TO VANADIUM STEELS CONTAINING CHROMIUM, MOLYBDENUM, TUNGSTEN AND MANGANESE

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(*Received* 20 *August* 1975. *Accepted* 17 *December* 1975)

N-Substituted hydroxylamines have long been regarded as group reagents for vanadium(V), forming coloured chelates with it. Because of their greater aromaticity, diaryl hydroxylamines, in general, produce greater intensity of colour. The nature and position of the substituents can also improve the selectivity.

Ever since the introduction of BPHA (*N*-benzoylphenylhydroxylamine) by Shome[1] as a reagent for vanadium, several of its analogues have been similarly used but none is entirely free from interference, expecially from the elements used to make alloy steels.

We have been unable to obtain satisfactory results with the *N*-benzoyl-*o*-tolylhydroxylamine method[2,3] or with the *N*-*p*-methoxybenzoyl-*m*-tolylhydroxylamine method[4] when analysing alloy steels containing chromium, molybdenum, tungsten, cobalt and vanadium. We therefore sought a new reagent of the hydroxylamine type, and have found one in the reagent described in this paper.

The colour is stable for several days. The stability of the vanadium chelate may be attributed to the increased basicity of the donor atom. The selectivity of the method may be attributed to steric hindrance due to the presence of one methyl group in the *ortho* position of each of the phenyl rings.

EXPERIMENTAL

Reagents

The reagent *N*-*o*-toluoyl-*o*-tolylhydroxylamine was prepared according to the method described earlier,[5] and used as a 0.4% solution in chloroform. All chloroform used was freed from alcohol and other impurities beforehand by washing first with a few drops of sulphuric acid and then successively with dilute ammonia and water, then distilled and dried over anhydrous sodium sulphate.

All reagents were of analytical-reagent grade. Solutions of niobium and tantalum were prepared by pyrosulphate fusion of the oxides and dissolution of the cooled melt in oxalate–tartrate solution.

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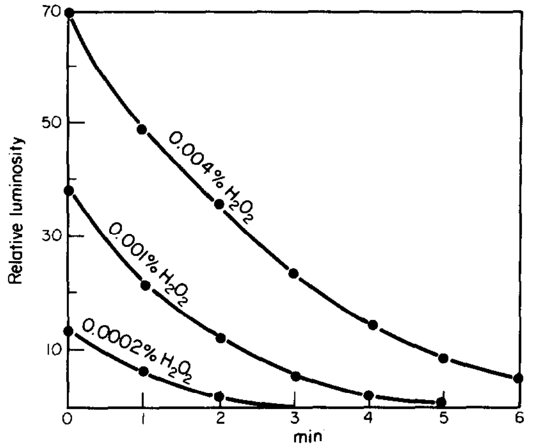

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The colour is stable for several days. The stability of the vanadium chelate may be attributed to the increased basicity of the donor atom. The selectivity of the method may be attributed to steric hindrance due to the presence of one methyl group in the *ortho* position of each of the phenyl rings.

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A standard solution of vanadium(V) was prepared from ammonium metavanadate dissolved in dilute ammonia and then diluted to a known volume with doubly distilled water; it was standardized by iron(II) titration.[6] Other standard solutions were prepared from it by appropriate dilution.

General procedure

An aliquot of vanadium(V) solution was mixed in a separating funnel with an equal volume of 8*M* hydrochloric acid, 5 ml of 0.4% reagent solution and 5 ml of chloroform. The mixture was shaken thoroughly for a few minutes and the reddish-violet chloroform layer was separated, dried over anhydrous sodium sulphate and quantitatively transferred to a 25-ml volumetric flask. The aqueous layer was similarly extracted with two further 5-ml portions of chloroform, separated, dried and transferred to the same 25-ml flask. The combined extracts were then diluted to 25 ml with chloroform. The absorbance was measured at the absorption maximum, 510 nm.

RESULTS AND DISCUSSION

Characteristics of the complex

The complex has maximum colour intensity in 2–6*M* hydrochloric acid medium. Maximum intensity is reached instantaneously at room temperature and is constant for about 4 days. A volume of 5 ml of reagent solution was found more than sufficient for complete development of the colour with 10 μg/ml of vanadium. Excess of reagent has no adverse effect.

The system obeys Beer's law over the vanadium concentration range 0.5–10 μg/ml. The optimum concentration range[7] is 2–8 μg/ml. The relative error per 1% absolute photometric error[8] is 2–7%. The Sandell sensitivity[9] calculated for an absorbance of 0.001 is 0.011 μg/cm^2. The molar absorptivity is 4.75×10^3 l. mole^{-1}.cm^{-1}.

Job's method,[10] the molar-ratio method,[11] and the slope-ratio method[12] all showed a 1:2 metal:ligand complex to be formed.

Effect of diverse ions

In determination of 4 μg of V(V) per ml, there was no interference from 20 mg (this is not the tolerance limit) each of Fe(III), Co(II), Ni, Cu(II), Cd, Hg(II), Ca, Mg, Be, Mn(II), Al, Cr(III), Cr(VI), $S_2O_8^{2-}$, Mn(VII), Mo(VI), W(VI), U(VI), Sn(IV), Zr, Hf, Ti(IV) (masked with fluoride), Nb, Ta, oxalate, citrate, tartrate, EDTA (disodium salt), fluoride, sulphate, nitrate and perchlorate. For Pd(II), the tolerance limit was found to be 5 mg. Both SCN^- and H_2O_2 cause negative errors.

Steel analyses

BCS Nos. 220 HS and 64b HS were analysed for vanadium by the method described below, the results being 1.31 and 1.37% for 220HS (certified value 1.35%) and 1.95, 1.97 and 2.00% for 64b HS (certified value 1.99%).

Procedure. About 0.6 g of the steel, in a covered 250-ml beaker, was treated with 10–15 ml of *aqua regia* and left aside for 10–15 min. When the initial brisk reaction had subsided, the solution was evaporated, on the hot-plate, to ~5 ml. Then 5 ml of concentrated hydrochloric acid were added and after heating for a few minutes the solution was cooled to room temperature, diluted with 10–15 ml of doubly distilled water and filtered. The precipitated tungstic acid was washed with hot 1*M* hydrochloric acid until free from iron (tested with thiocyanate). The combined washings and filtrate were transferred into a 100-ml volumetric flask and diluted to the mark with water. A 1-ml aliquot of this solution was pipetted into a separating funnel and treated with 2–3 ml of freshly prepared 4% potassium persulphate solution (or dilute permanganate solution until the solution appeared faintly pink) and an equal volume of 8*M* hydrochloric acid was added to make the acidity nearly 4*M*. The vanadium was then extracted and measured as in the general procedure.

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Summary—A newly synthesized reagent, *N*-*o*-toluoyl-*N*-*o*-tolylhydroxylamine is used in a sensitive and selective spectrophotometric method for determination of vanadium(V). The method has been successfully applied to vanadium determination in Mn–Mo–Cr–V steels. The system in 2–6*M* hydrochloric acid medium obeys Beer's law at 510 nm in the range of vanadium concentration from 0.5 to 10.0 μg/ml.

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AN AUTOMATIC ELECTROMETER RANGING CIRCUIT FOR A SPARK-SOURCE MASS-SPECTROMETER*

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Electrical measurements of ion-current signals from spark-source mass-spectrometers present unique experimental difficulties.[1] One of these is the automatic ranging of a sensitive electrometer amplifier during the sequential measurement of different ion-signals by peak-switching technique. These ion-signals, which commonly fluctuate between zero and high current,[2] are too erratic for commercial auto-rangers. This paper describes briefly an electronic circuit which satisfactorily performs automatic attenuation on a Cary 401 MR electrometer used for measuring spark-source mass-spectrometer ion-signals. The general electrical detection system has already been described.[3,4,5]

A block diagram of the circuit is given in Fig. 1. Electrical inputs required for the circuit are at the left of the figure. Electrical outputs are at the top, and operator switch controls are at the bottom of the figure. The purpose of the circuit is to find the proper range in which the average value of the electrometer signal for a specific spectral ion-beam (NUCLIDIC ION in Fig. 1) is closest to 25% of full scale. A variable time period (INTEGRATE TIME switch) determines the sampling time in which the ranging is performed. The instantaneous level of the TOTAL ION BEAM in the spectrometer, monitored by a separate amplifier, is also input to the circuit. If this total ion-current falls below a preset level during the ranging period, then the auto-ranger restarts the range-finding procedure. This is done because experience has shown that certain ion-signals are extraordinarily high (or low) just before failure of the ion-source to provide a spark-breakdown.

The auto-ranger determines the electrometer gain-setting in two steps, called COARSE RANGE and FINE RANGE, with a MASTER COARSE/FINE CONTROL. During coarse ranging the output of the electrometer is sampled to determine if it is between 10 and 95% of full scale. If the output is outside this range, the coarse range is appropriately changed and the output is again sampled. The fine range is determined by integrating the electrometer output for a preset time. The integrated value determines one of five ranges to be set for the measurement. Ranging will not go below a preset LOWEST RANGE. Both coarse and fine ranging are accomplished in the same manner. When ranging, two shift registers (SHIFT REGISTER logic) are used: one for up-ranging and the other for down-ranging. The outputs of the shift registers are applied to an up/down decade counter in RANGE CONTROL, which contains the range. Zero corresponds to the most sensitive range and 9 corresponds to the least sensitive range.

The auto-ranger can be operated in two modes, manual or auto, as selected by the operator. In the manual mode the decade counter is forced to the setting of the MANUAL RANGE switch and in the auto mode the decade counter is influenced by up or down clock inputs controlled by the SHIFT REGISTER logic. Activation of the auto-ranger for this mode is recognized by a signal on ACTIVATE AUTO-RANGE. Completion of auto-ranging is externally recognized by a high signal on AUTO-RANGE COMPLETE. RANGE DISPLAY is a seven-segment LED digit. The BCD to DECIMAL DECODER activates the appropriate RELAY DRIVERS and the RANGE RECORDING interface.

The timing sequence for the auto-ranger is given in Fig. 2. Three sequences are of interest: FINE CONTROL, COARSE CONTROL, and MASTER COARSE/FINE CONTROL, as shown in the figure. General control is maintained by MASTER COARSE/FINE and the sequence starts with START COARSE. After 1 msec

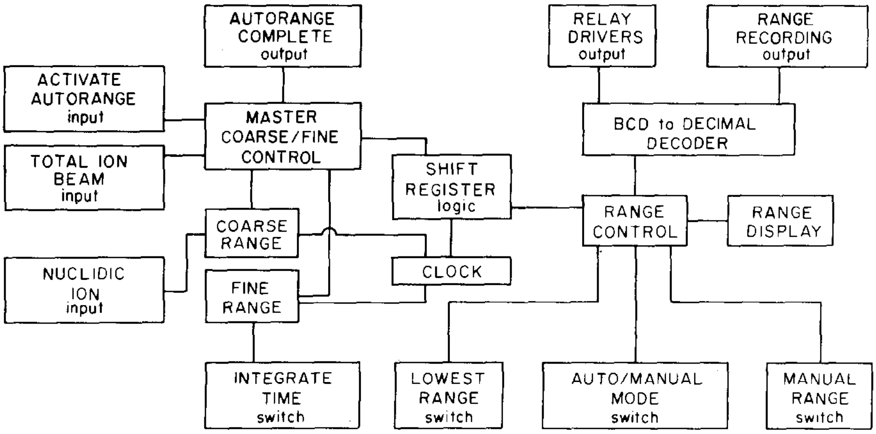

Fig. 1. Block diagram for auto-range circuit.

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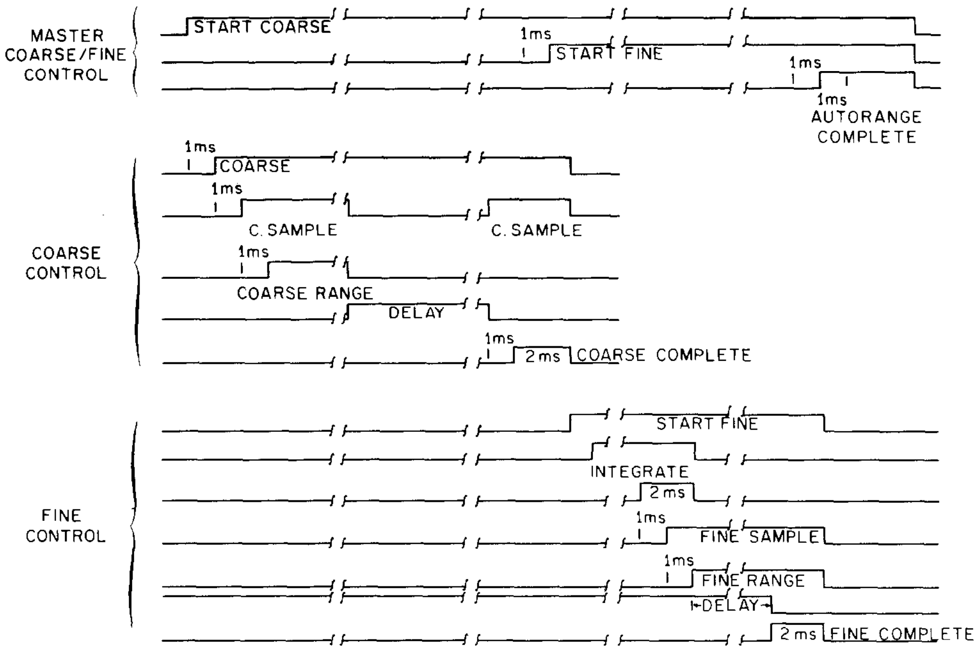

Fig. 2. Timing diagram.

COARSE CONTROL is initiated when signal COARSE goes high as indicated. The NUCLIDIC ION input is sampled at signal C SAMPLE. If the input is less than 10 or greater than 95% of full scale then a COARSE RANGE change occurs. When the coarse-range change is completed there is a DELAY before the input is again sampled. If the input is between the 10 and 95% levels the COARSE COMPLETE signal goes high, thus ending coarse ranging.

Fine ranging starts when START FINE is high. The fine-range sequence consists of a period of integration of the NUCLIDIC ION input, a sampling of an INTEGRATE output, a FINE RANGE change if necessary, and a DELAY for the electrometer to settle. The integration period is determined by an RC network which is controlled by the INTEGRATE TIME switch-setting. The most satisfactory integration period has been found to be approximately 3 sec. As a result of the integration sampling, the range is changed up or down by the number of clock pulses at the CLOCK input of an up-shift register or a down-shift register in the SHIFT REGISTER logic. After a delay, signal AUTO-RANGE COMPLETE ends the auto-ranging sequence. The circuit has performed satisfactorily for the past two years. A complete circuit diagram with pertinent annotation can be obtained upon request. Please address inquiries to Robert J. Conzemius, Ames Laboratory, Iowa State University, Ames, Iowa 50010. The authors wish to thank Harry J. Svec and Willard L. Talbert for their advice and support, and David F. Anderson who constructed the circuit.

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Summary—An auto-ranging circuit which accommodates the erratic nature of the electrometer output signals from a spark-source mass-spectrometer is described briefly.

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DETERMINATION OF 8-HYDROXYQUINOLINE WITH *N*,2,6-TRICHLORO-*p*-BENZOQUINONEIMINE

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8-Hydroxyquinoline (oxine) is used as an antiseptic, antiperspirant, and deodorant and is also widely used as an analytical reagent; for these and other reasons there are several methods for the determination of this compound. For determination of microamounts of oxine, spectrophotometric methods[1,2] are the most suitable. Microdetermination of oxine also provides indirect microdetermination of several cations.

It is well known that *N*,2,6-trichloro-*p*-benzoquinoneimine (chlorimide) forms blue indophenol derivatives with phenols which have an unsubstituted *para*-position,[3] and it has been used for determination of pyridoxine,[4–7] potassium guiacol sulphonate,[8] salicylamide,[9] and phenylephrine.[10]

In this paper we describe a new and convenient spectrophotometric method for the determination of 8-hydroxyquinoline in complex mixtures. This procedure is based on our observation that an isopropyl alcohol–water solution of 8-hydroxyquinoline forms at pH 8 a stable blue indophenol derivative with *N*,2,6-trichloro-*p*-benzoquinoneimine.

EXPERIMENTAL

Reagents

All chemicals and reagents used in this work were either USP or NF grade. *N*,2,6-Trichloro-*p*-benzoquinoneimine (Eastman Kodak) was used without further purification; a solution of 12 mg in 100 ml of isopropyl alcohol was prepared. This solution must be prepared fresh before use.

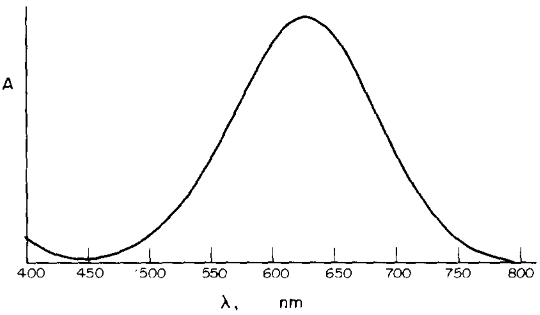


Fig. 1. Absorption spectrum for 8-hydroxyquinoline indophenol derivative.

The buffer solutions used were (*a*) 16 g of ammonium chloride and 16 ml of ammonia solution (sp.gr. 0.910) per 100 ml of solution, (*b*) 20% w/v sodium acetate solution.

A stock solution containing 35–60 mg of 8-hydroxyquinoline (accurately weighed) was prepared in 80 ml of ethyl alcohol and when dissolution was complete, the solution was diluted to 100 ml with ethyl alcohol; 10 ml of this solution were diluted to 100 ml with isopropyl alcohol, and 10 ml of this stock solution were diluted to 100 ml with isopropyl alcohol to provide the working standard solution.

Table 1

100 ml of solution contains						
8-Hydroxyquinoline, *mg*	Salicylic acid, *mg*	Benzoic acid, *mg*	Mint crystal, *mg*	Absorbance	8-Hydroxyquinoline found, *mg*	Recovery, %
0.708	12.04	13.15	220.7	0.54	0.703	99.3
0.590	10.04	10.96	183.9	0.45	0.589	99.8
0.708	24.09	26.30	321.4	0.55	0.716	101.1
0.590	20.08	21.41	267.8	0.45	0.590	100.0
0.472	16.06	17.53	214.2	0.36	0.473	100.2
0.236	8.03	8.76	107.1	0.18	0.242	102.6
0.708	30.12	32.88	551.7	0.54	0.705	99.6
0.590	25.10	27.40	459.3	0.45	0.589	99.8
0.472	20.08	21.92	367.4	0.36	0.473	100.2
0.354	15.06	16.44	275.6	0.26	0.345	97.5
0.236	10.04	10.96	183.7	0.18	0.240	101.5
0.590	10.04	10.96	183.7	0.45	0.588	99.7
0.472	8.03	8.76	147.1	0.36	0.475	100.5
0.354	6.02	6.57	110.3	0.27	0.354	100.1
0.236	4.01	4.38	73.6	0.18	0.244	103.6
0.590	4.01	4.38	73.6	0.46	0.590	100.0
0.354	6.02	6.57	110.3	0.28	0.359	101.5
0.295	6.02	6.57	110.3	0.23	0.300	101.7
0.236	6.02	6.57	110.3	0.18	0.236	100.0
0.177	6.02	6.57	110.3	0.13	0.177	100.0

Test solution

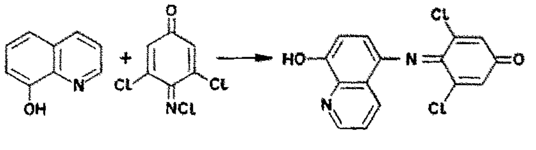
A weighed sample, equivalent to 35–60 mg of 8-hydroxyquinoline, was dissolved in about 80 ml of ethyl alcohol and diluted to 100 ml with the same solvent, then 10 ml of this solution were diluted to 100 ml with isopropyl alcohol. This solution was filtered through a dry Whatman No. 41 filter paper, and the first 30 ml of filtrate were discarded. Then 10 ml of the clear filtrate were diluted to 100 ml with isopropyl alcohol.

Procedure

Five ml of the test solution or the working standard are placed in a dry flask fitted with a ground-glass stopper. To this solution are added 2 ml of isopropyl alcohol, 1 ml of ammonia buffer, 1 ml of sodium acetate solution and 1 ml of *N*,2,6-trichloro-*p*-benzoquinoneimine reagent. The mixture is shaken for a few sec. After a few min the solution becomes blue. After 5–6 min the absorbance at 625 nm (Fig. 1) is measured against isopropyl alcohol in 1-cm cells. The oxine content is calculated by simple proportion from the data for the standard.

DISCUSSION

The reaction is



producing an acid–base indicator which is red at pH < 6.2 and blue at pH > 8.2. The colour intensity is therefore dependent on the pH, but the solutions are buffered at pH 9.2–9.4, so the pH is without effect. The normal colour of the isopropyl alcohol solution of the reagent is pale yellow, but it slowly turns pink on storage. The pink solution gives a green product with oxine and should not be used. The colour reaches maximum intensity within 5–6 min and remains stable for several hours.

An advantage of this method is that it is usable in the presence of salicylic acid, which interferes in the determination of 8-hydroxyquinoline with ferric ions as reagent. Generally phenol derivatives which have an unsubstituted *para*-position interfere with the determination. The double dilution and filtration are used to eliminate insoluble filler materials *etc*. from pharmaceutical and other preparations.

The error for 0.2–0.7 mg of oxine in the final 100 ml of solution is ±3% (Table 1) the relative standard deviation being 1.3%.

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Summary—This paper describes a photometric assay procedure for the determination of small amounts of 8-hydroxyquinoline, based on the formation of a blue indophenol derivative from the reaction of 8-hydroxyquinoline with *N*,2,6-trichloro-*p*-benzoquinoneimine.

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SOME OBSERVATIONS ON THE INTERFERENCES IN FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY OF MAGNESIUM

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Little has been said about the interference mechanism in flameless atomic-absorption spectrometry. Aggett and West[1] suggested that interferences in carbon-filament atomization occur in the vapour phase rather than as a result of a reaction on the filament itself and this idea is supported by the results of experiments with a double-filament arrangement. Aggett and Sprott established that the interferences may originate both on the surface of the graphite rod and in the vapour phase immediately above the rod.[2]

The present communication describes a detailed examination of interference effects, made on the magnesium system with a metal micro-tube atomizer[3] in an attempt to obtain understanding of the phenomenon.

EXPERIMENTAL

Apparatus

Atomic-absorption measurements were made with a Nippon Jarrell-Ash 0.5-m Ebert-type monochromator coupled to an R 106 photomultiplier tube (Hamamatsu TV Co.) and JEOL AA-HMA signal-control unit as a signal-amplifier. The output signal from the signal-control unit was displayed on an Iwatsu DS 5016 dual-beam "synchroscope" with a time constant of 1 μsec.

A molybdenum micro-tube (25 mm long and 1.5 mm i.d.)[3] was used as atomizer. Two small indentations (1 mm in depth and 1 mm in diameter) were made 3 mm apart in the central part of the interior of the micro-tube to accommodate the sample. The micro-tube assembly was mounted in the absorption chamber (300 ml volume) which was purged with argon at a flow-rate of 460 ml/min and hydrogen at a flow-rate of 20 ml/min. The micro-tube was fabricated and mounted on two supports so that there was no localized variation in tube temperature.

A magnesium hollow-cathode lamp (Hamamatsu TV Co.) was used as source. The radiation from it was unmodulated, for fast tracing of the output from the photomultiplier. The spectral line used was 285.2 nm. In order to limit radiation from the micro-tube reaching the photomultiplier, a slit was placed in front of the micro-tube. The voltage signal from the atomizer and the absorption signal were recorded simultaneously by using the two beams of the synchroscope, and the temperature was determined from the voltage signal, which was previously related to the temperature measured by optical pyrometer. A deuterium lamp was used for checking whether interferents absorbed radiation.

Reagents

Chloride solutions were used for all elements tested. Solutions were transferred to the indentation in the micro-tube with a home-made glass micropipette.

Measurement technique

Atomization from separate sample indentations. A magnesium solution was placed in one indentation in the micro-tube and the interfering ion (in 1000-fold amount) in the other, and the samples were dehydrated slowly by operating the tube at low power for about 30 sec. After cooling of the tube, high power was applied for atomization of magnesium and interferent. The diffusional mixing of the two atom-clouds in the micro-tube was assumed to be sufficient, on the basis of observations of the escape-times of the atom-clouds from both ends of the tube, and of the absorption profiles.

Mixture-atomization. A mixture of magnesium and interfering ion was placed in one of the indentations, and the tube was heated as above.

RESULTS AND DISCUSSION

Interference studies were carried out on 4 pg of magnesium and 1000-fold amounts of potentially interfering ions. Interfering ions studied include Na, Al, Ca, Cr(III), Mn(II), Fe(III), Co(II), Ni, Cu(II), Zn, Se, Sr, Sn, Pd, Te and Pb. Atomization was performed at 1600°, which was optimum for magnesium. Simultaneous synchroscope traces or temperature and absorption profiles showed that only 0.1 sec was needed to raise the tube temperature from 600 to 2000°, and the magnesium absorption was started after attainment of the selected temperature. The absorption profiles of magnesium in the presence of most potential interferents were similar to that of magnesium alone in both atomization processes, though the absorption of magnesium was somewhat reduced in the mixture-atomization process. A deuterium lamp was used to check for non-atomic absorption by the foreign ions. Exceptions were Zn, Pb, Mn and Cr. Zinc and lead caused broadened absorption profiles for magnesium, with a long tail when the mixture-atomization process was used, as shown in Fig. 1. These profile shapes may result from delayed atomization of magnesium, probably because of compound formation in the indentation. Chromium gave interfering effects (broadened absorption profiles) with magnesium in both atomization processes. Observation of the absorption profile for atomization from separate indentations would suggest that the interaction was partially occurring in the vapour phase. It is known that chromium(III) chloride reacts with hydrogen at 400° to form chromium(II) chlor-

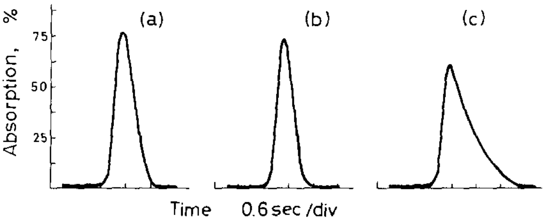

Fig. 1. Synchroscope traces of atomization of magnesium: *a*, pure magnesium; *b*, magnesium in one indentation and zinc in the other; *c*, mixture of magnesium and zinc in one indentation. Atomization temperature, 1600°.

ide, which is present as the dimer (Cr_2Cl_4) in the vapour phase at 1500°. The probable mechanism of chromium interference in atomization from separate sample indentations is delayed atomization of magnesium due to partial interaction with chromium chloride in the vapour phase. The absence of interference from other elements tested in atomization from separate indentations may be due to their chlorides being sufficiently dissociated at 1600° Aggett *et al.*[1,2] proposed an interference mechanism involving vapour-phase condensation or co-precipitation of analyte atoms in an atmosphere saturated with a large excess of gaseous foreign metal atoms or molecules, in carbon-filament atomization. McIntyre *et al.*[4] described the severe interference by chromium when copper and nickel were atomized with a molybdenum filament, and use of a purge-gas mixture of 5% hydrogen in argon, and suggested that the interelemental interference occurs at least partially in the vapour phase.

The use of hydrogen in the absorption chamber was necessary to protect the molybdenum tube from oxidation. Otherwise, atomization with a molybdenum tube was not possible. The metal micro-tube atomizer provides an environment with uniform temperature throughout it, and the effective lifetime of the free atoms may be considerably longer than when a filament system is used. Therefore, the dissociation may be more effective in the micro-tube than with the filament.

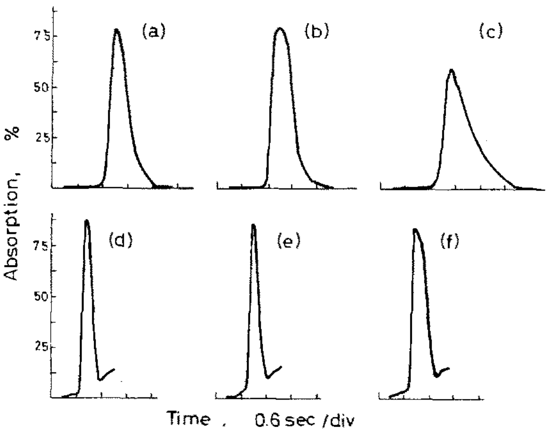

Fig. 2. Synchroscope traces of atomization of magnesium: *a* and *d*, pure magnesium; *b* and *e*, magnesium in one indentation and lead in the other; *c* and *f*, mixture of magnesium and lead in one indentation. Atomization temperature, 1600° for *a*, *b* and *c*; 2200° for *d*, *e*, and *f*.

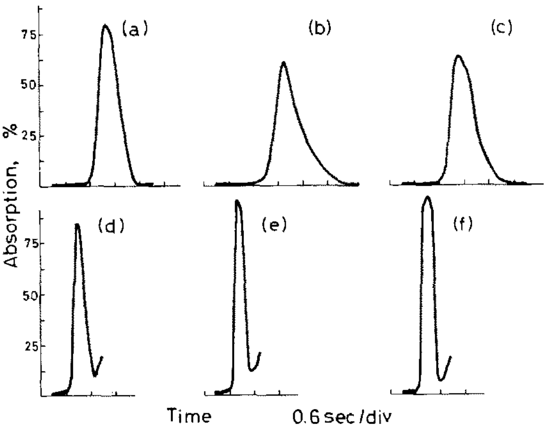

Fig. 3. Synchroscope traces of atomization of magnesium: *a* and *d*, pure magnesium; *b* and *e*, magnesium in one indentation and chromium in the other; *c* and *f*, mixture of magnesium and chromium in one indentation. Atomization temperature, 1600° for *a*, *b* and *c*; 2200° for *d*, *e* and *f*.

The interferences in mixture-atomization appear to be complex. No correlation could be found between interference effects and any physical properties, such as boiling points, melting points and vapour pressures of the magnesium salts or the interfering salts.

Elevated temperature (2200°) helped to reduce interferences as shown in Figs. 2 and 3. This may be due to effective atomization in the micro-tube atomizer. Atomization at higher temperature is recommended for minimizing interferences provided a fast-response detection system is applied.

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Summary—Interferences in flameless atomic-absorption spectrometry of magnesium were investigated by the use of a molybdenum micro-tube atomizer with a double indentation. Two atomization processes were compared in order to understand the interference mechanism: atomization from separate indentations, and mixture-atomization. Most elements tested gave no interference in atomization from separate indentations, whereas magnesium absorption was somewhat reduced in mixture-atomization. However, zinc and lead caused broadened absorption profiles in mixture-atomization. Chromium interfered in both atomization processes. The origin of these interferences is discussed.

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SELECTIVE STRIPPING VOLTAMMETRIC DETERMINATIONS EMPLOYING CELLS FOR ELECTROLYSIS WITH SIMULTANEOUS ION-EXCHANGE OR SOLVENT EXTRACTION

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Summary—Cells have been designed for stripping-voltammetry analyses employing graphite working electrodes and mercury film electrodes on a graphite support, permitting ion-exchange or solvent extraction separation simultaneously with the pre-electrolysis. The ion-exchange separation was tested on the determination of mercury in the presence of excess of copper(II), lead and cadmium and on the determination of bismuth in the presence of excess of copper(II). The solvent extraction separation was tested on the determination of mercury(II) in the presence of copper(II), lead and cadmium and the determination of copper(II) in the presence of bismuth. Very good results were obtained by using ion-exchange, where the sensitivity and precision of the determination are comparable with those obtained in the determinations without separation, the separation efficiency being very high, limited virtually only by the capacity of the ion-exchanger used. The solvent extraction separations yielded poorer results: the sensitivity of the determination is decreased substantially, the separation efficiency is not very high and difficulties arise from the adsorption of the organic phase on the electrode surface

The main problem in the application of stripping voltammetric techniques is that of achieving adequate selectivity in determinations on more complicated materials, while preserving as high a sensitivity as possible. Some aspects of this complex problem have already been treated in our previous papers.[1–3] Some improvement in the selectivity over classical stripping determinations with a mercury drop electrode can be achieved by using mercury-film electrodes and by using other than d.c. measuring techniques, such as a.c. voltammetry, square-wave voltammetry or pulse and differential pulse voltammetry. However, a preliminary separation step is frequently necessary. Preliminary separations are usually tedious and often lead to dilution of the sample, introduction of impurities and loss of the substance to be determined through adsorption, coprecipitation, *etc.* With solvent-extraction separations, some of these problems can sometimes be alleviated by performing the stripping determination directly in the organic phase after extraction (see, *e.g.*, refs. 4 and 5); however, the sensitivity of the determination is not very high, the stripping peaks obtained are usually broad and non-symmetrical, and the electrode surface may be affected by the organic solvents. Stripping voltammetry has already been combined with ion-exchange by pumping portions of the eluate from a chromatographic column into the electrolysis cell and performing the stripping determination in each portion of the solution.[6]

The present paper describes a technique for simultaneous separation and pre-electrolysis, which in many cases removes these difficulties.

EXPERIMENTAL

Chemicals and apparatus

All chemicals employed were of *p.a.* purity, obtained from Lachema, Czechoslovakia. Stock solutions of metal salts were obtained by dissolving the solid substances in water, except for mercuric nitrate solution, which was prepared by dissolving metallic mercury in dilute nitric acid. The solutions were standardized by EDTA titrations and dilute solutions for experiments were prepared immediately before the measurement.

Strongly acidic cation-exchanger Dowex 50W-X8 (50–100 mesh) in the H^+-cycle was employed for ion-exchange separations. For solvent extractions, ethyl acetate and a 0.0013% solution of dithizone in carbon tetrachloride was employed.

The solutions were deaerated by passage of nitrogen, freed from traces of oxygen by bubbling through solutions of sodium anthraquinone-β-sulphonate and chromium(II) chloride, regenerated with amalgamated zinc.

The stripping-voltammetry measurements were carried out by using two- and three-electrode polarographs constructed in the laboratory from operational amplifier modules connected to an EZ-7 linear recorder (Laboratorní přístroje, Czechoslovakia). A stream of nitrogen was employed for stirring the solutions and its flow-rate was kept constant by using a liquid manostat. The measuring cells employed will be described below in the sections dealing with the particular separation techniques.

A stationary graphite disk was employed as the working electrode. Spectral graphite (Elektrokarbon, Czechoslovakia) was impregnated under reduced pressure (water-pump) with paraffin at 100° for 5 hr. The electrodes (2 mm in diameter) were cemented in glass tubes and polished with metallographic papers (SIA, Switzerland; 2/0, 4/0, 6/0) and with damp velvet. In some experiments, glassy carbon (Le Carbone Lorraine, France) electrodes of the same dimensions, polished in the same manner, were employed. Mercury contacts were used. Mercury films were deposited *in situ* on the polished graphite or glassy carbon support according to Florence.[7] Platinum wire auxiliary and satu-

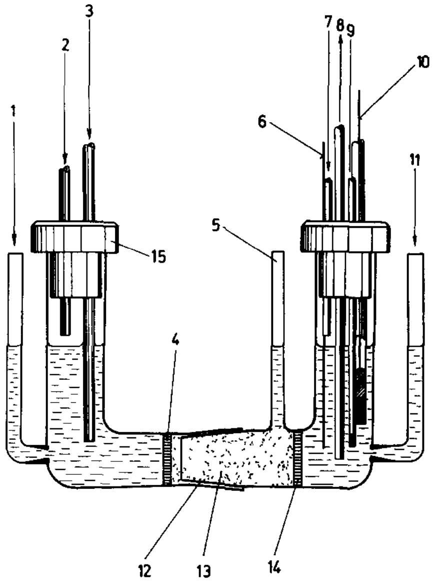

Fig. 1. Cell for stripping determinations with simultaneous separation on ion-exchanger with circulating solution (1,11)—nitrogen inlets for solution deaeration and stirring, (2,7)—nitrogen inlets for passage over the solution, (3,8)—tubes from and to the pump, respectively, for solution circulation, (4,14)—frits, (5)—air outlet tube, (6)—auxiliary platinum electrode, (9)—SCE liquid bridge, (10)—working graphite electrode, (12)—ground-glass joint, (13)—ion-exchanger, (15)—Teflon stopper.

rated calomel reference (K 401, Radiometer) electrodes were employed. All potentials are referred to the saturated calomel electrode at the experimental temperature, 20 ± 2°.

Procedure

Unless otherwise stated, the measuring procedure involved the following steps: 5-min deaeration by passage of nitrogen, followed by 5-min pre-electrolysis at −0.8 V in the solution stirred with nitrogen; then the stirring was stopped (nitrogen was passed over the solution) and after a 30-sec rest period the stripping voltammogram was recorded at a scan rate of 600 mV/min. The working electrode was repolished with damp velvet before each measurement.

RESULTS AND DISCUSSION

Stripping determinations with ion-exchange

The first cell employed is shown in Fig. 1. The left-hand compartment contains the test solution (5 ml), the right-hand one contains the pure base electrolyte (5 ml) and the electrode system. The two compartments are separated by an ion-exchange column and the solution is circulated by a simple peristaltic pump through the ion-exchanger from the sample compartment into the measuring compartment and back into the sample compartment at a rate of 0.5 ml/min. Simultaneously, pre-electrolysis at the required potential is carried out.

This principle was tested by using the separation of Hg^{2+} from Cd^{2+}, Pb^{2+} and Cu^{2+} in dilute hydrochloric acid.[8] Mercury is not removed by the ion-exchanger under these conditions, but passes through the column and can be determined, while the other ions are retained. An example of this determination is shown in Fig. 2, curve (*a*). Hydrochloric acid (0.2*M*) serves as both the ion-exchange medium and the base electrolyte. It is evident that perfect separation is achieved (the small lead peak is caused by the presence of Pb^{2+} in the acid originally present in the measuring compartment). The separation can be performed successfully with substantially higher excesses of the interfering elements and the upper limit is determined only by the capacity of the ion-exchange column. Therefore, this technique is especially advantageous for complicated systems and also for studying ion-exchange, as very small amounts of substances eluted from the ion-exchanger are immediately determined.

The main disadvantages of the cell for routine work are that washing of the apparatus between the measurements is rather tedious and that the detection limit is higher than in the determination without separation, because the sample is diluted by the base electrolyte present in the measuring compartment, and the efficiency of the pre-electrolysis is lower at the start, until the whole sample volume in the left-hand compartment has been pumped through the ion-exchanger into the electrode compartment. Therefore, longer pre-electrolysis times are required for low concentrations. On the other hand, the reproducibility of the measurements is good (the relative standard deviation generally amounts to a few per cent).

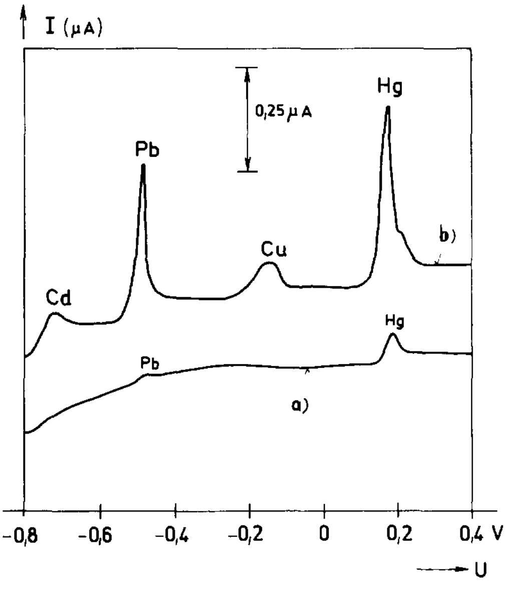

Fig. 2. Determination of $10^{-6}M$ Hg^{2+} in the presence of $10^{-4}M$ Cd^{2+}, Pb^{2+} and Cu^{2+}, employing simultaneous cation-exchange in 0.2*M* hydrochloric acid base electrolyte. Pre-electrolysis for 5 min at −0.8 V, volume of solution 5 ml. Scan rate 600 mV/min. (*a*) Determination in the cell depicted in Fig. 1, with circulating solution. (*b*) Determination in the cell depicted in Fig. 3, with cation-exchanger dispersed in the test solution.

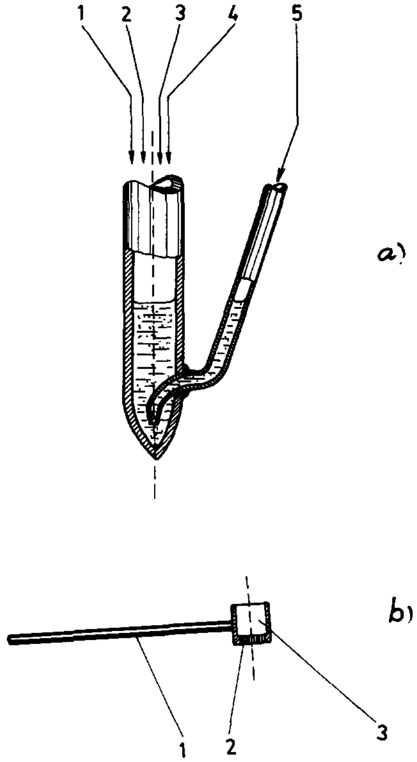

Fig. 3. (*a*) Cell for stripping determinations using ion-exchanger dispersed in the test solution. (1)—working graphite electrode, (2)—liquid bridge to SCE, (3)—auxiliary electrode, (4)—nitrogen inlet for passage above the solution, (5)—nitrogen inlet for solution deaeration and stirring. (*b*) Ion-exchanger measure. (1)—handle, (2)—frit, (3)—cylindrical glass vessel.

For routine determinations it is much more convenient to add ion-exchanger directly to the sample solution. The experimental technique is identical with that of common stripping-voltammetry determinations and the cell is very simple (see Fig. 3*a*). Constant amounts of pretreated ion-exchanger, stored in the base electrolyte, are added to the solution by using the measure depicted in Fig. 3*b*, after removal of the excess of solution from the resin by suction through the frit of the measure with a water pump (dry weight of resin added was 0.6 g). The solution is then deaerated for 5 min, electrolysed for 5 min, care being taken that the solution is sufficiently stirred with the stream of nitrogen, so that the cation-exchanger particles move through the bulk of the solution, and then the stripping voltammogram is recorded after settling of the exchanger.

The same determination was carried out as with the previous cell—see Fig. 2*b*. It can be seen that the separation is somewhat poorer than with the cell with solution circulation, owing to the smaller amount of ion-exchanger present, but the determination is substantially more sensitive, because the sample solution is not diluted and the pre-electrolysis efficiency is not decreased. Under the conditions used, the limit of detection was $2 \times 10^{-7}M$ Hg^{2+} (this value can be decreased substantially by using pre-electrolysis times longer than 5 min), the calibration curve was linear up to $5 \times 10^{-6}M$ Hg^{2+} and the maximum permissible concentration of interfering elements was $10^{-3}M$. Hence the separation efficiency was still very good. The standard deviation for relative determination of $10^{-6}M$ Hg^{2+} in the presence of $10^{-4}M$ concentrations of Cu^{2+}, Pb^{2+} and Cd^{2+}, calculated from 10 determinations, was 8.3% (for the determination of Hg^{2+} alone in the absence of the resin under these conditions, the limit of detection was $7 \times 10^{-8}M$ Hg^{2+} and the relative standard deviation for $10^{-6}M$ Hg^{2+} was 4.3%).

In order to test a determination employing the mercury-film electrode, bismuth was determined in the presence of copper. The test solution was $10^{-4}M$ in $Hg(NO_3)_2$ and the mercury film was deposited *in situ* during the 10-min pre-electrolysis at −0.8 V. The base electrolyte was 0.4*M* hydrochloric acid.[9] The determinations were carried out without and with 0.4 g (dry weight) of resin. Without ion-exchanger, Bi^{3+} down to $3 \times 10^{-9}M$ could be detected in the presence of up to 18 times as much Cu^{2+}. The relative standard deviation for the determination of $5 \times 10^{-8}M$ Bi^{3+} alone without the exchanger, calculated from 10 determinations, was 4.3%. In the presence of the exchanger, Bi^{3+} down to $10^{-8}M$ could be detected in the presence of up to $4 \times 10^{-5}M$ Cu^{2+} (4000-fold molar ratio). The calibration curve was linear for 10^{-8}–$10^{-7}M$ Bi^{3+} in the presence of $4 \times 10^{-5}M$ Cu^{2+}. The relative standard deviation calculated from 10 determinations

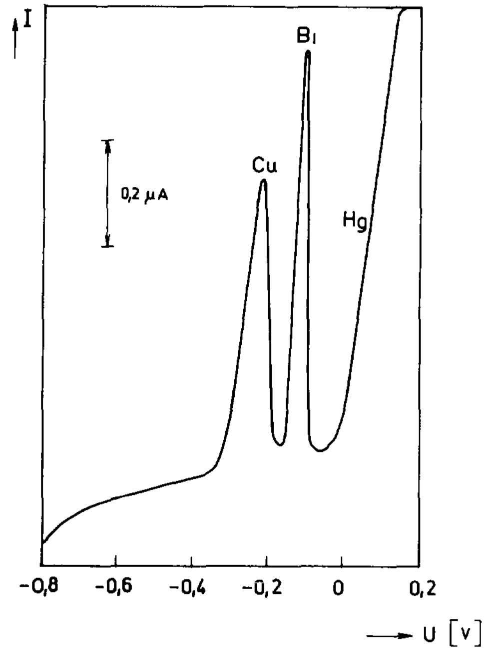

Fig. 4. Determination of $5 \times 10^{-8}M$ Bi^{3+} in the presence of $2 \times 10^{-7}M$ Cu^{2+} in the absence of the cation-exchanger. Pre-electrolysis 10 min at −0.8 V, base electrolyte 0.4*M* hydrochloric acid, $10^{-4}M$ Hg^{2+}, 2.5 ml sample volume, scan rate 800 mV/min.

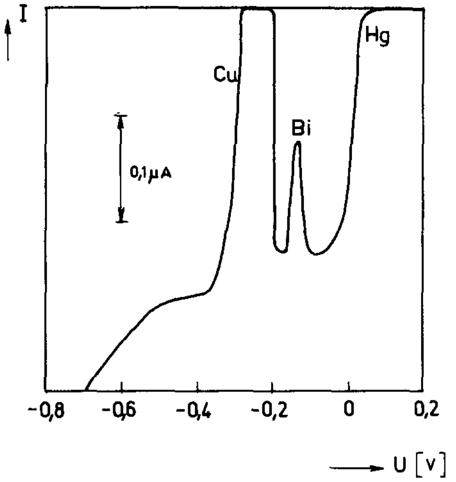

Fig. 5. Determination of $5 \times 10^{-8}M$ Bi^{3+} in the presence of $4 \times 10^{-5}M$ Cu^{2+}, with 0.4 g of the cation-exchanger dispersed in the solution. For experimental conditions see Fig. 4.

of $5 \times 10^{-8}M$ Bi^{3+} in the presence of $4 \times 10^{-5}M$ Cu^{2+} was 10.4%. Typical voltammograms are shown in Figs. 4 and 5.

It can be seen that the detection limit and reproducibility of the determination with the ion-exchanger present are not much poorer than in its absence and that good separations can be achieved. The procedure is very rapid and simple. No mechanical damage to the films deposited on the electrode, caused by the moving resin particles, was observed.

It can be generally concluded that simultaneous ion-exchange considerably improves the selectivity of stripping-voltammetric determinations, without adversely affecting the performance in any way. The ion-exchange equilibrium is established very rapidly under these conditions (in a much shorter time than the deaeration stage), so the separation efficiency depends only on the capacity of the ion-exchanger used. One limitation of these techniques lies in the necessity of using a base electrolyte which simultaneously satisfies the requirements of the separation and of the stripping determination. Only those systems can be analysed in which the species to be determined is not adsorbed on the resin but all the other species are: the capacity of the ion-exchanger must be large enough to remove all of the interfering species completely.

Stripping determinations with solvent extraction

The solvent extraction method is somewhat different from that involving the use of ion-exchangers. The sample solution and the base electrolyte are generally different and must be completely separated by a membrane containing the extraction system. The sample solution must have a composition that permits selective extraction of the determinand into the organic phase while the other components of the system remain unextracted, and the base electrolyte must ensure efficient back-extraction of the determinand into the aqueous phase. Moreover, the quickest possible passage of the substance through the organic layer must be ensured, to achieve sufficient sensitivity with reasonably short pre-electrolysis times. After several unsuccessful attempts, the cell depicted in Fig. 6 was finally constructed. The Teflon cell body contained two compartments separated by a layer of filter paper soaked with the appropriate organic phase. The compartments were placed at an angle to accommodate the electrodes and the nitrogen inlets as close to the membrane as possible in order to increase the sensitivity of the measurement.

The solutions (3 ml of each) were placed in the appropriate compartments and nitrogen was passed for 5 min. Then the pre-electrolysis was performed with the solutions stirred by the stream of nitrogen. The cell was tested for leakage by placing a solution of potassium permanganate in the left-hand compartment and water in the right-hand one. The compartments were separated by a layer of filter paper soaked in ethyl acetate. Traces of permanganate in the right-hand compartment were detected (spectrophotometrically) after 12 min.

The determination of $5 \times 10^{-6}M$ Hg^{2+} in the presence of 100 times as much Cd^{2+}, Pb^{2+} and Cu^{2+} was studied, using the extraction of mercuric ions into ethyl acetate from 0.125*M* hydrochloric acid and back-extraction into 0.1*M* nitric acid.[10] A typical stripping voltammogram is shown in Fig. 7. It can be seen that the separation is poorer than with ion-exchange and the sensitivity also considerably decreased ($5 \times 10^{-6}M$ Hg^{2+} yields a peak about 5 μA

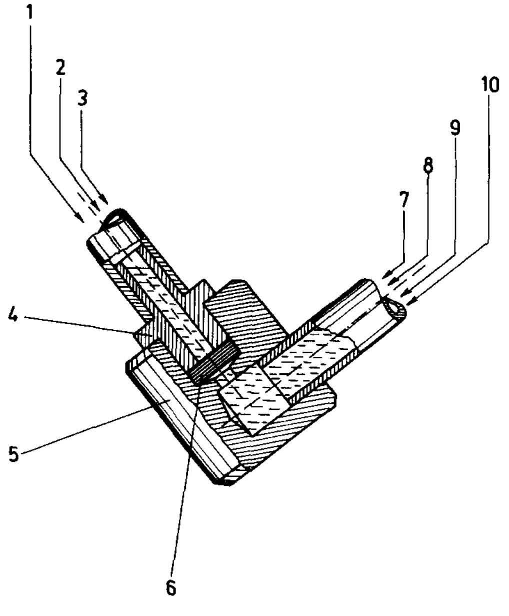

Fig. 6. Cell for stripping determinations with simultaneous solvent extraction. (1)—auxiliary electrode, (2,9)—nitrogen inlets for solution deaeration and stirring, (3,10)—nitrogen inlets for passage over the solution, (4,5)—Teflon body, (6)—layered filter paper soaked in the extractant, (7)—graphite working electrode, (8)—liquid bridge to SCE

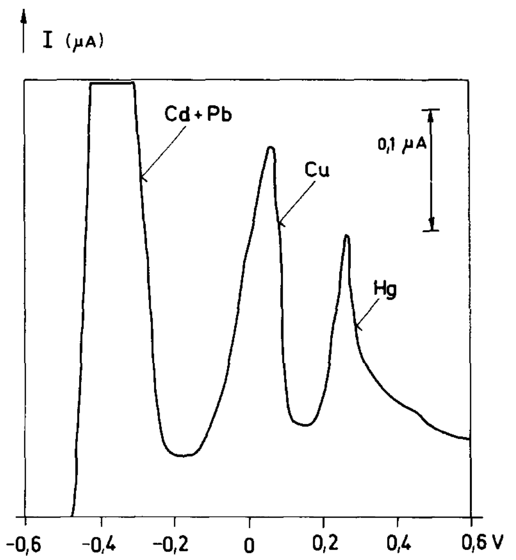

Fig. 7. Determination of $5 \times 10^{-6}M$ Hg^{2+} in the presence of $5 \times 10^{-4}M$ Cu^{2+}, Pb^{2+} and Cd^{2+} with simultaneous solvent extraction into ethyl acetate. Sample solution 3 ml, 0.125*M* in hydrochloric acid (left-hand compartment); 5 ml of 0.1*M* nitric acid (right-hand compartment); 5 min pre-electrolysis at −0.8 V, extraction layer 0.57 mm thick, scan rate 600 mV/min

Table 1. The effect of electrode passivation on the determination of mercury

Peak height, *μA*	Peak potential, *V*
0.42	+0.22
0.13	+0.15
0.04	+0.11
0.49*	+0.22

($5 \times 10^{-6}M$ Hg^{2+}, organic phase layer 1.35 mm thick, electric field applied across the membrane, other conditions identical with those described for Fig. 7).

* After a.c. prepolarization (±1.5 V, 50 Hz) for 3 min in the base electrolyte, followed by repolishing.

in height in the absence of the extractant, while in its presence the peak is only about 0.15 μA high). The reproducibility of this determination is also poorer than when using ion-exchange: the relative standard deviation, calculated from five experimental values, is 16%, compared with 4.4% in the absence of the extractant.

An attempt was made to improve the sensitivity and the efficiency by varying the membrane thickness and applying an electric field across the membrane (placing the auxiliary electrode in the sample compartment and carrying out electrolysis across the membrane). However, the use of thin membranes and of an electrical field leads to poor separation, while thick membranes render the measurement insensitive.

An additional difficulty lies in passivation of the electrode by the organic phase dissolved in the aqueous solution, occurring both with impregnated graphite electrodes and glassy carbon electrodes and manifested by a gradual decrease in the currents measured, and by a shift of the stripping peaks to more negative values. This phenomenon cannot be suppressed by simply polishing the electrode, and only prepolarization of the electrode in the base electrolyte for 3 min by applying 1.5 V a.c. (50 Hz) followed by polishing can restore the original state of the electrode surface (see Table 1). For this reason it is also impossible to carry out determinations in a two-phase system in the vessel, which otherwise would certainly be the simplest solution to the extraction–separation problem.

In order to test less polar organic systems which promise better separations, the determination of Cu^{2+} by using a mercury-film electrode was tested with separation from Bi^{3+} by extracting the copper from a solution of pH 1.5–2.0 (nitric acid) into a 0.0013% dithizone solution in carbon tetrachloride and back-extracting into 6*M* hydrochloric acid.[11] A typical stripping voltammogram is given in Fig. 8. The separation was very effective; copper ions passed through thick membranes, in the absence of an electric field across the membrane, and bismuth ions were not detected, but the passivation of the electrode, which could not be suppressed even by prepolarization, rendered the results irreproducible.

A certain advantage over the simple ion-exchanger method lies in the separation of the measuring space from the sample compartment, thus facilitating a much wider choice of media for the extraction and for the back-extraction with the electrochemical determination. Also the selection of organic extractants is very wide and applicable to a great variety of systems. However, it must be concluded that sol-

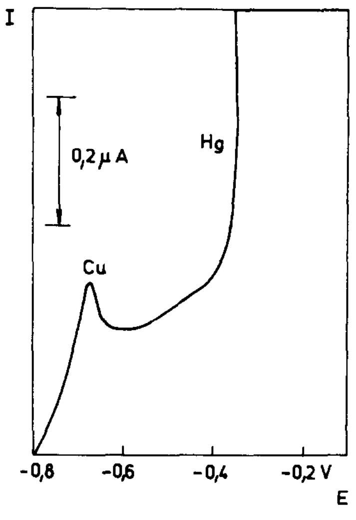

Fig. 8. Determination of $10^{-6}M$ Cu^{2+} in the presence of $10^{-5}M$ Bi^{3+} with simultaneous extraction into a dithizone solution in carbon tetrachloride. Sample solution 3 ml, pH 2 (left-hand compartment); 5 ml of $10^{-4}M$ Hg^{2+} in 6*M* hydrochloric acid (right-hand compartment); 5 min pre-electrolysis at −0.8 V, extraction layer 1.08 mm thick, scan rate 800 mV/min.

vent extraction is generally less suitable than ion-exchange if the technique described is to be useful in practice.

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DOSAGE COULOMETRIQUE PRECIS DES ACTINOIDES: APPLICATION A DE FAIBLES MASSES—I

URANIUM

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Résumé—Un dosage précis de faibles masses d'uranium par coulométrie à potentiel contrôlé est proposé. Ce dosage permet d'obtenir des précisions de l'ordre de 0,1% pour des prises d'essai d'uranium de 0,1 à 1 mg et de 0,5% pour de très faibles masses (15 μg). Les améliorations, permettant ces résultats, qui ont été apportées à l'appareillage et en particulier aux composants de la cellule, sont exposées et discutées.

Depuis la sortie des nouveaux intégrateurs de grande qualité, la coulométrie a pris une importance nouvelle, et voit l'éventail de ses applications s'élargir du fait de la fidélité, de la précision et de la spécificité inhérentes à cette technique. En particulier, le dosage de l'uranium par coulométrie à potentiel contrôlé, étudié par Thomason,[1] Shults,[2] Kelley,[3] Goode,[4] Angeletti[5] et par Molina et Brigaudeau[6] permet des dosages à 0,1% de précision en utilisant des quantités d'uranium de l'ordre de 5 à 20 mg par titrage. Désirant préparer des solutions de références d'uranium isotopiquement purs ^{233}U, ^{235}U, ^{238}U, nous avons été amenés, vu le prix très élevé de ces isotopes, à étudier une méthode de dosage coulométrique de l'uranium sur de faibles prises d'essai (0,1 à 1 mg), tout en conservant une bonne précision. Cette méthode est classique quant à son principe: coulométrie à potentiel contrôlé en milieu H_2SO_4, utilisant la réaction électrochimique:

$$UO_2^{2+} + 2e^- + 4H^+ \rightleftharpoons U^{4+} + 2H_2O$$

Souhaitant obtenir un dosage sensible et précis tout en gardant un temps d'électrolyse assez court, nous nous sommes attachés:

(*a*) à obtenir un coefficient de cellule le plus grand possible (étude de la géométrie de la cellule et du régime d'agitation);

(*b*) à abaisser le courant résiduel faradaïque (utilisation de réactifs ultra-purs, soins apportés au dégazage);

(*c*) à évaluer avec précision le courant résiduel capacitif (utilisation d'un ensemble d'intégration permettant de mesurer avec précision de très petites quantités d'électricité);

(*d*) à éliminer les parasites électriques.

PARTIE EXPERIMENTALE

Appareillage

Cellule. En coulométrie à potentiel contrôlé, on mesure la quantité d'électricité correspondant à l'intégration du courant d'électrolyse:

$$Q = \int_0^t i_0 10^{-At}\,dt = \frac{20}{2.303A}(1 - 10^{-At}) \qquad (1)$$

avec A = coefficient de cellule.

D'après Ravenel et Soret,[7] nous voyons que lors d'un dosage coulométrique direct la mesure peut être arrêtée lorsque le rapport concentration finale sur concentration initiale est inférieur à l'erreur relative admise (0,1% dans notre cas):

$$\frac{C_t}{C_0} = \frac{i_t}{i_0} = 10^{-At} < 10^{-3}$$

d'où

$$t > 3/A$$

Pour obtenir un temps d'électrolyse court, il faut donc avoir un coefficient de cellule (A) élevé. Ce coefficient de cellule dépend de la géométrie de la cellule et des conditions d'agitation; il est proportionnel à S/V, S désignant la surface de l'électrode et V le volume de solution d'électrolyte. Dans le cas d'une électrode de mercure, dans une cellule cylindrique: $S/V = 1/h$ (h = hauteur de la solution). Il faut donc obtenir h le plus petit possible. Nous utilisons des cellules en "Plexiglas" poli, usinées avec précision (figure 1). Le diamètre intérieur de ces cellules est de 33,5 mm. La hauteur minimum de solution à introduire est h = 4 mm, soit un volume minimum de 2,5 ml.

Des comparaisons expérimentales nous ont amenés à concevoir l'agitateur (figure 1) de diamètre = 16 mm. La surface de cet agitateur est polie. En rotation, il ne provoque pas de projections de solution sur les parois de la cellule. Il porte une pointe centrale qui évite d'emprisonner une bulle gazeuse au moment du contact avec la solution, augmente la surface portante sur le mercure et stabilise celui-ci dans son mouvement de rotation.

Les coefficients de cellules obtenus dans ces conditions sont de l'ordre de $A = 0{,}012/S$. Pour un dosage à 0,1% près, il nous faut donc un temps d'électrolyse supérieur à 4 min.

Le support de cellules employé, est celui mis au point par la Section de Chimie Analytique du Plutonium et d'Electroanalyse (C.E.A.-C.E.N./Fontenay-aux-Roses).[8–10] Il est équipé d'un moteur SF MI dont la vitesse constante de rotation est de l'ordre de 3000/min. Nous lui avons apporté quelques modifications, afin de l'utiliser dans des conditions optimales. Un niveau à bulle, des pieds antivibratoires, un réglet pour repérer la position de l'agitateur, un manomètre de contrôle de la pression d'argon ont été ajoutés. Un berceau en acier inoxydable, qui reçoit la cellule, permet la translation verticale ainsi que le verrouillage

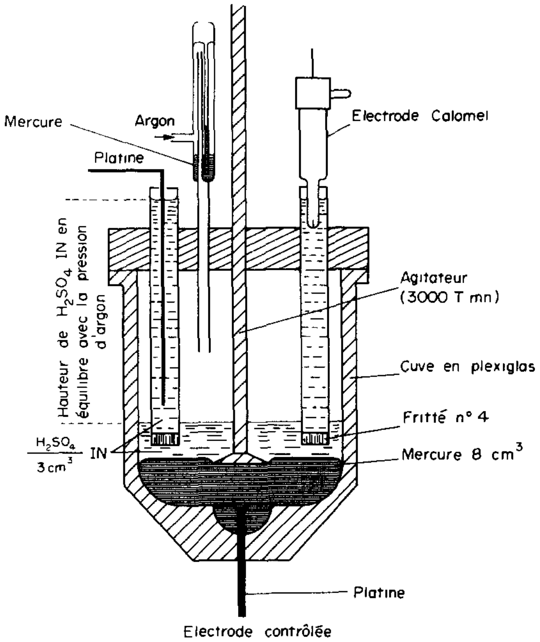

Fig. 1. Cellule de coulométrie.

de celle-ci sur le support, et assure la liaison électrique entre la masse et le fil de platine plongeant dans l'électrode de mercure. Cet appareil est placé dans une boîte à gants sous atmosphère d'argon.

Les caractéristiques de cet ensemble, l'utilisation de produits "ultra-purs", le soin apporté au dégazage, ont permis de réduire la valeur des courants résiduels de 10^{-5} à 10^{-6} A. D'autres améliorations portant sur l'ensemble d'intégration nous ont permis de réduire les courants parasites et de mesurer avec précision la quantité d'électricité non utilisée pour la réduction électrochimique des ions uranium.

Ensemble d'intégration. L'ensemble d'intégration se compose:

(*a*) d'un convertisseur tension-fréquence Hewlett-Packard type 2212 A, (taux de conversion: 10^5 impulsions par seconde pour 1 V; linéarité de 0,01% en pleine gamme; stabilité de ± 0,02% pour 8 hr) placé dans une cage de Faraday en cuivre;

(*b*) de résistances étalons AOIP type RE et REH (précision d'étalonnage de ± 0,02%);

(*c*) d'une échelle de comptage (compteur HVL type M 43 ou compteur ORTEC, modèle 715).

Nous vérifions périodiquement la linéarité de réponse de nos convertisseurs au moyen d'un générateur de tension continue Hewlett-Packard, modèle 740 B. Nous avons constaté que les convertisseurs sont d'une plus grande fiabilité dans la plage des tensions allant de 10^{-4} à 1 V.

Montage électrique (figure 2). Le montage électrique se compose:

(*a*) d'un potentiostat Tacussel, type PRT 20-2 X à réponse rapide;

(*b*) d'un enregistreur Tacussel, type EPL2 B fonctionnant en régime potentiométrique grâce à un tiroir type TV 11 GD [cet enregistreur placé aux bornes d'une résistance AOIP de 10 Ω trace la courbe $i = F(t)$ et permet de s'assurer du bon déroulement de la coulométrie (absence de parasites en particulier)];

(*c*) d'un voltmètre numérique Schneider, type Vn 954 qui contrôle le potentiel imposé à l'électrode de travail.

Ces appareils sont groupés dans une baie mobile alimentée en courant régulé à ± 1%. Un certain nombre de précautions ont été prises, afin de minimiser les perturbations d'origine électrique (liaisons par câbles coaxiaux, contacts en or, soudures à l'argent. Une diode placée dans le circuit supprime certains parasites réinjectés vers le potentiostat). Un commutateur de changement de gamme permet de choisir la résistance d'intégration en fonction de la quantité de l'élément à doser. Un interrupteur (*Z*) permet le contrôle de la dérive de la base zéro du convertisseur avant et après la coulométrie en court-circuitant la résistance de mesure. Une résistance de 500 Ω limite le courant dans le circuit, quand la mesure se fait sur la résistance étalon de 10 Ω.

Methode

Préparation de solutions d'uranium étalonnées. La préparation des solutions se fait à partir d'uranium métal électrolytique de très haute pureté. Un échantillon est décapé, puis séché sous courant d'azote et pesé dans une fiole conique préalablement tarée, dans laquelle se feront la dissolution et la mise en acidité convenable. Le métal est dissout dans l'acide perchlorique 11,5*M* à 60°, puis l'acide perchlorique est chassé par ébullition modérée en présence de l'acide sulfurique. Après refroidissement, on ajuste l'acidité à ≃ 1*N* avec de l'eau bidistillée (on opère de même avec l'oxyde d'uranium qui est préalablement porté à 900° dans un creuset en quartz, puis dissout en milieu acide nitrique 14*M*).

Préparation de la coulométrie On introduit dans la cellule environ 8 ml de mercure, puis 3 ml de l'acide sulfurique 1*N*. Le compartiment de l'électrode de référence et le compartiment de l'électrode anodique sont remplis de l'acide sulfurique 1*N* jusqu'à équilibre de la pression interne de l'argon. L'argon préalablement humidifié par barbotage dans une solution sulfurique 1*N*, est introduit dans la cellule au-dessus de la surface du liquide. Après un court dégazage, la solution subit une préréduction à −0,385 V/ECS jusqu'à l'obtention d'un courant résiduel constant (inférieur à 10^{-6} A). On procède alors à la mesure du "blanc" en prélevant dans la cellule 1 ml de solution préréduite que l'on remplace par 1 ml de solution acide ayant subi le même traitement que la solution d'uranium. On verrouille la cellule pour procéder à un dégazage de 5 min. La base zéro et le taux de conversion du convertisseur sont réglés, puis le potentiel 0,385 V/ECS est imposé et la mesure du blanc a lieu jusqu'à obtention du courant

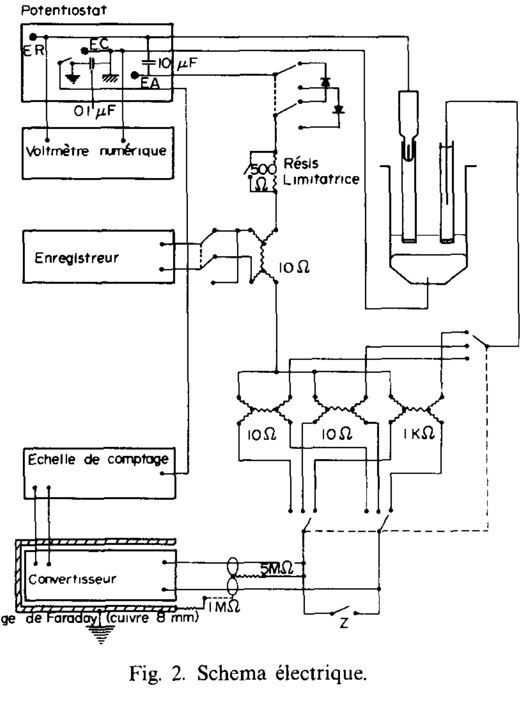

Fig. 2. Schema électrique.

Tableau 1

No de solution	Concentration théorique, *mg/g*	Prise d'essai, *mg*	Valeur moyenne, *mg/g*	Nombre de dosages	Correction moyenne de bruit de fond, %	Ecart à la valeur théorique, %	Ecart type relatif, S, %	Ecart moyen relatif, S_m, %
Metal U 8-1	8,822	8	8,826	8	0,10	0,05	0,06	0,02
Métal U 8-2	10,058	5	10,061	11	0 10	0 03	0,12	0,04
Metal U 8-4	10,334	5	10,332	10	0,015	0,02	0,11	0,03
^{233}U/U3-1		0,6	0,6114	10	0,20	—	0 09	0,03
Oxyde US-1	1,0581	0,5	1,0580	9	0,10	0,01	0,10	0,03
^{233}U-U3-2		0,5	0,6457	12	0,10		0,12	0,04
Oxyde US-1	1,0581	0,2	1,0597	2	0,25	0,15	—	—
Oxyde US-2	1,4392	0,2	1,4414	1	0,40	0,15	—	—
Oxyde US-3	0,02915	0,03	0,02935	1	3	0,50	0,30	—
		0,015	0,02920	2	6			—
^{235}U UD5		0,1	0,2636	5	0,6		0,08	0,04

résiduel (environ 10 min). On note le nombre d'impulsions sur l'échelle de comptage. Après la mesure, la dérive de zéro du convertisseur et la valeur du courant résiduel sont mesurées avec précision en plaçant le commutateur de changement de gamme sur 1000 Ω.

Pour la coulométrie de la solution d'uranium, 1 ml de solution d'électrolyte support est prélevé et remplacé par environ 1 ml de solution à doser. Le poids exact de cette aliquote est déterminé par différence de poids sur une balance Sartorius au 10 μg.

La suite des opérations se fait dans des conditions identiques à celles du blanc. La manipulation complète dure environ 1 hr.

Expression des résultats. La concentration cherchée est exprimée par la formule:

$$C = \frac{MN_u}{nFPKR} \tag{2}$$

ou M = masse atomique de l'élément; n le nombre d'électrons échangés; F = 96.487 C; K = le taux de conversion du convertisseur; R = la résistance de mesure; P = poids de la prise d'essai, $N_u = N_M - (N_R + N_Z + N_B)$; N_M = nombre d'impulsions lu sur le compteur; N_R = nombre d'impulsions ($N_R t$) correspondant à l'intégration du courant résiduel (I_R) pendant le temps de mesure (t); N_Z = nombre d'impulsions correspondant à la dérive éventuelle de la base zéro (Z_u) du convertisseur; N_B = nombre d'impulsions correspondant au blanc (ce nombre est à corriger du courant résiduel et de la dérive de la base zéro du convertisseur lors de la mesure de ce blanc). On a $N_Z = Z_u t$; en pratique $N_Z \leqslant N_u/5000$.

Les premiers résultats obtenus sur plusieurs solutions d'uranium sont consignés dans le tableau 1. Ils sont donnés dans l'ordre chronologique.

APPLICATIONS

Nous avons étudié la possibilité d'appliquer la méthode de dosage coulométrique à l'étalonnage d'une solution d'uranium 233 (teneur isotopique: 99,553%). Deux solutions étalonnées d'uranium naturel métal électrolytique et deux solutions étalonnées d'oxyde d'uranium naturel étalon ont été préparées et diluées à des aliquotes de la solution U3-2 dosée par coulométrie. Ces mélanges isotopiques ont été dosés en spectrométrie de masse, ce qui nous a permis de comparer les concentrations évaluées par chaque méthode. Les résultats sont donnés dans le tableau 2.

DISCUSSION ET CONCLUSION

Une étude statistique[11] montre qu'il n'y a pas de dérive détectable de l'appareillage et que notre méthode est reproductible. Nous avons obtenu un intervalle de confiance autour de la moyenne de +0,068%. La correction de bruit de fond ne dépasse pas 0,2% pour les quantités de l'ordre de 0,5 mg U. Enfin, nous avons constaté que les mesures sont justes dans le domaine considéré (0,5 à 8 mg d'uranium dosé).

Sur des quantités de 0,1 à 0,2 mg, les résultats sont encourageants. Bien que l'influence des corrections devienne plus importante, les résultats sont à peine différents de plus de 0,1% de la valeur théorique, ce qui est conforme à nos exigences de précision.

Ces résultats ont pu être acquis grâce à:

—des améliorations importantes sur les composants de la cellule et de son support, qui se sont traduites par un gain d'un facteur deux sur les coefficients de cellule précédemment publiés,

—l'élimination très poussée des parasites électrostatiques et hertziens, des surtensions à la fermeture du circuit,

—l'amélioration des contacts,

—l'emploi de réactifs ultra-purs.

Tableau 2

Coulométrie				Spectrométrie de masse		
Nombre de mesures	Concentration U total, *mg/g*	Concentration en ^{233}U pur. *mg/g*	S, %	Concentration en ^{233}U, *mg/g*	Nombre d'essais	S, %
12	$X = 0{,}6486$	$X_1 = 0{,}6457$	0,12	$X_b = 0{,}6461$	4	0,2

Nous avons réalisé des dosages sur des quantités de 15 à 30 μg. Les valeurs trouvées s'écartent de près de 0,5% de la valeur théorique; nous pensons cependant pouvoir améliorer ces mesures sur des faibles quantités (10 μg à 0,1% près), grâce à la conception d'une microcellule.

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USE OF LONG CHAIN ALKYLAMINES FOR PRECONCENTRATION AND DETERMINATION OF TRACES OF MOLYBDENUM, TUNGSTEN AND RHENIUM BY ATOMIC-ABSORPTION SPECTROSCOPY—III

TUNGSTEN IN GEOLOGICAL SAMPLES

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Summary—Tungsten is determined by atomic-absorption spectroscopy after its reduction to the W(V)–thiocyanate complex with tin metal and extraction with Alamine 336 into chloroform. Atomic absorbance is measured on a final MIBK solution after evaporation of the chloroform and redissolution of the residue in MIBK. Interference effects are shown to be negligible for diverse cations and anions, including Fe, Cu, Cr, Co, Mo, Al and Bi. Analysis of geological samples with an exceptionally wide range of W content from 2.8 ppm to 10% is achieved with relative standard deviations better than 5%.

A rapid and reliable method for the determination of traces of tungsten in geological samples is not at present available. Existing gravimetric and spectrophotometric methods[1–3] are generally insensitive and suffer from interference problems. Atomic-absorption methods for tungsten in geological samples have been reported[4–7] but are not applicable to trace determinations. Thomas *et al.*[4] improved the sensitivity by addition of potassium as ionization suppressor and phosphate as releasing agent. Keller and Parsons,[5] and Quin and Brooks,[6] determined tungsten in ores after dissolving digested ore residues in alkali. Rao[7] developed a method for solvent extraction of tungsten into 3% Aliquat 336 in di-isobutyl ketone, followed by direct aspiration of the extract into a nitrous oxide–acetylene flame. All of these methods are suitable only for per cent level quantities of tungsten in ore samples because of the poor sensitivity of tungsten determination by AAS.

Recent methods include determination by flame emission with vidicon tube detection,[8] proton-activation analysis[9] and visible spectrophotometry by complexing with hydroquinone,[10] but these have not been applied to analysis of geological samples. Microgram quantities of tungsten in natural waters have been determined by Korrey and Goulden[11] by extraction with benzoin *anti*-oxime. They found interference from Fe(III), V(V) and Mo(VI), making the method unsuitable for geological samples. A rapid spectrometric method for tungsten in steels and wolframite[12] is based on extraction of the yellow W(V)–thiocyanate complex with 2% tribenzylamine in chloroform and measurement at 410 nm. The method has few interferences and a sensitivity of 0.013 μg/ml. Beer's law is obeyed up to 24 μg/ml. However, the proving trials of the method related only to relatively high concentrations of tungsten in special steels and there were no details of applicability to trace amounts of tungsten in most geological materials. The same authors considered extraction of the tungsten(V)–thiocyanate complex with other amines.

We recently reported a general method[13] for extraction and preconcentration of molybdenum, tungsten and rhenium with long-chain alkylamines, before atomic-absorption analysis. In this paper, we describe a detailed application of this method to the determination of tungsten at ppm levels in geological samples.

EXPERIMENTAL

Reagents and apparatus

All reagents have been described previously.[13] The atomic-absorption spectrophotometer used was a Varian Techtron AA5 and instrumental settings have also been reported.[13]

Procedure

The general procedure described previously[13] for determination of tungsten was its extraction from 50 ml of 3*M* hydrochloric acid containing 2 ml of 20% stannous chloride solution and 2 ml of 20% potassium thiocyanate solution into a solution of a long-chain alkylamine in chloroform, followed by evaporation of the chloroform from the separated organic phase and dissolution of the residue in methyl isobutyl ketone (MIBK). Tungsten in the final MIBK solution was then determined by atomic-absorption spectrometry.

This general procedure was modified for determination of tungsten in soils and geological samples in order to eliminate interference problems, as follows. Samples (0.100–1.000 g, 150 mesh) containing less than 600 μg of tungsten were dissolved by the method of Kim *et al.*,[14] giving a final solution of approximately 20 ml in 10*M* hydrochloric acid in a 50-ml beaker. A granular piece of tin

Table 1. The concentration of Alamine 336–$CHCl_3$ for extraction and the final volume of MIBK

Approximate content of W, *μg*	Colour of W–SCN in aqueous phase	Concentration of Alamine 336–$CHCl_3$, %	MIBK, *ml*
20	Very weak yellow	0.5	1.0
10–40	Weak yellow	0.5	2 0
25–100	Yellow	1.0	5 0
50–200	Strong yellow	1.0	10.0
100–600	Very strong yellow	1.0	25.0

metal (0.5–1.0 g) was added, followed by 1 ml of 20% stannous chloride solution and the solution was boiled for 20 min (some tin metal should remain). The solution was then cooled rapidly in ice-water and 2 ml of 50% sodium thiocyanate solution were added. As a source of thiocyanate ion, sodium thiocyanate was preferred because potassium would be precipitated by the perchlorate remaining in solution after the dissolution procedure for the geological samples. After 20 min reaction time, the solution was transferred to a 100-ml separating funnel, the beaker and tin metal being rinsed with cold water and further water added to a final volume of about 50 ml.

The tungsten was extracted with 10 ml of 0.5–1.0% Alamine 336 in chloroform by vigorous shaking for 2 min. The organic phase was drained into a 25-ml beaker or a 25-ml weighing bottle, depending on the final volume of MIBK required and the aqueous phase was washed with a second 10-ml portion of Alamine 336 in chloroform. The combined extracts were heated on a steam-bath to evaporate the chloroform and a few ml of MIBK were added to dissolve the residue. On cooling, the solution was transferred to a 25-ml volumetric flask and made up to volume with MIBK washings from the beaker. For low tungsten concentrations, 1–5 ml of MIBK were added directly to the 25-ml weighing bottle instead of the 25-ml beaker and the residue was dissolved in the MIBK by gentle warming after the stopper had been placed on the bottle. The absorbance of this final MIBK solution was then measured relative to pure MIBK as a blank, with the instrumental parameters previously specified.[13] A range of concentrations of Alamine 336 in chloroform and also of the final MIBK volume was required, depending on the tungsten content of the sample, as shown in Table 1.

RESULTS AND DISCUSSION

The general method for extraction of the thiocyanate complex of tungsten into chloroform solutions of long-chain aliphatic amines has been described previously.[13] From this work, Alamine 336 was chosen as the most suitable extracting agent and the following results give a more detailed account of the use of this method of analysis for tungsten in geological samples. In particular, when the previous method was applied to analysis of ores, some modifications were found to be necessary because of interference effects reported earlier[13] and methods are given below to overcome these problems. It is shown that less than 10 ppm of tungsten can be determined by this technique.

Effect of acid and other reagents

The effect of hydrochloric acid concentration on the extraction of the W(V)–thiocyanate complex into Alamine 336 in chloroform was investigated as shown in Table 2. A single extraction with 10 ml of 1% Alamine 336 in chloroform was carried out, over a range of hydrochloric concentrations from 3*M* to 10*M* in the aqueous phase. After evaporation of the extract, the residue was redissolved in MIBK and made up to 10 ml. The extractability was constant up to 7*M*, but decreased markedly at higher concentrations. Extraction from less than 3*M* hydrochloric acid was not tested, because of difficulties in control of acidity after the initial reduction in 15 ml of 10*M* hydrochloric acid. The final concentration of hydrochloric acid was chosen to be between 4 and 6*M*. Table 2 also shows the measured absorbance as a function of volume of 20% stannous chloride solution used for reduction of 0.200 mg of tungsten in 20 ml of 10*M* hydrochloric acid. A single extraction was carried out with 10 ml of 1% Alamine 336 in chloroform after complexing with 2 ml of 20% potassium thiocyanate solution. In addition, Table 2 shows the effect of varying the volume of potassium thiocyanate solution with the volume of 20% stannous chloride solution

Table 2. Effect of reagents in W extraction*

HCl concentration†, *M*	Absorbance	$SnCl_2$ volume†, *ml*	Absorbance	KSCN volume†, *ml*	Absorbance
3.0	0.62	0.5	0.57	0.5	0.56
4.0	0.62	1.0	0.61	1.0	0.58
5.0	0.62	2.0	0.61	2.0	0.61
6.0	0.62	3.0	0.60	3.0	0.61
7.0	0.60	4.0	0.60	4.0	0.61
8.0	0.57	5.0	0.59	5.0	0.61
9.0	0.51				
10.0	0 43				

* Extraction of 0.200 mg of W from 50 ml of aqueous solution.

† Concentration of reagent varied with other reagent concentrations kept constant

Table 3. Effect of Alamine 336 on W extraction and absorbance

Concentration* of amine in $CHCl_3$, % v/v	Absorbance	Concentration of† amine in MIBK, % v/v	Absorbance
0.1	0.44	0.2	0.31
0.2	0.57	0.5	0.53
0.4	0.61	1.0	0.60
0.6	0.61	2.0	0.61
0.8	0.62	4.0	0.60
1.0	0.61	6.0	0.61
1 5	0.62	8.0	0.60
2.0	0.62	10.0	0.58

* Extraction of 0.200 mg of W into amine/$CHCl_3$ solvent.

† Solvent for final aspiration into the flame after evaporation of $CHCl_3$.

kept constant at 2 ml. Little effect on absorbance was observed with either reagent, as shown previously[13] with Amberlite LA-1 as the extractant. For the purpose of applying this procedure to the determination of tungsten in geological samples, some modification to the reduction system was required, however.

Effect of Alamine 336 on absorbance of tungsten in MIBK

Table 3 shows the effect of varying concentrations of Alamine 336 in MIBK on the tungsten absorbance after the evaporation of the chloroform and dissolution of the residue in 10 ml of MIBK. Low absorbance values were obtained at amine concentrations less than 0.5%, owing to incomplete extraction.

The results also show that Alamine 336 can be used over a much wider concentration range than Amberlite LA-1[13] without effect on absorbance. This was attributed to the lower viscosity of Alamine 336 in comparison to Amberlite LA-1. Furthermore, there was no background absorbance by the MIBK solution up to a 10% content of Alamine 336. Therefore, pure MIBK can be used as a blank solution for the adjustment of zero absorbance.

Recovery of tungsten

Quantitative recovery of 0.200 mg of tungsten was obtained by extraction with solutions of Alamine 336 in chloroform in the concentration range 0.4–2.0%, as shown in Table 3. The degree of extraction achieved was an approximately 25% improvement over the extraction previously reported.[13] In general, double extractions with Alamine 336 concentrations greater than 0.4% in chloroform were used, depending on the quantity of tungsten in the sample solution, in preference to a single extraction, for quantitative recovery.

Interference effects

A wide range of cations and anions likely to be present in geological samples was tested for interference in the extraction of tungsten (0.200 mg), as shown in Tables 4 and 5. Each ion was added to 0.200 mg of tungsten in 20 ml of hydrochloric acid, in 100-fold to 1000-fold w/w ratio to tungsten. The tungsten was then extracted from the aqueous solution containing 2 ml of 20% stannous chloride solution and 2 ml of 20% potassium thiocyanate solution, into two 10-ml portions of 1% Alamine 336–chloroform. Serious interference was observed in the presence of large excesses of copper, iron and molybdenum. Copper caused difficulties in extraction by formation of a white precipitate of CuSCN. It was found that iron(III) in large excess (200 mg) was incompletely reduced by 2 ml of 20% stannous chloride solution. Molybdenum caused complications because of co-extraction into Alamine 336-chloroform as the thiocyanate complex. All these interferences caused a negative error in the tungsten absorbance.

Several anions were also tested for interference as shown in Table 5. When added in large excess in quantities ranging from 1 to 10 mmole, only nitrate interfered severely with the extraction owing to its strong oxidizing effect in concentrated hydrochloric acid. Most interferences, however, were satisfactorily eliminated by the use of tin metal as a reductant.

Reduction with tin metal

Interferences from Fe(III), Cu(II) and Mo(V) were eliminated by exploiting differences between the reduction potentials of tungsten and of these cations. For the quantitative extraction of tungsten or molybdenum as the thiocyanate complex, their oxidation state must be +V. If Mo(VI) can be reduced to Mo(III), the extraction of molybdenum can be prevented because Mo(III) is only weakly complexed by thiocyanate.[15,16] We found that when Sn(II) or Ti(III) was used at hydrochloric acid concentrations greater than 8*M* for the reduction of tungsten in the presence of molybdenum, W(VI) was quantitatively reduced to W(V) while Mo(VI) was reduced to Mo(III). Under these conditions the reduction of molybdenum was incomplete and Mo(III) was readily re-oxidized on standing in air. This instability caused difficulties in the clean extraction of the tungsten thiocyanate complex.

It was finally shown that tin metal alone or with Sn(II) was superior to other reducing agents for the reduction of tungsten in the presence of Mo(VI), Fe(III) and Cu(II). It was necessary to heat the 10*M*

Table 4. Effect of cations on W extraction (200 mg taken)

Cation (salt used)	Amount added (as *mg* of metal)	Absorbance	Cation (salt used)	Amount added (as *mg* of metal)	Absorbance
No addition	—	0.60	Mg ($MgCl_2$)	20	0.60
Ag (Ag_2SO_4)	2	0.60		200	0.60
Al (metal)	20	0.59	Mn ($MnCl_2$)	20	0.60
	200	0.60		200	0.61
Au ($NaAuCl_4$)	2	0.55	Mo [$(NH_4)_6Mo_7O_{24}$]	20	0.58
				200	0.05
Ba ($BaCl_2$)	20	0.61	Na (NaCl)	20	0.61
	200	0.61		200	0.61
Bi ($BiCl_3$)	20	0.60	NH_4 (NH_4Cl)	20	0.61
	200	0.60		200	0.59
Ca ($CaCl_2$)	20	0.59	Ni ($NiCl_2$)	20	0.59
	200	0.60		200	0.60
Cd ($CdCl_2$)	20	0.60	Pb ($PbCO_3$)	20	0.61
	200	0.60		200	0.61
Ce [$Ce(SO_4)_2$]	20	0.61	Pd (PdI_2)	2	0.58
	200	0.57			
Co ($CoCl_2$)	20	0.60	Pt (PtO)	2	0.60
	200	0.61	Re ($KReO_4$)	2	0.60
Cr ($CrCl_3$)	20	0.60		20	0.57
	200	0.61	Rh (metal)	2	0.61
Cu ($CuCl_2$)	20	0.58	Sb ($SbCl_3$)	20	0.60
	200	0.47		200	0.62
Fe ($FeCl_3$)	20	0.60	Th ($ThCl_4$)	20	0.60
	200	0.25		200	0.60
Hg ($HgCl_2$)	20	0.61	Ti ($TiCl_4$)	20	0.60
	200	0.56		200	0.62
In ($InCl_3$)	20	0.61	V (NH_4VO_3)	20	0.57
	200	0.61			
K (KCl)	20	0.61	Zn ($ZnCl_2$)	20	0.60
	200	0.62		200	0.60
Li (LiCl)	20	0.60	Zr ($ZrOCl_2$)	20	0.60
	200	0.61		200	0.59

hydrochloric acid solution containing tin metal to ensure complete reduction to Mo(III) and the solution was then cooled in ice-water to prevent re-oxidation. Sn(II) was added along with the tin metal to increase the rate of reaction, and the rate of consumption of tin metal was further increased by the presence of other oxidizing elements such as Fe(III), Cu(II), Cr(VI) and nitrate.

Table 6 gives results for the determination of tungsten in the presence of molybdenum and iron after reduction with the Sn/Sn(II) system. At least 90% recovery was obtained in the presence of 1000-fold ratio of molybdenum to tungsten. In addition, large amounts of Cu(II) were spontaneously reduced to copper metal by tin metal with the solution at room temperature. Greater than 90% recovery of tungsten was obtained from a mixture of 0.200 mg of tungsten and 200 mg of Cu(II). Nitrate interference

Table 5. Effect of anions on W extraction

Anion (salt used)	Amount added		Absorbance
	mmole	*g*	
No addition*	—	—	0.60
Acetate	1	0.08	0.60
(CH_3COONa)	10	0.82	0.60
Borate	1	0.06	0.58
(HBO_3)	10	0.60	0.53
Citrate	1	0.20	0.60
[$C_3H_4(OH)(COOH)_3 \cdot H_2O$]	10	2.00	0.59
Nitrate	1	0.08	0.30
($NaNO_3$)	10	0.85	0.10
Perchlorate	1	0.14	0.61
($NaClO_4 \cdot H_2O$)	10	1.41	0.56
Phosphate	1	0.16	0.60
($Na_2HPO_4 \cdot 2H_2O$)	10	1.56	0.62
Silicate	1	0.28	0.59
($Na_2SiO_3 \cdot H_2O$)	10	2.84	0.50
Sulphate	1	0.32	0.61
($Na_2SO_4 \cdot 10H_2O$)	10	3.20	0.59
Tartrate	1	0.15	0.60
[$(CHOHCOOH)_2$]	10	1.50	0.58
Tetrafluoroborate	1	0.13	0.61
(KBF_4)	10	1.26	0.55

* W taken, 0.200 mg

Table 6. Effect of Mo and Fe on W extraction

W taken, *mg*	Mo added, *mg*	Fe added, *mg*	W found, *mg*
0.200	—	—	0.200
0.200	2	—	0.198
0.200	20	—	0.195
0.200	200	—	0.183
0.200	—	500	0.194
0.200	—	1000	0.183
0.200	2	100	0.194
0.200	2	200	0.198
0.200	20	100	0.195
0.200	20	200	0.183
0.200	100	100	0.183
0.200	100	200	0.183

Table 7. Analysis of soils and geological samples

Sample No.	Amount taken, *g*	Aliquot, *ml*	Concentration of Alamine 336–$CHCl_3$, %	MIBK, *ml*	No. of detns.	Mean	Range	RSD, %	Independent laboratory value	Mo, *ppm*	Fe, %	Cu, *ppm*
Soils, King Island, Tasmania												
						ppm	*ppm*					
1	0.400	—	1.0	10.0	7	439	430–440	0.8	—	340	9.0	92
2	1.000	—	0.5	2.0	5	28.8	28–30	3.0	—	250	4.9	44
3	1.000	—	0.5	2.0	5	6.9	6.7–7.0	1.9	—	240	5.8	70
4	1.000	—	0.5	2.0	5	9.1	9.0–9.6	2.8	—	110	5.3	48
5	1.000	—	0.5	2.0	5	5.2	5.0–5.4	3.3	—	270	4.5	31
Drill Cores, CRA, QLD.												
						ppm	*ppm*		*ppm*			
171389	1.000	—	0.5	5.0	5	63	60–65	3.4	61†	220	1.7	42
171390	1.000	—	0.5	1.0	5	2.8	2.7–3.0	4.5	<10†	200	1.3	31
171394	1.000	—	0.5	2.0	6	9.1	9.0–9.6	2.6	16†	104	1.5	37
Scheelites, Warman Equipment Ltd.												
						%	%		%			
22	0.050	5/100	1.0	25.0	5	8.4 (10.6)*	8.2–8.5	1.5	10.8 (WO_3)§	7500	11.0	1520
24	0.050	5/100	1.0	25.0	5	10.0 (12.6)	10.0–10.2	0.9	12.6 (WO_3)§	17,000	10.0	13,000
26	0.100	25/100	1.0	10.0	6	0.89 (1.12)	0.88–0.90	0.9	1.15 (WO_3)§	8000	6.5	13,200
33	0.250	—	1.0	10.0	5	0.55 (0.69)	0.54–0.56	1.6	0.92 (WO_3)‡	200	8.9	87
34	0.100	—	1.0	10.0	7	0.15 (0.19)	0.14–0.15	2.5	0.39 (WO_3)‡	150	10.9	40
41	0.100	5/100	1.0	10.0	5	3.2 (4.05)	3.0–3.4	5.3	4.10 (WO_3)§	3000	11.5	280
Soils (W-rich), USGS												
						%	%					
3-401	0.200	10/100	1.0	25.0	6	1.20	1.19–1.25	2.0	—	—	—	—
3-402	0.200	10/100	1.0	25.0	6	1.18	1.16–1.25	3.0	—	—	—	—

* Value in brackets given as WO_3.

† Determined by X-ray fluorescence.

§ Gravimetry.

‡ Colorimetry.

Table 8. Results of standard additions

Sample	W added, μg	W found, μg	No. of detns.	Mean, μg	Range, μg	RSD, %
Tasmania	5	11.8, 11.0, 11.1	3	11.27	0.8	4.19
Soil 3 (1 g)	10	16.0, 17.0, 16.0	3	16.33	1.0	3.62
Drill core	5	8.0, 8.0, 7.5	3	7.83	0.5	3.77
171390 (1 g)	10	13.0, 12.0, 12.5	3	12.50	1.0	4.73

was also satisfactorily eliminated by reduction with Sn/Sn(II).

Calibration curve

The absorbance was a linear function of tungsten concentration in the range 5–25 ppm tungsten when × 10 scale expansion was used. The calibration allows the determination of tungsten in the range from 1.0 to 600 ppm in a sample by use of a range of final MIBK volumes from 1 to 25 ml. An absorbance reading of 0.05 was found to correspond to approximately 1.5 ppm of tungsten, *i.e.*, 1.5 μg of tungsten in 1 g of sample. This low content can therefore be determined satisfactorily by the present procedure with 1 ml of MIBK as the final solvent volume. The standard solutions were prepared by dilution of a stock solution of 100 ppm tungsten in the form of a W–SCN–Alamine 336–MIBK stock solution. These solutions were stable for more than two months, but absorbance measurements of solutions of geological samples must be completed within one or two days after preparation because of the complex nature of such solutions.

Results of sample analysis

Table 7 shows the analytical results for four different kinds of sample. The analytical results for the scheelites were in good agreement with the gravimetric values determined by Warman Equipment Ltd., except for the values obtained by colorimetry (No. 33 and 34). We assume that the high colorimetric results are a consequence of interference from iron and molybdenum. The analytical data from C.R.A., Queensland, for the drill core samples were obtained by X-ray fluorescence spectrometry *without* matrix correction. Results were generally in good agreement with independent laboratory values.

Studies of standard additions of tungsten to two different samples were also made and results are given in Table 8. Quantities of 5 and 10 μg of tungsten were added to 1 g of each sample before the solvent extraction. Total tungsten recoveries were in good agreement with the original values shown in Table 7.

All the results shown in Tables 7 and 8 gave relative standard deviations not exceeding about 5% over a wide range of tungsten concentration from 2.8 ppm to 10%. The method is rapid and determinations can be carried out batchwise with up to 50 samples, in an average time of about 10 min for each determination after the dissolution of the solid sample.

CONCLUSIONS

It has been found that tungsten can be determined in geological samples over a wide concentration range by atomic absorption, without serious interference from excesses of many metals, particularly iron and molybdenum, which interfere in the colorimetric method[12] when present in large excess. High sensitivity has been achieved by the extraction–preconcentration procedure with Alamine 336. The method has been shown to provide a rapid, sensitive procedure and has been applied for the first time to analysis of samples containing tungsten concentrations as low as 2.8 ppm and ranging up to 10%, with standard deviations better than 5%.

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THE DETERMINATION OF PLATINUM IN REFORMING AND EMISSION-CONTROL CATALYSTS BY DIFFERENTIAL SPECTROPHOTOMETRY

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Summary—Differential spectrophotometry is used in conjunction with the stannous chloride method to determine platinum with <1% relative error in reforming and emission-control catalysts. Detailed instructions are given for decomposition of the samples.

Because platinum-bearing catalysts have the ability to reform or rearrange the molecular structure of hydrocarbons, "reforming catalysts" have become of great importance to the petroleum industry.

Further, the enactment of the Federal Clean Air Act requires the introduction of platinum- and platinum–palladium-bearing catalysts in the form of catalytic converters in automobiles from 1975 models onward, to achieve satisfactory control of exhaust emission.

Both the reforming catalysts (~0.3 or ~0.6 Pt) and the emission-control catalysts (0.035–0.11% Pt) contain the platinum as a deposit on a substrate consisting mainly of γ-alumina, or, in the case of "octafining" catalysts, of γ-alumina plus silica. Rhenium (~0.3% or ~0.6%) is frequently present in reforming catalysts, and palladium (0.015–0.04%) in emission-control catalysts. The amount of α-alumina is usually small in fresh reforming catalysts. Spent reforming catalysts which, because of their platinum content, are usually recycled, may be contaminated with a variety of metallic impurities and carbon. In addition, because of high-temperature applications of some of these catalysts, part of the acid-soluble γ-alumina may be converted into α-alumina, which is acid-insoluble. The platinum in spent emission-control catalysts is not at present recovered.

Since the use of platinum-bearing catalysts involves substantial investment of money, the accurate determination of platinum represents a *sine qua non* in all financial transactions. Agreements between producers and consumers of both types of catalyst therefore generally specify platinum results to agree within 1% relative. This requirement can be met more easily in the case of the reforming catalysts, which have the higher Pt content.

The literature on determining platinum in catalysts is not extensive. For reforming catalysts an X-ray fluorescence approach was described by Lincoln and Davis.[1] Distillation of the platinum as the chloride, followed by the spectrophotometric *p*-nitrosodimethylaniline procedure, was suggested by Conrad and Evans.[2] Dissolution of the catalyst in hydrochloric acid, followed by a spectrophotometric stannous chloride finish, was used by Maziekin *et al.*[3] A gravimetric method based on the precipitation of platinum with dimethylphenylbenzylammonium bromide was suggested by Kuebler[4] who also recommended a spectrophotometric diaminobenzoic acid procedure for the determination of small amounts of platinum. There is no literature yet on the determination of platinum in emission-control catalysts, although it is known that the producers of the catalysts, as well as the A.C. Spark Plug Division of General Motors, have been investigating extensively various approaches using X-ray fluorescence spectroscopy.[5] Because of the high and fluctuating background, due to the various forms in which the alumina may be present, and because of the lack of meaningful standard samples, this technique does not yet appear to be capable of meeting the requirements for precision and accuracy, but may serve as a tool in quality control. The determination of platinum (and palladium) in emission-control catalysts by atomic absorption after collection of the platinum and palladium with either tellurium[6] or sodium formate[7] as precipitant has recently been reported. This technique is at present capable of providing platinum results with a relative standard deviation of about 1.5%. This falls somewhat short of the desired accuracy (error less than 1%).

The spectrophotometric determination of platinum by the stannous chloride system appears to be the best suited approach for the determination of platinum in both types of catalyst. It has been thoroughly investigated.[3,8–12] Ayres and Meyers[9] showed that it can be used for differential spectrophotometric measurement of platinum. It is this particular feature which makes the method attractive for the precise determination of platinum in both types of catalyst.

EXPERIMENTAL

Apparatus

Spectrophotometer. Beckman DU equipped with matched 1-cm cells.

Vitreous graphite crucibles. Obtainable from Société Le Carbon Lorraine, Paris, and Boonton, N.J.

Normal laboratory equipment. Muffle furnace, stoves, steam-bath, H_2S cylinders, glassware, alumina crucibles, Rose crucibles.

Optional equipment. Fire-assay furnace, scorifiers, and cupels.

Reagents

Sodium dimethylglyoximate solution, 2%.

Stannous chloride solution, 30%. Dissolve 300 g of $SnCl_2 \cdot 2H_2O$ by warming with 500 ml of concentrated hydrochloric acid and dilute to 1 litre with water.

Sodium formate solution, 25%.

Saturated solution of bromine in water.

Collection of the platinum

Fresh reforming catalysts containing only platinum. Decompose four different sample weights ranging between 10 and 12 g (Pt ~0.3%) or 7 and 9 g (Pt ~0.6%) in 600-ml beakers by heating with 200 ml of 6*M* hydrochloric acid on a hot-plate with a surface temperature of about 100°. (For precautions to guard against the pick-up of moisture and for the determination of "total solids" see reference 3.) Add from time to time a few ml of 30% hydrogen peroxide to aid in the dissolution of the platinum. Maintain the volume with 6*M* hydrochloric acid until dissolution is complete and the solution clear, then transfer to 1000-ml volumetric flasks. Should, however, a haze persist after 12 hr of heating, filter, and wash with hydrochloric acid (1 + 99). Transfer the clear solutions to 1000-ml volumetric flasks.

Platinum–rhenium catalyst. Decompose four different sample weights (chosen as above) in 600-ml beakers, by heating gently and with intermittent stirring, in a mixture of 100 ml of water, 20 ml of 25% sodium formate solution and 150 ml of sulphuric acid (1 + 1). When decomposition is complete, dilute to 400 ml with hot water, and simmer until the platinum has coagulated. Allow to cool, filter off on a retentive paper, and wash the beaker twice and the paper thoroughly with sulphuric acid (1 + 99). Wipe the beaker with a piece of moistened filter paper and add this to the funnel. Wash beaker and paper finally once with warm water. Keep the precipitation beaker, and either discard the filtrate or use it for the determination of rhenium.

Char the filter paper in a small porcelain crucible, gradually increase the temperature, and finally heat at about 750° for 10–20 min. After cooling, transfer the residue with a small stream of hot water to the precipitation beaker. Clean the crucible with 10 ml of hot *aqua regia* and add the solution to the beaker. Add an additional 15 ml of *aqua regia* to the beaker, heat for 5 min on a steam-bath, dilute with 25 ml of water, filter through a small paper into a 150-ml beaker, and wash the paper thoroughly with nitric acid (1 + 9).

Evaporate the solution to dryness on a steam-bath and repeat the evaporation twice with addition of 3 ml of 3*M* hydrochloric acid between successive evaporations. Dissolve the salts in 20 ml of 6*M* hydrochloric acid. Transfer the solutions to 1000-ml volumetric flasks.

Spent reforming catalysts. Heat four different sample weights ranging between 8 and 12 g in porcelain dishes for about 5 hr at 550° to destroy carbonaceous matter. Depending on the solubility of the alumina, treat the residue remaining after the ignition step either with sulphuric acid (1 + 1) and sodium formate as for Pt-Re catalysts or with sulphuric and phosphoric acids as for emission-control catalysts. Transfer the final solutions of the platinum to 1000-ml volumetric flasks.

Emission-control catalysts. The preferred method involves fire assay for the recovery of platinum and palladium in the residue.

Transfer different sample weights ranging between 12 and 18 g to 600-ml beakers. Add 50 ml of phosphoric acid and stir thoroughly with a rod to break up any lumps. Add 25 ml of water and stir. Add 50 ml of sulphuric acid, stir and place on a hot-plate with a surface temperature not exceeding 200°. Stir the solution intermittently during the heating. After the water has been expelled (5–10 min), dissolution of the sample is usually complete in about 20 min. If decomposition appears incomplete, cool for a few minutes, add 25 ml of water, and reheat.

Allow to stand, cool for about 10 min, add 100 ml of water, 15 ml of hydrochloric acid, and an excess of bromine water to effect dissolution of the platinum and palladium. Dilute with hot water to 400 ml and boil for a few minutes to expel excess of bromine. Small amounts of residual bromine do not interfere.

Add to the solution 5 mg of copper as chloride or sulphate solution, dilute to 500 ml with hot water, and pass hydrogen sulphide into the hot solution for about 20 min at a rate of about 300 ml/min. Again heat the solution to near boiling and repeat the treatment with hydrogen sulphide.

Filter off the sulphides on a 12-cm retentive paper containing a little filter pulp. Wipe the beaker and H_2S-tube with moistened filter paper and add this to the sulphides on the paper. Wash the beaker twice with sulphuric acid (5 + 95) containing some hydrogen sulphide, then once with cold water, adding the washings to the funnel. Set the beaker aside for further cleaning (see next paragraph). Wash the paper at least 12 times with the sulphuric acid (5 + 95) containing hydrogen sulphide, to remove the aluminium salts and phosphoric acid. Discard the filtrate.

Char the paper in a small alumina crucible in a muffle furnace at a low temperature, then heat to about 700° for 10 min. To the cooled crucible add 5 ml of hydrochloric acid and 2 ml of nitric acid, cover, and warm to dissolve the platinum and palladium. Wash the solution into a 150-ml beaker. Treat the 600-ml precipitation beaker with a little hot *aqua regia* and wash this solution also into the 150-ml beaker. Boil the combined solution to dissolve the platinum and palladium completely. Filter the solution through a small filter paper, into a 250-ml beaker, and wash thoroughly with nitric acid (2 + 98).

The residue may require treatment as below, if there is more than a few mg and it is discoloured. Otherwise, discard it, evaporate the filtrate to dryness on a steam-bath, and continue with the separation of Pt and Pd, as described below.

For treatment of the residue, ignite the paper in a 2-in. scorifier. Add 50 g of test lead, 20 mg of silver, and cover with 3 g of borax. Scorify until a lead button weighing about 20–25 g is obtained (this requires about 25 min at 900° and is complete when the molten lead is reduced in size to approximately 1 cm diameter in the centre of the molten slag). Cupel the lead button at approximately 900–950°. The resulting silver bead contains the traces of platinum and/or palladium retained by the material insoluble in *aqua regia.* Dissolve the silver in a 150-ml beaker in 20 ml of hot nitric acid (1 + 4). Add 3 ml of hydrochloric acid to precipitate the silver and dissolve platinum and palladium. Boil for about 5 min, dilute with 100 ml of water, and warm until the silver chloride has settled. Cool, filter off, and wash twice with nitric acid (2 + 98). Discard the silver chloride. Combine the filtrate with the main platinum- and palladium-bearing solution and evaporate to dryness on a steam-bath.

To separate platinum and palladium, dissolve the salts by heating with 30 ml of a mixture of concentrated perchloric and hydrochloric acids and water (2:1:97 v/v), cool, transfer the solution to a 125-ml separatory funnel, add 5 ml of sodium dimethylglyoximate solution and mix. Palladium will precipitate. Extract the palladium by shaking for 30 sec with 15 ml of chloroform. Run the chloroform phase into a 150-ml beaker if a palladium determination is required, otherwise discard it. Repeat the chloroform extraction until the solution is clear, indicating quantitative removal of the palladium.

Transfer the aqueous phase back to the 150-ml beaker previously used and evaporate the solution to dryness on a steam-bath. Add to the residue 10 ml of nitric acid and 5 ml of perchloric acid and evaporate to dryness at a low temperature. Stir the residue with a glass rod to ensure that all free perchloric acid is expelled. However, do not bake the salts.

Dissolve the residue by heating with 40 ml of 6*M* hydrochloric acid on a steam-bath. If the platinum content of the sample is 0.035% or less, wash the solution into a 100-ml volumetric flask. For a platinum content between 0.035 and 0.07% wash the solution into a 200-ml volumetric flask. For platinum contents between 0.07 and 0.15% use a 500-ml flask. Continue with the determination as in the next section.

If no fire-assay facilities are available, proceed as follows. Decompose the sample as already described. Filter the cold solution through a 12-cm retentive paper containing a little filter pulp, preferably by suction. Wipe the beaker with a piece of moistened filter paper and add this to the funnel. Wash the beaker twice and the paper ten times with dilute sulphuric acid (5 + 95). Reserve the filtrate. Ignite the paper in a vitreous graphite crucible at about 550°. Cool the crucible, wet the residue with a little water, add about 5 ml of hydrofluoric acid and 2 drops of sulphuric acid, and heat on a hot-plate until the silica and finally the acids have been expelled. Add 3–5 g of sodium bisulphate to the crucible, cover with a quartz or porcelain lid, and heat in a muffle furnace at 650° for about 20 min. Allow the crucible to cool, leach the melt in a 250-ml beaker with 50 ml of water and 5 ml of hydrochloric acid. Add a little bromine water to ensure complete dissolution of any platinum and/or palladium. Combine this solution with the filtrate reserved from initial dissolution. Precipitate the platinum and palladium with hydrogen sulphide as described above, omit the fire-assay treatment and continue with the separation of platinum and palladium.

Determination of platinum

Preparation of standards. The maximum concentration of platinum suitable for measurement is 65 μg/ml. The platinum for the standards must be weighed with an error of <0.1%. In view of the normal weighing error on microbalances, this means that a minimum of about 5 mg of platinum is needed. To make the standards, weigh on a microbalance such quantities of platinum that the platinum concentration in each sample will fall between that of two standards 5 μg/ml apart in concentration. The volumes of the standard solutions when ready for measurement (*i.e.*, after the reaction *etc.*) are best matched to those of the samples for which they are to be used. This means a maximum of 6.5 mg for a 100-ml flask, with 0.5-mg intervals between standards, 13 mg and 1-mg intervals for 200-ml flasks, 32.5 mg and 2.5-mg intervals for 500-ml flasks, 65 mg and 5-mg spacing for 1000-ml flasks. An alternative is to use appropriate portions of a platinum stock solution, always provided that the measurement error is <0.1% (weight fractions could be used, for example).

Transfer the standards to covered 50-ml beakers, and dissolve the platinum by warming with 5–15 ml of *aqua regia* (depending on the amount of platinum). After dissolution, wash off the cover-glass, evaporate the solution to dryness on a steam-bath, and repeat the evaporation twice, with addition of 1–2 ml of hydrochloric acid (1 + 3) in between. Dissolve the residue in 10 ml of hydrochloric acid (1 + 3), and transfer the solution to an appropriate volumetric flask.

Add to the volumetric flasks enough concentrated hydrochloric acid to make the final concentration 35% by volume. Add cold water until the flasks are three-quarters full and mix. Cool the solutions to 20 ± 2°. Add enough stannous chloride solution to make its final concentration 3% w/v. Dilute to volume and mix.

Allow the solutions to stand for 15 min to obtain maximum colour development, then measure the absorbance of standards and sample solutions as follows. Transfer sample solution and the two standards nearest to it in concentration to 1-cm cells. Using a wavelength of 403 nm, set the spectrophotometer zero with the lower standard in the light-beam. Then, measure the absorbance of the other standard and the sample relative to the lower standard. Repeat until the absorbance can be established within ±0.005 or better. Repeat for the other samples, using the appropriate pairs of standards.

Calculations. Calculate the amount of platinum in the sample as follows.

$$C_3 = \frac{(C_2 - C_1)A_2}{A_1} + C_1$$

where C_1 = mg of Pt in lower standard, C_2 = mg of Pt in higher standard, C_3 = mg of Pt in sample, A_1 = absorbance of higher standard, A_2 = absorbance of sample.

DISCUSSION

The decomposition steps described are applicable to any type of reforming and emission-control catalysts with the exception of those where, because of heat treatments, the catalyst has been largely converted into α-alumina. In the latter case, however, reasonably good recovery of platinum (about 99%) can be obtained as follows.

Mix the catalyst with a third of its weight of ammonium carbonate (to prevent the volatilization of any platinum halide) gradually heat to 1200°, cool, extract the platinum with *aqua regia*, and repeat the heating and extraction cycle on the insoluble residue. Alternatively, fuse the catalysts by fire-assay procedures with a flux consisting of litharge, borax, sodium carbonate and a reducing agent, such as starch, using silver and gold as collectors. Scorify the resulting lead button, if necessary, and cupel it to obtain a silver–gold bead containing the platinum. Dissolve the bead in dilute nitric acid, filter off the gold, and precipitate the silver as chloride. In the filtrate of the silver chloride determine the platinum as described in the main procedure. (For a discussion of various critical aspects of the fire-assay procedure and the treatment of the silver–gold bead see reference 14.)

Differential spectrophotometry

For a discussion of the optimum conditions for the colour development see reference 3. However, tests carried out in our laboratory indicate that it is not necessary to add aluminium chloride to the standards as required by reference 3. A 45-μg/ml platinum standard read against a 40-μg/ml standard gave identical absorbances of 0.213 ± 0.001 when read in the presence or absence of 45 mg of $AlCl_3 \cdot 6H_2O$ per ml.

The rationale for preferring differential measurement is as follows. A 20-μg/ml platinum solution will give an absorbance of about 0.8 in a 1-cm cell when

Table 1. Precision measurements

Amount of platinum used for zero adjustment setting, *mg*	Amount of platinum used to measure precision, *mg*	Volume, *ml*	Average absorbance reading	Precision of readings
0	0.50	100	0.203	±0.0025
5.00	5.51	100	0.204	0.0012
10.00	11.00	200	0.205	0.0014
25.03	27.52	500	0.204	0.0010
30.00	35.03	1000	0.203	0.0013
35.03	39.98	1000	0.203	0.0011
39.98	45.03	1000	0.204	0.0010
45.03	50.01	1000	0.204	0.0012
50.01	55.00	1000	0.203	0.0014
55.00	60.02	1000	0.203	0.0012
60.02	65.04	1000	0.202	0.0013
65.04	70.02	1000	0.198	0.0020

measured against water as reference. Suppose the measurement error is 1%. If an attempt is made to decrease the error by a factor of three by taking three times the concentration of platinum, the absorbance will be too high to be read even approximately. If, however, instead of water, standard platinum solutions are used for the zero-absorbance settings and the difference in platinum concentration of any pair of neighbouring standards is the same, then the difference in absorbance between neighbouring standards should also be the same (See Table 1), and correspond (if Beer's law is obeyed) to an absorbance of about 0.2 for a 5-μg/ml difference. Thus for a 54-μg/ml sample measured with the aid of 50 and 55 μg/ml standards (themselves prepared with <0.1% error) the overall error will be only about a tenth of the actual absorbance measurement error, so an absorbance error of 4% would still give an overall error of only about 0.4%.

In order to ensure that the measurements of the absorbances are matched by corresponding improvements in the platinum collection procedure, sample weights are intentionally chosen in the proposed methods so that they require the use of at least four different standards.

The maximum concentration of platinum which can be handled by the procedure is about 65 μg/ml in the solution measured. Above this, the slit-widths cannot be further adjusted and the colour system apparently departs from Beer's law. However, a small departure from Beer's law can be tolerated, if the platinum concentration does not exceed 70 μg/ml and not such a high degree of accuracy is required, since the measurement is still differential. Likewise, if the same concentration slightly exceeds that of the highest standard, meaningful results are obtained, as is illustrated by the following experimental results:

$$C_1 = 50.00\ \text{mg} \qquad C_1 = 55.05\ \text{mg}$$

$$C_2 = 55.05\ \text{mg} \qquad C_2 = 60.00\ \text{mg}$$

$$A_1 = 0.213 \qquad A_1 = 0.208$$

$$A_2 = 0.228 \qquad A_2 = 0.016$$

$$C_3 = \frac{(55.05 - 50.00)}{0.213} \times 0.228 + 50.00 = 55.41\ \text{mg} \qquad C_3 = \frac{(60.00 - 55.05)}{0.208} \times 0.016 + 55.05 = 55.42\ \text{mg}$$

Table 2

Type of catalyst	Pt reported, % Lab. A.	Lab. B	Umpire determination by proposed procedure, Pt, %	Relative standard deviation, %
Fresh catalyst (Pt only)	0.342	0.350	0.343	0.35
	0.330	0.340	0.333	0.40
	0.623	0.607	0.625	0.30
	0.644	0.632	0.640	0.28
Fresh catalyst (Pt–Re)	0.336	0.343	0.341	0.40
	0.328	0.320	0.321	0.43
Octafining catalyst	0.394	0.387	0.392	0.42
	0.399	0.409	0.403	0.57
Spent catalyst	0.297	0.313	0.301	0.35
	0.335	0.325	0.325	0.43
	0.343	0.352	0.344	0.42
	0.595	0.606	0.604	0.65
	0.613	0.627	0.614	0.70
	0.104	0.110	0.104	0.50

However, if an attempt is made to extend the measurements much beyond 0.25 absorbance units, because the system follows Beer's law, serious mistakes can be introduced as is demonstrated below.

Platinum concentration µg/ml	Absorbance measurement
25.06	0
30.06	0.197
35.06	0.387
40.06	0.559
45.00	0.694

The increase in the platinum colour follows Beer's law. The measuring device (photo tube), however, is unable to determine the linearity. Therefore the linearity cannot be proven by constructing a calibration curve, but only by the expedient of measuring differences in the absorbances in the range between 0 and 0.2.

Separation of platinum and palladium

For the determination of platinum in emission-control catalysts the platinum is separated by the dimethylglyoxime–chloroform extraction technique.[11,13] A re-examination of the optimum acid conditions led to the proposed perchloric acid–hydrochloric acid–water (2:1:97) medium. No palladium was found in the platinum fraction (detection limit 10 µg) and no palladium in the platinum fraction (detection limit 5 µg), when up to 10 mg of palladium was separated from up to 25 mg of platinum. Palladium can be determined in the chloroform extracts by evaporating off the chloroform layer, treating the residue with *aqua regia*, evaporating the solution to dryness, dissolving the salts in a measured volume of 2% potassium cyanide solution and determining the palladium by atomic-absorption spectroscopy, with palladium standards in cyanide medium.

Table 3. Effectiveness of the proposed procedure when applied to emission-control catalysts

Platinum added, *mg*	Palladium added, *mg*	Platinum found, *mg*	Error, %
5.035	2.0	5.04	+0.1
5.005	2.0	4.97	−0.7
5.515	2.2	5.53	+0.3
5.527	2.2	5.48	−0.8
6.528	2.6	6.47	−0.9
8.502	3.4	8.52	+0.2
9.005	3.6	8.95	−0.6
9.474	3.8	9.44	−0.4
10.051	4.0	9.99	−0.6
10.567	4.2	10.60	+0.3

Verification of accuracy of procedures

No standard samples of either type of catalyst were available. However, in the case of fresh reforming catalysts, in the course of determining platinum by the proposed procedure on an umpire basis, comparative results became available which are reported in Table 2.

It should be emphasized that the proposed methods of separation are also applicable if ordinary spectrometry is employed and the consequent lower accuracy is acceptable.

Since neither standard samples nor reliable comparison samples of emission-control catalysts were available, the following tests were carried out to prove the effectiveness of the collection steps. To the filtrates from the hydrogen sulphide separation, obtained while analysing catalysts from three different producers, measured amounts of platinum and palladium were added in the form of solutions of the chlorides, the platinum metal being weighed individually on a microbalance. The solutions containing the platinum and palladium were then carried through all remaining steps of the procedure. The results are reported in Table 3.

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SHORT COMMUNICATIONS

ATOMIC-ABSORPTION SPECTROMETRY OF LASER-NEBULIZED SAMPLES

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In flame-emission and atomic-absorption spectrometry, the solid sample introduction techniques applicable with simple table instruments have been the subject of several investigations. In recent developments some type of flameless atomization device such as a graphite tube furnace, a tantalum filament, an electric arc or a laser beam is used. The free atoms generated in this way can be detected directly. An alternative method involves the transport of the fine particles from the primary vaporization source into a secondary high-temperature zone where the aerosol particles are atomized and detected. The primary heating process can be considered as *thermal nebulization*. The following combinations of thermal nebulization and atomization–excitation sources are known: spark and flame,[1] d.c. arc and capillary arc,[2] d.c. arc and flame[3] and tantalum filament and inductively coupled radiofrequency plasma.[4] The arc and flame combination was developed in our laboratory for use with powdered samples.[5] Recently, a laser and flame combination has been introduced. Experiments with metals, solutions and non-metallic solid samples are described in this paper.

EXPERIMENTAL

In Fig. 1 an arrangement for a laser–flame combination is shown, which has a very simple transport system. A glass chamber is fixed by a rubber gasket around the mount of the objective lens. The chamber is open at the base to allow the exit of the laser beam and the entry of the sample vapours, and connected to the mixing chamber by the "ejector" which transports the sample by suction. A stoichiometric acetylene–air flame was used with an observation height of 10 mm. An air flow-rate of 11 l./min through the ejector nozzle produced a flow-rate of 3.2 l./min as carrier gas.

A Zeiss, Jena, Model LMA-1 laser microprobe apparatus was used, having a neodymium-doped glass laser rod, emitting at 1060 nm. The energy input and output are about 1000 and 1 J respectively at maximum. This apparatus operates without a Q-switch mode, and the pulse duration is 500 μs, comprising approximately 250 laser spikes. A Unicam Model SP 90A atomic-absorption spectrometer was used. Although the pulse duration of the laser beam was in the millisecond range, the duration of the half-peak absorption signal from the flame was about 1 sec, corresponding to the transit time of the aerosol through the transporting and mixing systems. No special demand on the response time of the detection unit is made and this is a critical point when direct laser atomization is used.[6,7] Statistical treatment of the peak signal and the integrated signal measurements has shown an equal precision, so that no integration is necessary with the laser–flame method.

The dimensions of the laser crater were studied for nickel-base alloys, as a function of the energy input and the focus. A distance of about 0.3 mm between the focus points of white light and of the infrared laser radiation was estimated. The best precision and absolute sensitivity were obtained with medium energy input and with focusing of the laser beam a distance of 0.3 mm above the sample surface (a displacement of 0.6 mm for the adjusting white light). Under these conditions a circular crater of 0.35 mm diameter was produced. No formation was detected of large droplets which might cause poor precision and low absolute sensitivity. Morton and co-workers[8] were able to produce deep conical craters without large droplet formation when perfect focusing and Q-switched laser beams were used.

In Fig. 2 an analytical curve for iron in nickel-base alloys is shown, each point representing an average of 5 measurements. The concentration range of iron is 8–92% and some alloys with high chromium and cobalt contents are also compared. The absorbance is proportional to iron concentration between 8 and 65% and variation of the major component has little effect. An average relative standard deviation of 7% was found.

In the application of the laser–flame method to solution analysis a photographic plate was used as the target. The photographic emulsion was developed after a strong exposure and showed high absorptivity for the laser light. A solution volume of 0.2 μl was applied to the emulsion surface and the residue was vaporized by a laser beam of medium energy. Analytical curves for sodium were linear up to 25 ng per 0.12 mm^2 whether plotted as peak absorbances without blank corrections or as integrated values from which the blank signal of the emulsion had been subtracted. Analytical curves having a similar character

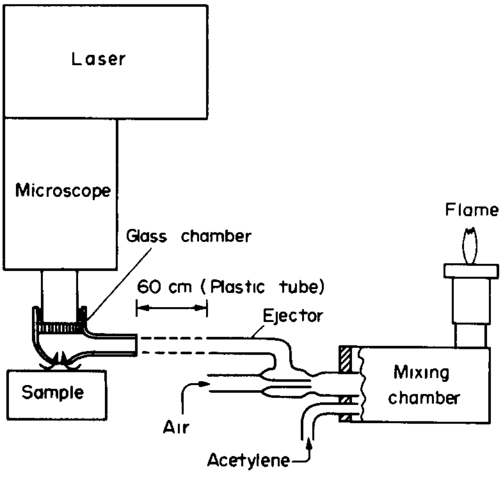

Fig. 1. Schematic diagram of the laser–flame combination.

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* Presented in part at EUROANAL II, Budapest, August, 1975.

Table 1. Analytical performance

Element and matrix	Energy input, # *J*	Out-of-focus,‡ *mm*	Detection limit¶ %	Detection limit¶ *ng*	Rel. std. devn., %	Concentration range, %
Fe*	920	0.0	0.5	20	24	10–90
Fe*	650	+0.3	0.9	7	6.8	10–90
Fe†	820	−0.3	0.1	4	9 4	0.1–0 8
Na§	1020	0.0	0.009	0.2	12	0.04–0.2
Na†	820	−0.3	0.008	0.3	13	0.02–0.2
Cd†	820	−0.3	0.01	0.4	8.2	0.02–0.2
Cu†	820	−0.3	0.04	2	12	0.1–0.8
Zn†	820	−0.3	0.01	0.4	10	0.05–0.5

* Nickel-base alloy.

† Gelatine with silver grains, developed photographic plate.

§ Pressed corundum plates.

\# Energy input was varied by the voltage on the flash lamp.

‡ Out-of-focus corresponds to the distance of the infrared laser beam focus above (positive) or below (negative) the sample surface.

¶ The most sensitive resonance line for each element was selected.

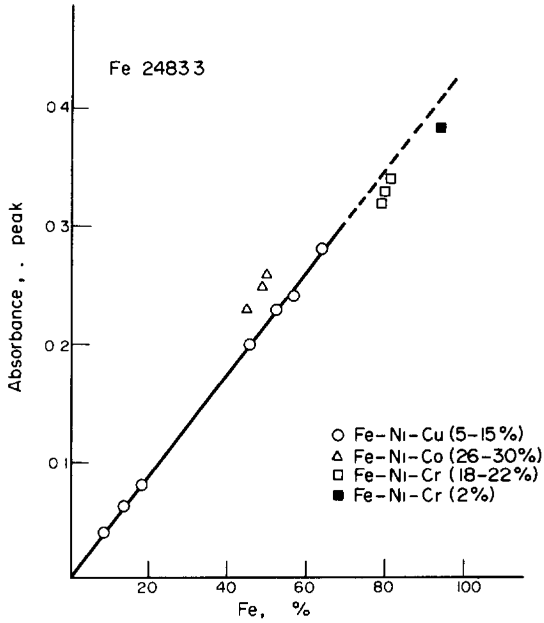

Fig. 2. Analytical curves for iron in nickel-base alloys.

were established for iron, cadmium, copper and zinc solutions.

Sodium in the 0.04–0.2% concentration range could be determined in the corundum plates used in the electronics industry. A series of these plates was analysed by other methods and were used as standards for the laser–flame method, the highest energy input being used.

RESULTS

In Table 1 the analytical performance for metals, solutions and solid (corundum) samples is summarized. In the first row data are given for those cases in which deep craters in alloys were produced. Some improvement in the relative detection limits appears, with a high loss in precision and absolute detection limit, but the average relative standard deviation is 10% and this is sufficient for many purposes. The absolute detection limits are in the ng range for the elements studied. Relative detection limits are calculated from the weight of gelatine (as organic matrix) removed by the laser beam.

CONCLUSIONS

These experimental results suggest that the formation of solid aerosols at elevated temperatures is governed by laws which allow us to use this process in quantitative analysis. The concentration of fine particles is proportional to the amount of the sample evaporated even under the conditions of non-stationary vaporization. The techniques are simple and make possible separate optimization of the nebulization and the atomization–excitation steps.

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Summary—Thermal nebulization of nickel-base alloys, corundum plates and residues of solutions was performed with a laser beam. The solid aerosol was aspirated into an acetylene–air flame by an ejector. Linear analytical curves in wide concentration ranges were established and an average relative standard deviation of 10% was found. The detection limit is in the ng range for iron and copper, and lower for zinc, cadmium and sodium.

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ACID-BASE EQUILIBRIA IN ETHYLENE GLYCOL—III
SELECTION OF TITRATION CONDITIONS IN ETHYLENE GLYCOL MEDIUM, PROTOLYSIS CONSTANTS OF ALKALOIDS IN ETHYLENE GLYCOL AND ITS MIXTURES

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The main purpose of this series of papers[1,2] is the development of a general approach for the selection of the most appropriate conditions for volumetric determination of acids and bases in ethylene glycol (EG). For many non-aqueous solvents this selection is usually made empirically, but in the present treatment a somewhat different approach is proposed. EG has properties very similar to water: amphiprotic behaviour, relatively high dielectric permeability, tendency to form hydrogen bonds *etc.*, which is why some methods used for the selection of suitable titration conditions in water could, in principle, be applied to EG. A number of methods based on examination of the titration curve are used for this purpose,[3–6] but the graphical method[5,6] is probably the easiest. For its application, the acid-base constants of all protolytes taking part in the titration equilibrium have to be known. That is why in the previous papers the autoprotolysis constants of EG and its mixtures[1] and the constants of some acid-base indicators[2] were determined.

The present paper describes the method for selection of the titration conditions. Since EG is most frequently used as a solvent medium for the titration of water-insoluble weak bases,[7] a number of alkaloids were studied in this investigation, and this necessitated determination of their protolysis constants in EG medium.

EXPERIMENTAL

Reagents

Ethylene glycol, its mixtures and the titrants were purified, prepared and standardized as described earlier.[1,2] Reagent-grade codeine and ephedrine were used after drying in a vacuum desiccator, without purification. Morphine, papaverine and quinine were prepared by making alkaline aqueous solutions of their hydrochloride and recrystallization from ethanol–ether mixture.

Apparatus and procedure

The protolysis constants were determined by potentiometric titration using a cell without liquid junction, equipped with a glass and a silver–silver chloride electrode:

$$\begin{array}{c} \text{glass} \\ \text{electrode} \end{array} \Big\| \, 0.1M(\mathrm{B + KCl + HCl}),\ \mathrm{SH} \,\Big|\, \mathrm{AgCl\text{-}Ag}$$

The experimental arrangement and the procedure was the same as before.[1] The temperature was kept at 25° ± 0.2°. Standardized 0.1*M* hydrochloric acid was used to titrate *ca.* 0.01*M* alkaloid solution in 0.1*M* potassium chloride. The titration was continued after the equivalence point so as to yield data which were used to calibrate the electrochemical cell for the particular experiment.

The e.m.f. of the cell (E) at 25° is given by the equation

$$E = E^{0'} - 0.05916 \log[\mathrm{SH_2^+}] \qquad (1)$$

The $E^{0'}$-value of the cell was calculated from the titration data after the equivalence point by means of equation (1). From this equation it follows that

$$\mathrm{p}c_{\mathrm{H}} = -\log[\mathrm{SH_2^+}] = \frac{E - E^{0'}}{0.05916} \qquad (2)$$

The protolysis of the conjugate acid ($\mathrm{BH^+}$) of the alkaloid (B) in EG or EG mixture (SH)* can be presented by the equation

$$\mathrm{BH^+ + SH = B + SH_2^+} \qquad (3)$$

The concentration ($K^c_{\mathrm{BH^+}}$) and the thermodynamic ($K_{\mathrm{BH^+}}$) protolysis constants are given by the equations:

$$K^c_{\mathrm{BH^+}} = [\mathrm{SH_2^+}]([\mathrm{B}]/[\mathrm{BH^+}]) \qquad (4)$$

$$K_{\mathrm{BH^+}} = \{\mathrm{SH_2^+}\}(\{\mathrm{B}\}/\{\mathrm{BH^+}\}) = K^c_{\mathrm{BH^+}} f_{\mathrm{SH_2^+}} (f_{\mathrm{B}}/f_{\mathrm{BH^+}}) \qquad (5)$$

Since $[\mathrm{BH^+}] = [\mathrm{HCl}] + [\mathrm{S^-}]$ and $[\mathrm{B}] = [\mathrm{B}]_{\mathrm{tot}} - [\mathrm{HCl}] - [\mathrm{S^-}]$, from (2) and (4) a relationship can be written, which is used in practice for calculation of the $\mathrm{p}K^c_{\mathrm{BH^+}}$-values:

$$\mathrm{p}K^c_{\mathrm{BH^+}} = \frac{E - E^{0'}}{0.05916} + \log \frac{[\mathrm{HCl}] + [\mathrm{S^-}]}{[\mathrm{B}]_{\mathrm{tot}} - [\mathrm{HCl}] - [\mathrm{S^-}]}$$

where [HCl] is the molar concentration of the added acid, $[\mathrm{B}]_{\mathrm{tot}}$ is the total concentration of the alkaloid base determined by a Gran plot,[8] and $[\mathrm{S^-}]$ is the molar concentration of the lyate ion of the solvent. The latter was calculated only for $\mathrm{p}c_{\mathrm{H}} > 10$, from the values of the concentration autoprotolysis constants.[1]

As an illustration of the method used for calculation of the protolysis constant, the experimental data from a potentiometric titration and their treatment for the determination of the $\mathrm{p}K^c_{\mathrm{BH^+}}$-value of codeine in EG are shown in Table 1.

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* In this work as in the previous one,[1] the EG mixtures are treated as separate solvents with their own acid–base properties and dielectric constant.

Table 1. Experimental data and their treatment for the calculation of $pK^c_{BH^+}$ of codeine in ethylene glycol

V_{HCl}, *ml*	E_{meas}, *mV*	$E^{0}_{''}$ *mV*	pc_H	$-\log[BH^+]/[B]$	$pK^c_{BH^+}$
0.600	+95.4		9.773	−0.415	9.358
0.800	+85.5		9.597	−0.230	9.367
1.000	+76.2		9.448	−0.064	9.384
1.200	+66.9		9.291	+0.097	9.388
1.400	+56 9		9.112	+0.265	9.387
1.600	+45.4		8 927	+0.456	9.383
1.800	+30.4		8.669	+0.699	9.368
2.300	−293.5	−482.9	Mean $pK^c_{BH^+}$ = 9.376 ±0.011*		
2.400	−307.2	−482.9			
2.500	−315.8	−482.7			
2.600	−322.0	−482.4			
2.800	−331.6	−482.6			
3.000	−338.5	−482.7			
3.200	−343.9	−482.8			
Mean $E^{0'}$ = −482.7 ± 0.2*					

Conditions: 20 ml of $1.08 \times 10^{-3}M$ codeine titrated with 0.1001 *M* hydrochloric acid in ethylene glycol 0.1*M* in potassium chloride. The base was neutralized with 2.160 ml of hydrochloric acid (this volume was determined by Gran plot).

* Confidence interval ($p = 0.95$)

If it is assumed that the activity coefficients in equation (5) are $f_{SH_2^+} = f_{BH^+}$ and $f_B = 1$, then the concentration constants determined in the described manner are equal to the thermodynamic ones. The identical values obtained for the constants by measurements at two different ionic strengths (0.1 and 0.05), confirm the validity of this assumption.

The protolysis constants of the conjugate acids of some alkaloids (pK_{BH^+}) determined in the present work in both EG and its mixtures are given in Table 2. In the same table the protolysis constants for the corresponding bases (pK_B) computed by the well-known relation $pK_B = pK_S - pK_{BH^+}$ are also given. The K_S values are the autoprotolysis constants of the solvent, determined in the previous work.[1]

OUTLINE OF THE METHOD

The theoretical titration curves of all the alkaloids were constructed. The curves were drawn by a graphical method,[6] based on the logarithmic concentration diagram, (lc-diagram). This type of diagram is widely used for the presentation of acid–base equilibria in aqueous media, but so far has not been applied to a non-aqueous medium. An essential difference when the lc-diagram is applied to a non-aqueous solvent is the length of the pH-scale, which, as well known, is defined by the autoprotolysis constant (pK_s) of the solvent. In Fig. 1 the construction of a titration curve for 0.01*M* codeine is shown. The left hand part represents an lc-diagram. Note that the length of the pH-scale, in accordance with the autoprotolysis constant of EG, is 15.7 units. The basic principles and construction details of the lc-diagram are discussed in full by Sillén[9] and other authors,[10,11] and therefore no details will be given here. It will only be mentioned briefly how titration curves are constructed by using an lc-diagram.

Point 1 in the lc-diagram (see Fig. 1) represents the initial pH-value of the EG solution 0.01*M* in alkaloid (B). This point is transferred to the right-hand part of the figure at position 1′ at $Y = 0\%$ added titrant. Point 2 represents the pH-value of a 0.001*M* solution of BH^+, hence 10% of the alkaloid **B** present has been converted into its conjugate acid BH^+. Therefore point 2 is transferred to 2′ at $Y = 10\%$. The crossing point 3 corresponds to the equality $[B] = [BH^+]$, hence this point is transferred to $Y = 50\%$ (3′). Point 4 corresponds to a pH-value of a solution which contains 10% of the initial concentration of the free base and point 4 is transferred to 4′ where $Y = 90\%$. Similar considerations transfer point 5 to 5′ at $Y = 99\%$, 6 to 6′ at $Y = 99.9\%$. Point 7 is the pH-value of a 0.01*M* solution of BH^+, hence 7 is transferred to 7′ at $Y = 100\%$. After this point the lyonium ions are in excess, consequently their concentration can be read from the SH_2^+-line. It is obvious then, that point 8 corresponds to a surplus of the acid, or $Y = 100.1\%$. Similarly, points 9, 10 and 11

Table 2. Protolysis constants* of alkaloids in ethylene glycol and its mixtures†

	EG		EG–E		EG–W		EG–EMK–Ch	
Alkaloid	pK_{BH^+}	pK_B	pK_{BH^+}	pK_B	pK_{BH^+}	pK_B	pK_{BH^+}	pK_B
Quinine I	5.23	10.49	5.25	10.66	4.49	10.36		
Papaverine	7.25	8.47	7.30	8 61	6.52	8.33	7.14	8.67
Codeine	9.38	6.34	9.42	6 49	8.71	6.14		
Morphine	9 51	6 21	9.47	6.44	8.81	6.04	9.31	6.50
Quinine II	9.90	5.82	9.94	5.97	9.18	5.67		
Ephedrine	11.29	4.43	11 21	4.70	10.46	4 39		

* Confidence interval pK_{BH^+} ± 0.01 ($p = 0.95$)

† Symbols: EG—ethylene glycol, E—ethanol (10%), W—water (5%), EMK–Ch—ethyl methyl ketone–chloroform (5 + 5%).

are transferred to $Y = 101$, 110 and 200%. After the main points of the titration curve are known, it is an easy matter to draw the full line as shown in Fig. 1. The part of the titration curve which covers the pH-values corresponding to $Y = 99.9$–100.1% may be called the *equivalence region* of the titration curve. For end-points within this range of pH-values the error of the titration is less than or equal to $\pm 0.1\%$. It must be added that the equivalence region is easily found from the lc-diagram as shown by an arrow in Fig. 1.

After the theoretical curve is known, an appropriate acid–base indicator can be chosen for the detection of the end-point. Obviously the transition interval of the indicator must coincide with the equivalence region of the titration curve. As can be seen from Fig. 1, Bromophenol Blue (BPB) is a very suitable indicator for the accurate ($\pm 0.1\%$) determination of codeine in EG.

There is quite good agreement between the theoretical titration curve and the experimental data as shown in Fig. 1, where the open circles denote the experimentally measured pH-values. Also in accordance with theory, a very sharp colour change was observed with Bromophenol Blue as indicator.

Figure 2 shows the theoretical curves for $0.01M$ solutions of the alkaloids investigated, constructed similarly.

DISCUSSION

The results from this series of investigations show that acid–base equilibria in EG are simple and similar to those in water. This allows the application of methods commonly used in investigations of acid–base equilibria in water solutions. The utility of EG and its mixtures as a medium for the determination of water-insoluble weak bases has been proved by means of a detailed study.

From the theoretical curves (Fig. 2) it is shown that the visual titration error is $\pm 0.1\%$ for 0.01 or $0.1M$ solution of these alkaloids in EG and its mixtures, except for quinine and papaverine where the error may be up to $\pm 0.5\%$. The water content (5%) of EG, though it makes the titration conditions worse by shortening the equivalence region of the curve, does not affect the accuracy of the determination. It is found both theoretically and experimentally that the most suitable indicator for titration of the alkaloids investigated was Bromophenol Blue ($pK^c_{HI} = 6.49$), except for quinine, for which Bromocresol Green ($pK^c_{HI} = 7.38$) was best.

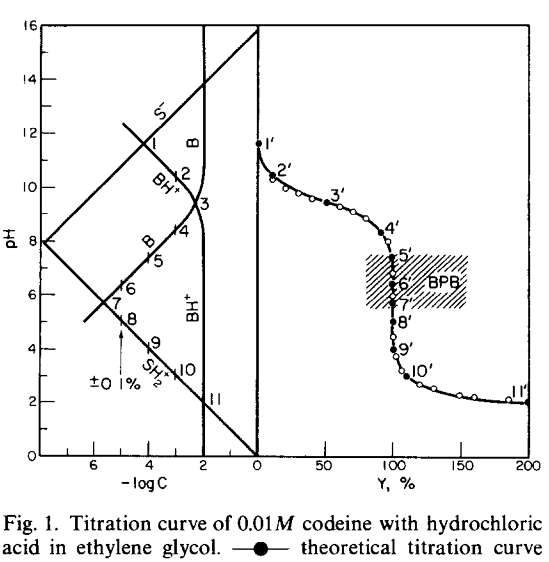

Fig. 1. Titration curve of $0.01M$ codeine with hydrochloric acid in ethylene glycol. —●— theoretical titration curve ○ experimental data

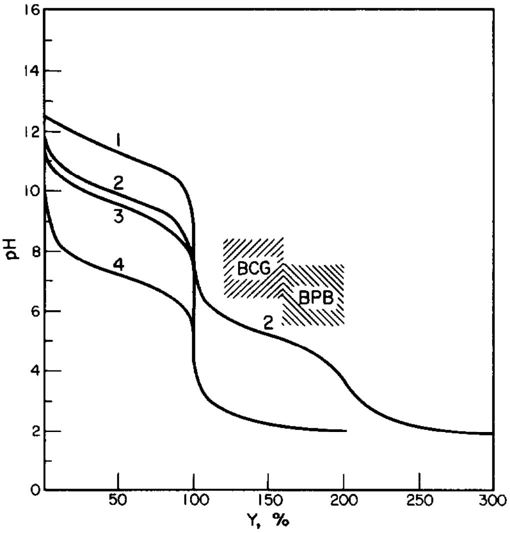

Fig. 2. Theoretical titration curves of $0.01M$ solutions of ephedrine (1), quinine (2), morphine (3) and papaverine (4) in ethylene glycol.

According to theoretical considerations,[12] the titration of bases is improved in solvents that decrease the K_S/K_B ratio, *i.e.*, increase the pK_{BH^+}-value. The pK_{BH^+}-values of the alkaloids in EG and EG mixtures, compared with the corresponding values in water, 10% acetone–water, methanol and formic acid[12] show that EG as medium provides better titration conditions.

The pK_{BH^+}-values in EG (Table 2) are on average 1.5 units higher than those in water. Since the protolysis of charged acids of the type BH^+ does not involve any charge separation [equation (3)], the decrease of the acid strength can be attributed to the lower basicity of EG.[13] Because EG is more acidic than water,[1,13] a greater basicity of the alkaloids should be expected. Nevertheless, Table 2 shows that the pK_B-values are on average 0.3 units higher in EG than in water. Since the protolysis of an uncharged base (B) is accompanied by charge separation, this difference can be explained by the influence of the lower dielectric permeability of EG. The addition of ethanol (10%) and ethyl methyl ketone–chloroform (5 + 5%) does not affect significantly the strengths of the bases and their conjugate acids. The addition of water, as expected, leads to an increase in the acid strength—the pK_{BH^+}-values are on an average 0.7 units lower in EG–water (5%) mixture than in pure EG.

The results obtained in this series of papers provide a means of avoiding the empirical approach for the selection of titration conditions for this non-aqueous solvent. The convenient potentiometric method permits an accurate determination of the constants needed for the construction of the theoretical titration curves. These curves constructed by the lc-diagram method allow a rapid and accurate enough prediction of the titration conditions, *viz.* evaluation of the titration error, choice of a proper indicator, appropriate concentration of the base to be titrated, *etc.* There is reason enough to expect that the same approch could be extended to other amphiprotic solvents possessing properties similar to those of EG.

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Summary—Theoretical titration curves are used for the selection of appropriate conditions for the acid–base volumetric determination of weak bases in ethylene glycol medium. The theoretical curves for titration of some alkaloids are deduced graphically on the basis of the logarithmic concentration diagram. The acid–base constants used for the construction of the theoretical titration curves were determined by potentiometric titration in a cell without liquid junction, equipped with a glass and a silver–silver chloride electrode. It is shown that the alkaloids investigated can be determined accurately by visual or potentiometric titration. The same approach for the selection of titration conditions seems to be applicable to other non-aqueous amphiprotic solvents.

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CONCENTRATION AND SEPARATION OF TRACE METALS WITH AN ARSONIC ACID RESIN*

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Because of their selectivity for heavy metals, chelating resins have been used for the concentration and separation of trace metals in food extracts,[1,2] oil-field brine,[3] industrial waste waters,[4] geological samples,[5] and sea-water.[6–8] Most of this work was performed on Dowex A-1 (Chelex 100), which has an iminodiacetic acid functional group. Dowex A-1 is a gel-type resin which undergoes pronounced swelling and shrinking. This resin has rather slow kinetics and a comparatively high affinity for calcium and magnesium.[6,9]

To meet the growing needs of ecological research in pollution control[10] and elsewhere, new chelating resins are continually being developed. Among those showing promise for trace metals are dithiocarbamate,[11,12] natural polymer,[13] 8-aminoquinoline,[14] polyamine–polyurea[15] and isothiouronium[5] exchangers. Hirsch *et al.*[16] started with a macroporous polystyrene–DVB resin and prepared a resin containing the iminodiacetic acid functional group and another containing an arsonic acid group. Macroporous resins are much less susceptible to swelling and shrinking and appear to have faster reaction kinetics than gel-type chelating resins.

A series of macroporous arsonic acid resins has now been prepared by a synthetic method similar to that used by Hirsch *et al.*[16] The effect of varying pore diameter and surface area on the properties of the final resins has been studied. These arsonic acid resins are now proposed for the concentration of trace metal ions from hard water and sea-water.

EXPERIMENTAL

Apparatus

A Milton Roy Pump No. 19-60029-003 or helium pressure was used to maintain a constant flow-rate through the resin column.

An RIDL AEC 320-3 single-channel analyser was used for counting the activity of the radiotracers, at a window setting of 1.3 MeV.

Plasma emission analyses were performed on the ICP-OES system built at Ames Laboratories.

Reagents

XAD-1, -2, and -4 macroporous resins were obtained from Rohm and Haas. The 150–200 mesh resin was prewashed with acetone and concentrated hydrochloric acid

For all trace analyses 0.5 g of resin IV was packed in a column measuring 2.8 × 0.6 cm.

^{54}Mn, ^{65}Zn, and ^{59}Fe gamma-emitters with 99% radiometric purity were obtained from New England Nuclear

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Co. Synthetic sea-water was made according to Lyman and Fleming.[17]

All chemicals were of the highest available purity.

Synthesis

The synthesis used was adapted from methods used by Hirsch.[16] The resin was nitrated with a 60/40 v/v mixture of sulphuric and nitric acids at 65–70° after addition at 0°. It was reduced to the amine with mossy tin in conc. hydrochloric acid at 70–75°. The reduction product was slurried with 1*M* sodium hydroxide to remove tin salts, chilled to 0° in conc. hydrochloric acid, and diazotized by slow addition of 1*M* sodium nitrite. The resin was washed with sodium carbonate solution and coupled with sodium arsenite in aqueous soln at 70–75°. All reactions other than diazotization were allowed to proceed for half a day.

Infrared spectra of the phenylarsonic acid resins I, II and IV and the monomeric acid were taken on a Beckman IR7.

The 2.9 μm arsonic acid O–H stretch was visible for each of the three resins and matching bands in the region of 11.0–13.0 μm were found in the resins and the monomer that can be ascribed to the arsonic acid group.

Recovery

The recovery of trace metal ions was determined as a function of the effluent pH. One litre of distilled demineralized water containing 0.5 ppm of the metal ion was buffered to the appropriate pH and passed through the resin at a flow-rate of 7 ml/min. After collection and washing, the adsorbed metals were stripped from the column with 25 ml of 4.0*M* perchloric acid and determined by plasma emission, atomic absorption or colorimetrically with Arsenazo I.

Complexing agents

To 250 ml of distilled demineralized water containing 10 ppM (parts per milliard) of metal ion (including radiotracer) and 10 ppm of complexant, 5 or 6 drops of orthophosphoric acid were added. The phosphoric acid was added as a buffer and was necessary for 100% recovery of iron(III). The pH was adjusted to 5.0 and the solution was passed through the column at 7 ml/min. The metals were then stripped from the column with 25 ml of 4*M* perchloric and the activity of an aliquot of the effluent was measured.

Recovery of trace metals

One litre of distilled demineralized water, tap-water, or synthetic sea-water at pH 5 and containing 0.5 ppm of heavy metals was passed through the resin at 7 ml/min, followed by 100 ml of metal-free pH-5.0 solution, and the metals were eluted with 25 ml of 4*M* perchloric acid and determined by plasma emission or atomic absorption.

For trace metals at sub-ppM level, the procedure was similar, but with 5 ml of 2 μCi/ml tracer solution replacing the 0.5 ppm of heavy metals. Detection was by gamma emission.

In the analysis of the tap-water, no metal ions were added.

Separation of uranium(VI) from other heavy metals

A 1-litre sample containing 0.5 ppm of uranium(VI) and other heavy metals and 0.01*M* in EDTA was buffered to pH 5.0 with orthophosphoric acid and ammonia and passed through the resin column at 7 ml/min. The column was then washed with 100 ml of 0.01*M* EDTA at pH 5.0 and 100 ml of pH-5 wash-solution (both solutions buffered with phosphoric acid and ammonia). The column was then stripped with 25 ml of 4*M* perchloric acid. The uranium was determined colorimetrically and the other heavy metals were determined by plasma emission

Separation of thorium(IV) from other heavy metals

A litre sample containing 0.5 ppm of thorium(IV) and other heavy metals and 0.1*M* in perchloric acid was passed through the resin at 7 ml/min. The resin column was washed with 100 ml of 0.1*M* perchloric acid and the thorium was then stripped from the column with 25 ml of conc. perchloric acid and determined by plasma emission.

Batch abstraction of trace metals

Resin IV, 0.5 g, was added to 250 ml of pH-5.0 solution containing 2.0 ppm of the heavy metals. The solutions were stirred for 2, 6, or 24 hr before collection of the resin. The adsorbed metals were washed from the resin with 25 ml of 4*M* perchloric acid.

RESULTS AND DISCUSSION

Arsonic acid resins were prepared from XAD-1, -2, and -4, which are macroporous polystyrene–DVB resins of varying pore size and surface area. The arsonic acid resins are designated I, II and IV, corresponding to the numbers of the XAD-resin starting material. The physical properties of the three resins are summarized in Table 1. Each of the three resins contains a nitrogen-containing group as an impurity although less than reported by Hirsch.[16] The resin IV synthesis was repeated and the yield in each step was estimated by analysis for the appropriate functional group. Nitration gave approximately 1.2 nitro groups per benzene ring. Reduction to the amine gave approximately 0.8 amine group per benzene ring, 67% yield. Conversion into the arsonic acid then gave approximately 0.6 arsonic acid group per benzene ring for an overall yield of about 50%.

The ratios of arsonic acid group per benzene ring and acidic hydrogen atoms per benzene ring were calculated from the arsenic and hydrogen analyses, the average molecular weight per resin unit being based on the calculated arsonic acid content and the remainder assumed to be 50% styrene and 50% DVB. The acidic hydrogen content is more than the 2:1 ratio of H:As expected for an arsonic acid group and probably represents titratable protonated amine. Although the exact values may be somewhat in question the trend seems clear; conversion into the arsonic acid is highest in resin I and lowest in resin II The large pores in XAD-1 appear to lead to high reactivity In XAD-4 the very high surface area is able to compensate for the smaller pores and good conversion into the arsonic acid was obtained.

Table 1. Properties of the XAD-arsonic acid resins

	Surface area, m^2/g	Pore diam., Å	As/benzene ring	H/benzene ring	C, %	H, %	N, %	Kinetics
AsO_3H_2-XAD I	100	205	2.4	5.2	52.8	5.2_5	3.3	Slow
AsO_3H_2-XAD II	300	90	0.3	0.8	58.1	5.4	5.0	Rapid
AsO_3H_2-XAD IV	784	50	0.75	1.8	51.3	5.2	3.2	Rapid

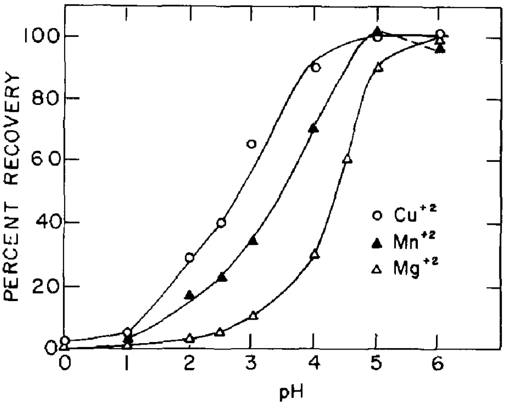

Fig 1. Effect of pH on recovery of Cu(II), Mn(II) and Mg(II).

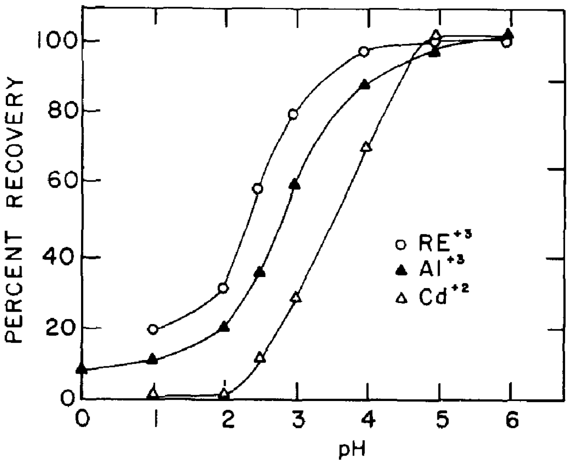

Fig. 3. Effect of pH on recovery of RE(III), Al(III) and Cd(II). (RE = rare earths).

Column experiments with various metal cations indicated that the kinetics of resins II and IV are excellent and those of resin I somewhat slow. Because of this and the higher capacity of resin IV (compared to resin II), resin IV was chosen for all subsequent experiments. This resin has little swelling tendency and is stable even in the concentrated acid and base solutions used to wash the resin and to strip some metal ions from the resin.

Small columns packed with resin IV were equilibrated with buffered aqueous solutions. Then solutions of various metal ions buffered to the same pH were passed through the column and the amount of metal ion retained by the column was determined. The degree of retention as a function of pH is plotted for various metal ions in Fig. 1–3. The selectivity order for metal ions, based on the assumption that the more stable complexes are retained at lower pH, is as follows: $Th^{4+} > UO_2^{2+} > RE^{3+} > Cu^{2+} > Pb^{2+} > Al^{3+}, Fe^{3+} > Zn^{2+} > Ni^{2+}, Co^{2+} > Cd^{2+}, Mn^{2+} > Mg^{2+}$ (RE = rare earths). This is in agreement with the order reported by Hirsch[16] of $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$.

Separation of thorium(IV) from all other metal ions studied was possible because of the affinity of resin IV for thorium at low pH values. Recovery of thorium at pH 1.0 was 102.5% (from spectrophotometric determination), with less than 1% of any of the other metal ions being retained. A successful separation of uranium(VI) from other metal ions was accomplished by adding EDTA to complex the foreign metal ions. Spectrophotometric analysis showed 98.3% recovery of uranium(VI) at pH 5.0 in 0.01*M* EDTA medium. Chromium(III) was the only interference (11% recovery).

Eight trace metals were added to demineralized water, tap-water and synthetic sea-water, the pH was adjusted to 5.0 and 1-litre samples were passed though a resin IV column. The sorbed metal ions were then eluted with 25 ml of 4*M* perchloric acid and the metal ions determined by plasma emission or atomic-absorption spectroscopy. The results, shown in Table 2, indicate excellent recovery except for chromium(III), which has a very slow reaction rate with ligands. With use of radiotracers, the experiment was repeated for three metal ions at the ppb (parts in 10^{12}) level. As shown in Table 3, the recovery is still quantitative within experimental error, even in the presence of a large

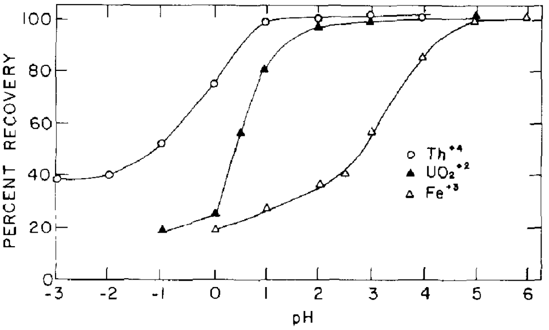

Fig. 2. Effect of pH on recovery of Th(IV), U(VI) and Fe(III).

Table 2. Recovery of trace metals in aqueous media with resin IV

Metal ion	Recovery,* % Pure water	Recovery,† % Tap-water	Recovery,† % Sea-water
Cd^{2+}	102	98.7	100.5
Co^{2+}	100	102.3	104.0
Cr^{3+}	74^5	57^3	—
Cu^{2+}	103	96.8	101.0
Fe^{3+}	101^5	101.2	102.0
Mn^{2+}	97	97.2	22
Ni^{2+}	101	100.5	105
Pb^{2+}	98	100.3	100.3
Zn^{2+}	98	96.0	100.8

* Plasma emission.
† Atomic absorption

Table 3. Recovery of metals at ultra trace level in aqueous media with resin IV

Metal	Conc., *ppb**	Recovery, % Pure water	Recovery, % Tap-water	Recovery, % Sea-water
Fe^{3+}	38	105.6	101.2	106.3
Mn^{2+}	5	96.2	97.2	94.6
Zn^{2+}	32	97.2	94.9	100.8

* Parts per billion (10^{12}).

Table 4. Recovery of trace metals in ISU tap-water with resin IV, *ppM**

	Ni	Zn	Fe	Pb	Mn	Cu
No. 1	41.2	66.2	123.7	11.2	91.3	900
No. 2	40.0	68.8	123.7	11.2	56.3	1160
No. 3	36.2	65 0	127.5	16.2	105.0	1160

* Parts per milliard (10^9).

excess of sodium, magnesium and calcium salts. Triplicate analyses of tap-water were also carried out (Table 4).

The effect of complexing agents on the recovery of zinc(II), manganese(II) and iron(III) at 10 ppm concentrations was studied by adding a thousandfold w/w ratio of various complexing reagents. The added reagents included acetate, anthranilate, chloride, citrate, glycine, phosphate, salicylate, succinate, urea and EDTA. The recovery of manganese and zinc was unaffected by any of the complexants except EDTA. The recovery of iron was low in the presence of substances that form complexes having a stability constant greater than 10^8.

Comparative studies showed resin IV to be more effective for retention of trace metal ions when used in a column than for batch collection. For example, by the batch method recoveries were only about 90% for copper(II) and lead, 70% for iron(III), 40% for nickel, and 15% for cadmium.

Some calcium and magnesium is retained by the arsonic acid resin column at pH 5.0. If desired, about 95% of the calcium and magnesium retained by the column can be removed by elution with pH 4.0 buffer before the trace metal ions are stripped with 4–12*M* perchloric acid.

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CATION-EXCHANGE OF Mn(II), Cd(II), Co(II), Ni(II), Cu(II), Al(III) AND Fe(III) IN TARTRATE MEDIA*

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The ion-exchange behaviour of inorganic ions in citric[1] and formic[2] acid media has been reported. Anion-exchange in tartaric acid media has been studied by Pitstick *et al.*[3] and Morie *et al.*[4,5] who describe the separation of some transition metals. Cation-exchange studies[6–9] have resulted in the resolution of a limited number of metal ions. Qureshi *et al.*[10] have separated Fe(III) and other metal ions in formic, oxalic, tartaric and citric acid media, but the only comprehensive investigation was made by Rouchaud *et al.*[11] They examined both cation- and anion-exchange and determined distribution coefficients for several ions in tartaric acid media containing nitric acid.

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* This work was supported in part by C.N.R. of Italy

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The ion-exchange behaviour of inorganic ions in citric[1] and formic[2] acid media has been reported. Anion-exchange in tartaric acid media has been studied by Pitstick *et al.*[3] and Morie *et al.*[4,5] who describe the separation of some transition metals. Cation-exchange studies[6–9] have resulted in the resolution of a limited number of metal ions. Qureshi *et al.*[10] have separated Fe(III) and other metal ions in formic, oxalic, tartaric and citric acid media, but the only comprehensive investigation was made by Rouchaud *et al.*[11] They examined both cation- and anion-exchange and determined distribution coefficients for several ions in tartaric acid media containing nitric acid.

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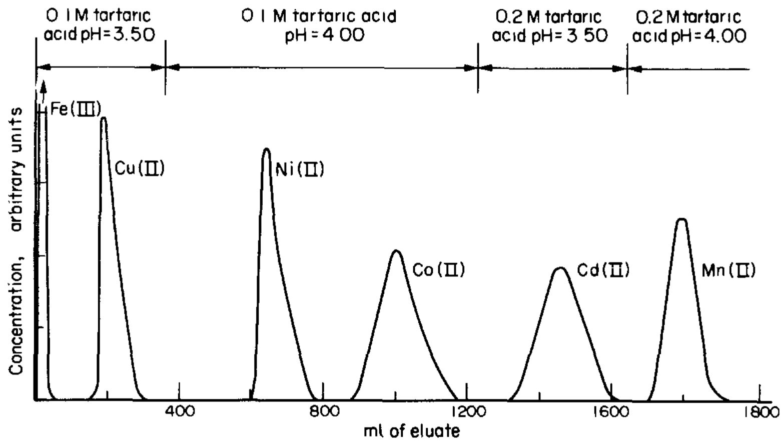

Fig. 1. Elution curves of Fe(III), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) in tartaric acid. Resin Dowex 50 W X8 (200–400 mesh), NH_4^+ form

In the present work we describe the cation-exchange of the ions Mn(II), Cd(II), Co(II), Ni(II), Cu(II), Al(III) and Fe(III), in tartaric acid solution at molarities between 0.1 and 1.0 and at pH values up to 10.

EXPERIMENTAL

The resin used was Dowex 50W X8, 200–400 mesh. It was converted into the NH_4^+-form with 3*M* ammonium chloride and washed with demineralized water. For the

Table 1. K_d values on Dowex 50W X8 resin (200–400 mesh), NH_4^+ form in tartaric acid at various molarities and pH

Ion	Tartaric acid concn., *M*	K_d in tartaric acid at pH values of							
		the free acid*	3 00	3.25	3.50	4.00	8.00	9.00	10 00
Mn(II)	0.1	s.a.	1423	782	339	135	74	ox.	ox
	0.2	s.a.	299	165	73	24	14	ox.	ox.
	0.3	4826	129	57	30	8.2	1.3	ox.	ox.
	0.5	4326	41	21	—	—	ox.	ox	ox.
	1.0	4326	—	—	—	—	ox	ox	ox.
Cd(II)	0.1	s.a.	931	725	260	87	45	294	656
	0.2	s.a	183	120	42	10.1	16	102	237
	0.3	s.a.	108	23	21	17	6.0	58	119
	0.5	s.a.	33	17	—	—	4.6	28	57
	1.0	s a.	—	—	—	—	2.5	13	22
Co(II)	0.1	s a.	710	323	128	32	19	1 8	154
	0 2	s.a	115	58	6.6	n a.	n.a.	n.a	152
	0.3	s.a.	36	22	n a.	n.a.	n.a.	n.a.	109
	0.5	s.a.	2.6	n.a.	—	—	n.a	n.a.	121
	1.0	2136	—	—	—	—	n.a.	n.a.	102
Ni(II)	0 1	s.a.	520	247	72	8.3	7 6	94	505
	0.2	4637	67	30	n.a.	n.a.	0.9	48	256
	0.3	3282	8.9	5.0	n.a.	n.a.	n.a.	34	122
	0.5	2860	n.a.	n.a.	—	—	n.a.	21	70
	1.0	2860	—	—	—	—	n.a	14	25
Al(III)	0 1	s.a.	443	183	33	3.1	n.a.	n.a.	n a
	0.2	s.a.	57	n.a.	n.a	n.a	n.a.	n.a.	n.a.
	0.3	s.a.	n.a.	n.a.	n.a	n.a.	n.a.	n a	n.a.
	0.5	s.a.	n.a.	n a.	—	—	n.a.	n a.	n.a
	1 0	s a.	—	—	—	—	n.a.	n a.	n.a.
Cu(II)	0.1	3143	96	18	7.7	n a.	6.4	142	452
	0.2	2493	n.a.	n.a.	n.a.	n.a.	6.7	88	444
	0.3	1806	n.a.	n.a.	n.a.	n.a.	7 1	51	189
	0.5	490	n.a.	n.a.	—	—	5.6	39	77
	1.0	329	—	—	—	—	4.1	4.1	5.9
Fe(III)	0.1	1324	n.a.	n.a.	n.a.	n a.	n.a	n.a.	n a
	0.2	1273	n.a.	n.a.	n.a.	n.a	n.a.	n.a.	n.a.
	0.3	465	n.a.	n.a.	n.a.	n.a.	n a.	n.a.	n.a.
	0 5	277	n.a.	n.a.	—	—	n.a.	n.a.	n.a.
	1.0	164	—	—	—	—	n.a.	n.a.	n.a.

* pH values for tartaric acid of a given molarity are, 0.1*M*, pH 2.10; 0.2*M*, pH 1.90; 0.3*M*, pH 1.80; 0.5*M*, pH 1 70, 1.0*M*, pH 1.50.

n a. not adsorbed; s.a strongly adsorbed, ox. oxides.

batch experiments the resin was air-dried to constant weight at 70° and stored in a desiccator over silica gel.

The metal ions examined were used as 0.2*N* solutions of the chloride or nitrate salts, after standardization.

Eluents

The eluents were prepared from reagent grade chemicals. Tartaric acid was used at molarities of 0.1, 0.2, 0.3, 0.5 and 1.0. The pH was adjusted between 3.00 and 10.00 by the addition of ammonia or sodium hydroxide solution. Solid sodium hydroxide was used for the pH values 3.00, 3.25, 3.50 and 4.00 to avoid the precipitation of ammonium salts. For the pH values 8.00, 9.00 and 10.00, adjusted with conc. ammonia solution, increasing K_d values were obtained, while the uptake of the ions was zero from solutions adjusted with sodium hydroxide.

Determination of K_d values

The distribution coefficients (K_d) were determined by the batch equilibration method. Resin (0.5 g dry weight), 50 ml of the appropriate tartaric acid solution and 2 ml of the metal ion solution, were shaken for 15 hr at room temperature. After equilibration, the resin phase was separated by filtration and the ion concentration was determined on an aliquot of the filtrate, by atomic-absorption spectrophotometry, using the standard addition method.

Columns

For column experiments borosilicate glass tubes were used, 1.2 cm i.d., 28 cm long, fitted with sintered glass plates. The resin bed was 22 cm deep. Fractions (10 ml) were collected automatically and analysed by atomic-absorption spectrophotometry.

RESULTS AND DISCUSSION

Table 1 gives the distribution coefficients (K_d) obtained in the present work. In tartaric acid the K_d values decrease regularly with increase in the acid concentration. All the values are too high, however, to allow separations to be achieved in a short time with practical elution volumes. The K_d values decrease with increasing tartrate concentration at constant pH and with rising pH at constant tartrate concentration. The value for Fe(III) differs markedly from that reported by Qureshi.[10] The K_d values are in accord with the tendency of the ions to form tartrate complexes.[12] When amonia is used to adjust the pH, there is a regular decrease of K_d with increasing tartrate concentration at constant pH, and a regular increase of K_d at constant tartrate concentration with increasing pH, with the exception of Mn(II) which oxidizes, and Fe(III) and Al(III), which are not absorbed. The increase of K_d values can be ascribed to the formation of cationic ammine complexes.

From Table 1 we can predict the possibility of achieving several interesting separations.

Separation

Fe(III), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) were separated. The resin was preconditioned with five bed-volumes of the first eluent and samples were added in the same medium (0.1*M* tartaric acid at pH 3.5). The elutions were effected at an overpressure of 190 mmHg and the loading of the resin bed was 0.1 meq of each ion used. The flow-rate was 2.5 ml/min. Elution curves are shown in Fig. 1 and it can be seen that the peaks are sharp and well separated.

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Summary—The cation-exchange behaviour of Mn(II), Cd(II), Co(II), Ni(II), Cu(II), Al(III) and Fe(III), in tartaric acid media was studied. Separations of Fe(III), Cu(II), Ni(II), Co(II), Cd(II) and Mn(II) on Dowex 50W X8 have been achieved.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AS V(III) OXINATE

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Almost all the numerous photometric methods for vanadium determination are based on vanadium(V) complexes. Only a few are based on vanadium(IV) complexes. There are even fewer methods[1–4] based on vanadium(III). Although some of them are highly sensitive, it would be advantageous to have methods with higher tolerance limits to analytically important elements to avoid preliminary separations. The limitation in using vanadium(III) appears to be its production and the stability of its complexes Electrolytic,[5] amalgam[6] or stannous chloride[4] reduction is frequently used for producing vanadium(III). A greater choice of reagents and conditions should be possible if introduction of metal ions can be avoided in the reduction.

Accordingly, we present below a method of producing vanadium(III) by sodium dithionite reduction and its extraction by oxine for its spectrophotometric determination.

EXPERIMENTAL

Reagents and solutions

Vanadium solution. A stock solution (10 mg of V/ml) was prepared from sodium metavanadate and standardized by the oxine method;[7] suitable dilution gave 100- and 10-μg/ml solutions.

8-Hydroxyquinoline. A 2% solution in carbon tetrachloride.

Sodium dithionite

Solutions of other elements. Prepared by dissolving suitable salts in water or dilute sulphuric acid to give 10 or 1 mg of element per ml.

Samples. Synthetic samples were prepared by mixing solutions of the ions to give the required compositions (see Table 4).

Rutile and ilmenite Finely powdered sample (1.0 g) was fused[8] with 5 g of fusion mixture in a platinum crucible for nearly 30 min. The melt was cooled and taken up in hot water. The insoluble residue was filtered off on Whatman No. 41 paper and washed 4 times with 5 ml of hot water each time. The filtrate was just acidified to litmus with dilute sulphuric acid and boiled to expel carbon dioxide. Any precipitate was filtered off, and washed twice with 5-ml portions of hot water. The filtrate and washings were cooled and made up to 5 ml. Aliquots of this solution were then used for the determination of vanadium by the procedure.

Determination procedure

To 20 ml of solution containing $\leq 175\ \mu$g of vanadium at pH 3–10, in a 150-ml separatory funnel, solid sodium dithionite (0.5–2.0 g) was added. After waiting for 2 min the funnel was stoppered and shaken gently for 2 min with 10 ml of the oxine solution in carbon tetrachloride, care being taken to release the pressure occasionally. After the layers had separated, the solvent phase was removed and passed through Whatman No. 41 paper (moistened with carbon tetrachloride) into a 25-ml volumetric flask. The extraction was repeated with another 10 ml of the oxine solution. Any complex sticking to the filter paper was washed into the flask, with oxine solution added dropwise. The solution was made up to the mark with carbon tetrachloride and mixed. The absorbance of the yellow complex was measured in 1-cm cells at 420 nm with a Beckman DU spectrophotometer, against a similarly treated reagent blank. The latter gave an absorbance of 0.006 against oxine in carbon tetrachloride.

Samples containing other elements. Masking agents were added after the reduction to vanadium(III), as shown in Table 3. In the case of tungsten, the tartrate was added to the solution at pH 8.5–10, before reduction.

RESULTS AND DISCUSSION

When sodium dithionite is added to mg amounts of vanadium(V) in slightly alkaline or acid solution, the pH decreases gradually, depending upon the amount of the reductant. The green solution obtained shows an absorption spectrum similar to the one obtained for vanadium(III) prepared by electrolytic reduction[2] or mercury reductor.[9]

When the solution is shaken with oxine in carbon tetrachloride a yellow complex is extracted quantitatively, showing an absorption peak at 420 nm. An initial pH of 3–10 before addition of dithionite gives a constant absorbance; the absorbance is lower if the initial pH is outside this range. Carbon tetrachloride is found to be the best solvent (Table 1), giving the highest absorbance. A single extraction with 10 ml of solvent was made from 20 ml of aqueous phase. The colour is not stable in other solvents except benzene, and in it has lower absorbance at the same λ_{max}.

The effect of various parameters on the V(III)-oxinate absorbance in carbon tetrachloride is shown in Table 2, the other conditions in each study being kept at the lower end of the optimum range. The optimum conditions for maximum absorbance are, initial pH of the aqueous phase 3–10, reduction with 0.5–2.0 g of sodium dithionite, 2 min waiting after mixing and 2–3 min equilibration with 2–4% oxine solution in carbon tetrachloride. A single extraction with oxine in carbon tetrachloride removes more than 99% of the vanadium but a second extraction with 10 ml of the solvent is recommended for 100% recovery

On the basis of Job's curves, the extracted species has a 3:1 ligand:metal composition.[10] The species has an

Table 1. Absorbance of vanadium(III)-oxinate complex in different solvents (V 5 μg/ml in the aqueous phase)

Solvent	Absorbance
Carbon tetrachloride	1.03
Benzene	0.995
Chloroform	0.858
Methyl isobutyl ketone	0.940
Amyl acetate	0.920
Amyl alcohol	0.662

Table 2. Dependence of the V(III)-oxinate extraction on different parameters (V 5 μg/ml in the aqueous phase)

Oxine/CCl_4, %	0.02	0.05	0.1	0.2	0.5	1.0	2.0–4.0
Absorbance	0.70	0.96	0.98	0.99	1.005	1.016	1.03
Sodium dithionite, *g*	0.1	0.2	0.5–2.0				
Absorbance	0.7	0.98	1.03				
Time of contact, *min*	0.25	0.5	1.0	2.0–3.0	5.0		
Absorbance	0.93	1.00	1.01	1.03	1.01		

absorption maximum at 420–425 nm, with sensitivity for vanadium of 0.004 μg/cm^2 (Fig. 1). At wavelengths shorter than 370 nm, the blank absorbs highly. There is no other peak at wavelengths up to 850 nm even at 0.8 mg/ml vanadium concentration. Beer's law is obeyed up 7 μg of V per ml of solvent phase. The absorbance remains constant for 45 min

Effect of diverse ions

Sodium chloride (5 g), sulphate (5 g), tartrate (2 g), acetate (3 g), thiourea (1 g) and ascorbic acid (1 g) have no effect on the extraction of vanadium. Only limited amounts of sulphosalicylic acid (0.4 g), thioglycollic acid (0.6 ml) and potassium cyanide (0.2 g) can be tolerated. Nitrate can be tolerated up to 5 mg/ml. Phosphate (2 g of the sodium salt) decreases the extraction. Fluoride and oxalate in ≥50 mg/ml and EDTA in ≥5 mg/ml concentrations mask the vanadium extraction completely.

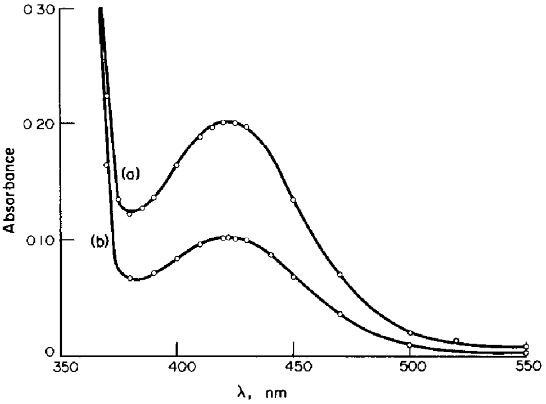

Fig. 1. Absorption spectrum of V(III)-oxinate; V—(a) 0.8, (b) 0.4 μg/ml of solvent phase.

Table 3. Extraction of diverse elements

Element	Tolerance limit *mg*/20 *ml**	Colour of extract	Masking agent§
Al(III)	100	Yellowish green	SSA†(0.4 g)
Zn(II)	100	Yellow	SSA†(0.4 g)
Cu(II)‡	20	Yellow	SSA†(0.4 g)
U(VI)	10	Yellow	SSA†(0.4 g)
Fe(III)	2	Blackish brown	SSA†(0.4 g)
Co(II)	15	Yellow	SSA†(0.4 g) or cyanide (0.2 g)
W(VI)	80	Faintly yellow	Tartrate (0.5 g)
Th(IV)	30	—	Citrate (0.05 g)
Ti(IV)	1	Faintly yellow	Tartrate (2.0 g)
Sn(II)	100	Yellow	TGA¶(0.6 ml)
Sb(III)	30	Yellow	TGA¶(0.6 ml)
Ni(II)	15	Greenish yellow	Cyanide (0.2 g)
Cr(VI)	50	Yellow	Ascorbic acid (1.0 g)
Cr(VI), Ce(IV)	5	Colourless	—
Ca(II), Cd(II)	20	Colourless	—
Bi(V)‡	20	Colourless	—
As(V)	40	Colourless	—
Pb(II)	50	Colourless	—
Hg(II), Mn(II), Mg(II), Sr(II), Ba(II)	100	Colourless	—

* For an absorbance ≤ 0.002, in presence of masking agent, if any.

§ Added after reduction by sodium dithionite unless otherwise stated; cyanide and citrate were added as potassium salts and tartrate as the sodium salt.

† SSA = sulphosalicylic acid.

¶ TGA = thioglycollic acid added before reduction.

‡ Precipitates formed after dithionite reduction were filtered off before extraction.

On reduction with sodium dithionite at pH 3–7, mercury and lead give black, arsenic brown and cadmium yellow sulphide precipitates; strontium and barium give white precipitates of their sulphates. These precipitates need not be filtered off as they do not affect the extraction of vanadium. Any slight emulsion appearing at the interface is removed in the filtration of the organic phase. Bismuth and copper form black sulphide precipitates which should be filtered off before the extraction. Even then, some copper seems to be left, giving a yellow solution after extraction with oxine in carbon tetrachloride. This can be prevented by masking with sulphosalicylic acid after the reduction. Other elements, such as aluminium, zinc, uranium, iron, cobalt, nickel, titanium, antimony, tin and chromium give yellow or yellowish green solutions because of extraction of their oxinates. This can be prevented (up to the tolerance limit) by using the masking agents shown in Table 3. Addition of sulphosalicylic and thioglycollic acids lowers the pH but the same maximum extraction is obtained by increasing the time of equilibration to 4 min in the first extraction.

When the vanadium sample solution is brought to the desired pH, some of the hydrolysable ions precipitate. Dithionite is added without filtration of these precipitates as they do not interfere with the process of extraction. Only in the case of tin and antimony is thioglycollic acid to be added to the neutral solution before the reduction. Under these conditions, tin does not give any precipitate but antimony gives the orange-red sulphide which remains at the interface. If thioglycollic acid is not added, tin and antimony sulphides are precipitated and give an emulsion on shaking with the solvent. The thioglycollic acid also prevents the extraction of oxinates of these elements. In the case of titanium, the vanadium is adsorbed on the hydrolytic precipitate and hence the tolerance is very low. Molybdenum gives a brown precipitate on shaking with oxine in carbon tetrachloride, forming unbreakable emulsions and being partly extracted. Therefore, molybdenum must be separated. The tolerance limits cannot be raised because of the upper limits of masking agents for vanadium extraction.

Applications

The sensitivity of the method is double that obtained by using oxine or its derivatives with vanadium(V) and is rarely exceeded by other photometric methods for vanadium. With the masking agents suggested, the limits of tolerance of interfering elements are much higher than in the other methods. Only molybdenum interferes seriously. The reduction of V(V) to V(III) by dithionite is very convenient and rapid. The method uses ordinary reagents and takes 10 min or less in series. The use of a single heavier solvent is also an advantage.

Table 4. Analysis of samples by the proposed method

Sample composition		
Matrix*	V added, μg	V found, μg
Fe(1.7) Cr(0.24) Co(0.015)†	15	15.0
Fe(1.5) Cr(0.12) W(0.35)‡	6	5.9, 6.0
Sn(40) Sb(15) Ce(5)	40	40.3
Th(30)	40	40.0
W(50)	30	30.0, 30.1
Rutile (V = 0.125%)§	—	0.125%
Ilmenite (V = 0.0911%)§	—	0.0912%

* The number of mg of the element in the aliquot taken for analysis is given in brackets.

† Analogous to Crocar.

‡ Analogous to High Speed Steel.

§ By ferron method

The scope and applicability of the method is shown by the satisfactory analysis of different synthetic samples and of rutile and ilmenite (Table 4).

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Summary—Vanadium(V) is rapidly reduced by dithionite to V(III) which is extracted as the oxinate into carbon tetrachloride. Vanadium is determined by measuring absorbance of the complex at λ_{max} = 420–425 nm with a sensitivity of 0.004 μg/cm^2 and Beer's law range of 0–7 μg/ml. Several mg of some important elements can be tolerated if they are masked. Molybdenum interferes seriously The method has been applied to synthetic samples, rutile and ilmenite with satisfactory results. Using ordinary reagents and taking 10 min or less in series for a determination, the method has a sensitivity rarely exceeded by others with a much higher tolerance for other elements.

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GRAVIMETRIC DETERMINATION OF TUNGSTEN WITH TETRAPHENYLARSONIUM CHLORIDE AFTER ITS EXTRACTION AS THIOCYANATE

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Analysis for low and high amounts of tungsten is required for natural and industrial samples containing some of the elements silicon, calcium, iron, manganese, cobalt, chromium, nickel, vanadium, molybdenum, copper, tin and bismuth. Except for the recent method of determination with iron(III) in thiocyanate medium,[1] the volumetric methods for tungsten are likely to give inconsistent and unreliable results.[2a] The gravimetric methods[2b,3a,4a] are based on precipitation as tungstic acid or as the tungstate of organic bases or easily volatilized cations. The process is hindered and the precipitates are contaminated by several elements of importance in tungsten materials, *e.g.*, phosphorus, silicon, iron, vanadium, chromium, arsenic, antimony and tin.[3b] The precipitates do not have definite composition and must be ignited to tungstic oxide. The barium and calcium tungstate methods are inconsistent and inaccurate[5] and the lead tungstate method requires preliminary precipitation of tungstic acid.[4b] All these methods are rather slow. The semimicro oxinate method is said to be unsuitable.[6]

Precipitation as tungstic acid in the presence of cinchonine is the most useful method for macro amounts, but is tedious, and contaminating elements have to be removed. The chromatographic,[3c] ion-exchange,[3c] precipitation,[3d] and solvent extraction[3e] methods handle only semimicro or micro amounts of tungsten and other elements in specific mixtures.

In view of the industrial importance of tungsten, we present a method for its gravimetric determination as the tetraphenylarsonium salt, after its extractive separation as the thiocyanate from interfering elements.

EXPERIMENTAL

Reagents and solutions

Tungsten solution. Sodium tungstate solution was standardized volumetrically with iron(III).[1]

Tetraphenylarsonium chloride solution, 1%.

Potassium thiocyanate solution, 5*M*.

Tribenzylamine solution (*TBA*). A 2% w/v solution in distilled chloroform.

Mercury. Purified with nitric acid.[7]

Procedure

Determination as tetraphenylarsonium tungstate. To a slightly alkaline solution containing 5–60 mg of tungsten, add tetraphenylarsonium chloride solution in 50% excess or till precipitation is complete. Dilute to about 40 ml and adjust the pH to 2 (pH-meter) with hydrochloric acid (caution: tungstic acid starts to precipitate at pH < 1.5). Wash the electrodes with 1 ml of 0.01*M* hydrochloric acid and filter off on a sintered-glass crucible (porosity 4). Wash the precipitate successively with 4, 2, 2, 1, 1 and 1 ml of 0.01*M* hydrochloric acid. Dry for 45 min at 110–115°, cool it over fused calcium chloride in a desiccator and weigh it.

Extractive separation of tungsten as thiocyanate. Place the solution, containing not more than 50 mg of tungsten, in a 100-ml separating-funnel and adjust it to be 0.4*M* in potassium thiocyanate and 4*M* in hydrochloric acid in a final volume of 25 ml. Add 2 ml of mercury and shake the funnel vigorously for 1 min. Extract the tungsten thiocyanate complex with 25 ml of TBA/chloroform solution by shaking for 1 min. Separate the mercury and then transfer the solvent layer to another separating-funnel. Repeat the extraction with 5 ml of solvent. Strip the tungsten from the combined extracts with two 25-ml portions of water made just alkaline to litmus and containing 2 ml of 6% hydrogen peroxide, shaking for 1 min each time. Filter, then boil the combined back-extracts with enough hydrogen peroxide to oxidize tungsten and destroy the excess of thiocyanate. Acidify to pH $\nless 2$ and boil to destroy the hydrogen peroxide. Cool the solution and determine tungsten.

Modification for presence of vanadium and titanium. When vanadium and/or titanium are present, scrub the TBA extract with 20 ml of 7*M* hydrochloric acid for 1 min before stripping the tungsten.

Modification for presence of iron and silica. With up to 100 mg of iron and/or 50 mg of silica present, shake with mercury for 2-3 min, before extracting with TBA in chloroform.

Modification for presence of molybdenum. When molybdenum is present, adjust the sample solution to 2*M* in hydrochloric acid and to contain 3 g of tartaric acid for each 100 mg of tungsten, in a final volume of 10 ml. Then separate molybdenum by the xanthate method.[8] After separation of the last chloroform extract, adjust the aqueous phase to 4*M* in hydrochloric acid and 0.4*M* in potassium thiocyanate in a final volume of 35 ml, and then follow the general procedure.

RESULTS AND DISCUSSION

Determination as tetraphenylarsonium tungstate

Tungstate condenses to paratungstate (pH 3–4) and metatungstate (pH 1.5–3),[9] which are precipitated as tetraphenylarsonium salts. The precipitation starts at pH ~ 6 but the weight of the salt from a given amount of tungsten is quantitative and reproducible only for the pH range 1 5–4. The conversion factor tungsten/tetraphenylarsonium tungstate is 0.4468. A lapse of up to 1 hr between pH-adjustment and filtration, or a change of temperature from 25° to 40° has no effect. The filtrate and washings contain 1 μg of tungsten per ml; therefore the minimum possible volume should be used. The precipitate is highly soluble in hot water and acetone, and less so in alcohol, ether and chloroform. Tartaric, citric and oxalic acids prevent precipitation. In the presence of even traces of a large number of other elements,[10] heteropolytungstates are formed which are also precipitated by the tetraphenylarsonium ion. It is, therefore, possible to use this method only after prior separation of almost all other elements, as proposed in the procedure above.

Extractive separation of tungsten as thiocyanate

Generally, the methods already available suffer interference from iron, vanadium, chromium, cobalt, nickel, copper and especially molybdenum. The recent mercury–thio-

Table 1 Effect of anions on extraction of tungsten thiocyanate (W = 50.0 mg)

Salt added	Amount, *g*	Extraction of tungsten,* %
None	—	99.7
Sodium chloride	2.0†	99.6
Potassium acetate	1.0	99.6
Sodium sulphate	2.0†	99.3
Trisodium phosphate	2.0†	99.1
Potassium citrate	1.0	98.3
Sodium tartrate	1.0†	98.2
Potassium oxalate	1.0	97.8

* By difference.

† Added before reduction.

Table 2. Analysis of samples by the proposed method*

Sample composition,† *mg*	Tungsten added, *mg*	Tungsten found, *mg*
Co(37.4), Cr(18.7)	18.70	18.72
Fe(171)	9.35	9.34
Fe(75), Cr(6), V(0.3)	17.00	16.97
Fe(114), Cr(7), Co(90)	18.70	18.73
Fe(158), Cr(46), Ni(16), Mn(1.1)	8.00	8.01
Fe(6.6), Mn(5), Sn(0.6), Bi(0.12), Ca(0.05)	29.92	29.89
Ferrotungsten A, 75.2% W	—	75.33%
Ferrotungsten B, 73.3% W	—	73.39%
High Speed Steel, 19.61% W (BCS 241/1)	—	19.73%

* Decomposed as described earlier.[11]

† The first six samples are analogous to stellite, tungsten steel, high-speed steel, K.S. magnet steel, Midvale HR and Spanish wolframite respectively.

cyanate–TBA method[11] for spectrophotometric determination of tungsten suffers interference only from molybdenum and niobium and is simple and rapid. It was therefore chosen for the extractive separation of tungsten.

Various parameters for extraction of 50 mg of tungsten were checked. The degree of extraction increases with acidity up to 4*M* hydrochloric acid and then decreases at higher acidity. It is maximal from 0.2 to 0.4*M* potassium thiocyanate, but the layers do not separate well at lower concentrations. A 2% solution of TBA in chloroform and 1 min reduction time gives maximum extraction but these levels are not critical. A single 1-min equilibration with an equal volume of just alkaline hydrogen peroxide solution strips the tungsten quantitatively, but repetition is recommended as a safety precaution. Smaller volumes of aqueous phase cause emulsions. The conditions selected give 99.7% extraction.

Alloying elements other than molybdenum (25% extracted) and niobium (10% extracted), titanium and vanadium accompany tungsten either not at all or only in traces. Titanium and vanadium can be almost completely removed by scrubbing with 7*M* hydrochloric acid before the stripping, without affecting tungsten. The traces of other elements are removed as the hydroxides by filtration of the alkaline peroxide solution. No tungsten is lost by adsorption on the small hydroxide precipitate. Thus tungsten can be separated practically quantitatively from iron, nickel, cobalt, chromium, vanadium, titanium, copper, bismuth, manganese, uranium, lead, zirconium, arsenic, antimony and silicon. Only molybdenum and niobium still accompany tungsten. Molybdenum can be conveniently removed quantitatively without loss of tungsten by xanthate extraction[8] from the initial sample solution in 2*M* hydrochloric acid containing tartaric acid. The aqueous phase is then adjusted to the optimum conditions for the mercury–thiocyanate–TBA extractive separation, in a total volume of 35 ml. Thus only niobium accompanies tungsten, and then only in part, but fortunately is rarely encountered in tungsten materials.

Chloride and acetate decrease the extraction of tungsten very slightly, sulphate, phosphate, citrate, tartrate, oxalate do so in that order (Table 1). Silicic acid does not cause any difficulty and therefore need not be removed for preparation of the tungsten sample solution.

Applications

The extractive separation method is generally applicable to all tungsten materials both natural and industrial. The separation and determination together take less than 2 hr for a single sample and much less in series. The method gives highly satisfactory results with a relative overall error of 0.1–0.2% over a range of 5–60 mg of tungsten (Table 2).

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Summary—Small amounts of tungsten in natural and industrial samples can be freed from all important interfering elements by extraction of molybdenum by xanthate, reduction of tungsten by mercury and extraction of tungsten(V) thiocyanate into tribenzylamine, and finally back-extraction. The tungsten can be then determined as tetraphenylarsonium tungstate by precipitating it at pH 2–4, filtering it off and drying it at 110° for 45 min. An overall error of 0.1–0.2% is obtained for 5–60 mg of tungsten.

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ESTIMATION OF CYANIDE ION IN METAL SALTS AND COMPLEXES BY MEANS OF CHLORAMINE-T AND DICHLORAMINE-T

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Cyanides have industrial applications such as extraction of noble metals, use as insecticides, in photography and the paper industry and in the preparation of various cyanogen derivatives. Reagents such as silver nitrate,[1] alkaline potassium permanganate[2] and iodine in alkaline medium[3] are used for the estimation of cyanide. We have now found chloramine-T (CAT) and dichloramine-T (DCT) give a two-electron oxidation of cyanide. Direct titration was found impracticable and a back-titration procedure was developed. The method can be extended to estimation of both cyanide and thiocyanate in a mixture.

EXPERIMENTAL

Reagents

CAT was purified by the method of Morris *et al.*[4] An approximately 0.1*N* solution was prepared and standardized by the iodometric method. DCT was prepared and purified by the method of Jacob and Nair.[5] An approximately 0.1*N* solution in glacial acetic acid (containing 10% acetic anhydride) was prepared and standardized by the iodometric method. Compounds of accepted grades of purity were used in preparing other solutions. Standard buffer systems were employed.[6]

Zinc cyanide was prepared by mixing zinc sulphate and potassium cyanide solutions in 1:2 molar ratio. The precipitate was washed with water and dried over anhydrous calcium chloride. Zn: theoretical 55.68%; found 55.8%.

Lead cyanide was prepared by mixing lead acetate and potassium cyanide solutions in 1:2 molar ratio. The precipitate was washed with ice-cold water and dried over anhydrous calcium chloride. Pb: theoretical 79.92%. Found 80.4%.

$K_2Zn(CN)_4$, $K_2Pd(CN)_4$, $K_2Hg(CN)_4$ and $KAg(CN)_2$ were prepared by standard methods[7] and their composition was checked.

Procedures

Soluble cyanides with CAT. Adjust the pH of the aqueous solution (containing 0.01–4.0 mmole of cyanide) to 4 with acetate buffer. Add it to a known volume (30–40% excess) of 0.1*N* CAT in an iodine flask and set aside for about 30 min, shaking occasionally. Rinse down with 20 ml of water, add 10 ml of 2*N* sulphuric acid and 10 ml of 20% potassium iodide solution and titrate with 0.1*N* sodium thiosulphate (V_1 ml). Run a blank with the same volume of CAT solution alone (V_2 ml of thiosulphate needed). The amount (x mg) of cyanide ion is given by $x = 13.00y(V_2 - V_1)$ where y is the normality of the thiosulphate.

Soluble cyanides with DCT. Add 0.01–4.0 mmole of cyanide dissolved in water or pH 4 buffer to a known volume (~70–80% excess) of 0.1*N* DCT containing about 30% of acetic anhydride. Complete the determination as with CAT.

Insoluble cyanides with CAT. For zinc cyanide dissolve the solid in dilute acetic acid, adjust the pH to 4, then treat as for soluble cyanide but with 1 hr standing time. For lead cyanide treat samples in pH-4 buffer as for soluble cyanides, but keep at about 70° for 30 min.

Insoluble cyanides with DCT. For zinc cyanide proceed as for soluble cyanides but allow 1 hr standing time. For lead cyanide add samples in pH-4 buffer to 70–80% excess of DCT, then enough acetic anhydride to react with all the water in the mixture, keep at about 40° for 30 min and complete as before.

Complex cyanides with CAT. Proceed as for soluble cyanides for potassium tetracyanozincate; for potassium tetracyanopalladate(II) do the same but boil for about 30 min before the back-titration; for potassium tetracyanomercurate keep at about 40° for 30 min; for potassium dicyanoargentate let stand at room temperature for 1 hr.

Complex cyanides with DCT. For the tetracyanozincate proceed as for soluble cyanides; for the other three compounds add the excess of DCT and enough acetic anhydride to remove the water, keep at room temperature for 30 min for the mercury complex, 60 min for the silver complex, and at 50° for 30 min for the palladium complex, and complete as before.

Blank titrations with CAT or DCT are carried out under the same conditions as for the determinations.

Table 1. Estimation of potassium cyanide in presence of halides

Composition of mixture, *mg*					KCN found, *mg*
NaF	KCl	KBr	KI	KCN	
12.4	10.1	11.3	10.7	6.74	6.77
20.8	19.8	21.2	20.5	16.75	16.84
40.5	39.7	38.9	41.3	33.7	33.9
102.3	100.2	99.8	101.6	101.0	101.7
204.4	201.1	203.9	200.5	202.0	202.8
501.3	500.0	502.3	504.6	403.9	404.2

Table 2. Estimation of potassium cyanide and thiocyanate with chloramine-T

Composition of mixture, *mg*		Weights found, *mg*			
		Procedure I		Procedure II	
KCN	KCNS	KCN	KCNS	KCN	KCNS
3.37	3.93	3.34	3.97	3.34	3.96
6.74	7.87	6.68	7.92	6.71	7.89
16.83	19.67	16.75	19.79	16.75	19.78
33.7	39.3	34.0	39.3	34.0	39.3
50.5	59.0	50.5	58.9	50.7	58.7
67.3	78.7	67.3	78.6	67.7	78.3
84.2	98.3	84.1	98.3	84.1	98.3
101.0	118.0	100.9	117.9	100.9	118.0

Soluble cyanide in presence of halide. Add excess of $\sim 0.5M$ zinc sulphate to precipitate zinc cyanide; filter it off, wash it with about 30 ml of ice-cold water till free from halide, dissolve it in dilute acetic acid and analyse as above.

Soluble cyanide and thiocyanate in a mixture. Determine the sum of cyanide and thiocyanate as for soluble cyanide, and then the cyanide (in another sample) by the procedure for cyanide in presence of halide (procedure I). Alternatively (procedure II) determine the thiocyanate in the filtrate as for soluble cyanide. If there is only enough for one sample, analyse the precipitate for cyanide and the filtrate for thiocyanate. The equivalent weight of thiocyanate is 7.25 g.

RESULTS AND DISCUSSION

The stoichiometry of oxidation of KCN by CAT (or DCT) can be represented by

$$\mathrm{KCN + RNClNa\,(or\ \tfrac{1}{2}RNCl_2) + H_2O \rightarrow KCNO + RNH_2\,(or\ \tfrac{1}{2}RNH_2) + NaCl\,(or\ HCl)}$$

where $R = p\text{-}CH_3C_6H_4SO_2$. The presence of KCNO in the reaction products was detected by spot-tests.[8,9] The sulphonamide was detected by paper chromatography. Benzyl alcohol saturated with water was used as the solvent, with 0.5% vanillin in 1% hydrochloric acid in ethanol as the spray reagent ($R_f = 0.91$)

In preliminary experiments it was found that the degree of oxidation of potassium cyanide in 30 min was maximal at pH 3–5, and quantitative with a 30–40% excess of CAT. With a 10–20% excess the reaction is complete only after 1 hr. In other media quantitative oxidation takes 2 hr with 30–40% excess of CAT. With DCT, oxidation was found to be quantitative if the titration medium contained 30% acetic anhydride.

Several methods[10–14] have been reported for the determination of cyanide and thiocyanate in a mixture. Rao and Murthy[15] have shown that CAT oxidizes thiocyanate in acid medium (pH 1–6) in about 30 min, with an eight-electron change per mole.

The maximum error in determination of 2–220 mg of various cyanides, simple and complex, ranged from 3% at the bottom of the sample weight range to just under 1% at the top. Results for mixtures are shown in Tables 1 and 2.

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Summary—A simple and accurate method for the estimation of cyanide in salts and complexes is based on oxidation with chloramine-T (in pH 4 buffer) or dichloramine-T (in presence of acetic anhydride). The oxidation involves a two-electron change. Halides interfere with the estimation of KCN, but the interference can be eliminated by precipitating and determining zinc cyanide. A method for estimating KCN and KCNS in mixtures is also described.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM AND OSMIUM WITH THIOBENZHYDRAZIDE

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Several organic reagents[1,2] containing the $-CS-\overset{|}{N}-N<$ group, *e.g.*, 1,4-diphenylthiosemicarbazide[3,4], 2,4-diphenylthiosemicarbazide,[4] *o*-hydroxythiobenzhydrazide,[5] have been proposed for the spectrophotometry of ruthenium and osmium. In the present communication thiobenzhydrazide is recommended as a suitable reagent for the extraction of ruthenium and osmium in chloroform and for the subsequent photometric determination of those metals in the presence of a moderately large excess of diverse ions commonly associated with them.

EXPERIMENTAL

Reagents

Ruthenium(III) chloride hydrate was dissolved in dilute hydrochloric acid and the solution standardized by the hydrolytic precipitation method.[6] Standard osmium solution[7] was made by dissolving a weighed amount of osmic acid in 0.1*M* caustic soda. Solutions for spectrophotometric measurements were prepared by appropriate dilution of the stock solution. Sodium acetate solution and dilute hydrochloric acid were used for the regulation of pH. All the reagents and chemicals used were of analytical-reagent grade.

Preparation and properties of thiobenzhydrazide. Thiobenzhydrazide was first prepared by Holmberg.[8] A slightly modified procedure was used, as follows. Dissolve 2.12 g of carboxymethyldithiobenzoate[9] in 15 ml of 1*M* sodium hydroxide and cool the solution in ice. Slowly add 1.0 ml of hydrazine hydrate (80%) dissolved in 10 ml of 1*M* sodium hydroxide. Allow the mixture to stand for 2 hr in an ice-bath. Neutralize with cold, dilute hydrochloric acid (the pH should remain between 5.5 and 6.5), leave in the ice-bath for 1 hr, filter, crystallize from tepid water and dry in vacuum. The pure compound melts at 71–72°.

Thiobenzhydrazide is appreciably soluble in water and highly soluble in most organic solvents. It is stable towards acids and very dilute alkalis, but is decomposed by concentrated nitric acid and strong oxidizing agents. The reagent should preferably be stored at below 15°.

An approximately 0.01*M* solution of thiobenzhydrazide solution was prepared in spectroscopic grade ethanol.

Spectrophotometric determination of ruthenium

Place a measured volume of ruthenium(III) chloride solution in a 100-ml separatory funnel, and dilute to 20 ml with hydrochloric acid and water so that the final hydrochloric acid concentration of the solution is 1–4*M*. Add 2–3 ml of 0.01*M* thiobenzhydrazide and heat on a boiling water-bath for 20–25 min. Cool and extract with four successive 5-ml portions of chloroform. Combine the extracts, dilute to 25 ml, dry with anhydrous sodium sulphate and measure the absorbance at 520 nm against chloroform.

Spectrophotometric determination of osmium

Place an aliquot of osmic acid solution in a 100-ml separatory funnel and dilute to 15 ml. Add 2 ml of 5% EDTA solution to mask the interfering ions, if any, and adjust the pH of the solution to 2.3–4.8. Add 2 ml of 0.01*M* thiobenzhydrazide (the final volume should be <20 ml) and allow to stand for 10 min. Extract with three successive 5-ml portions of chloroform, combine the extracts in a 25-ml volumetric flask and make the volume up to the mark. Dry the extract with anhydrous sodium sulphate and measure the absorbance at 385 nm or 480–490 nm against a reagent blank.

RESULTS

Characteristics of the complexes

The absorbance spectra of the thiobenzhydrazide complexes of ruthenium and osmium in chloroform are shown in Fig. 1. The absorbances remain constant for at least 24 hr. The concentration ranges for conformity to Beer's law are 0.73–7.33 μg/ml at 520 nm for ruthenium and 1.20–12.04 μg/ml at 385 nm and 1.20–18.06 μg/ml at 480–490 nm for osmium.

The optimal acidity for complete extraction of ruthenium is 1.0–4.5*M* hydrochloric acid and for osmium pH 2.30–4.80. The extraction coefficients and degrees of extraction of the ruthenium and osmium complexes into various solvents are shown in Table 1. From these data four successive extractions with 5-ml portions of chloroform should extract 99.9% of the ruthenium, and three such extractions should extract 99.8% of the osmium present.

The minimal reagent:metal ratios for complete colour development with ruthenium and osmium were 15:1 and 10:1 respectively. Molar-ratio studies[10] indicated that osmium (VI) forms a 1:2 metal: ligand complex. The composition of the ruthenium complex, however, could not be determined.

It may be pointed out that both ruthenium (VI) and ruthenium (III) give the same colour reaction with thiobenzhydrazide. Similarly osmium (VIII) and osmium (VI) produce the same colour with the reagent. It appears that ruthenium (VI) and osmium (VIII) are reduced to ruthenium-(III) and osmium (VI) respectively before complex formation.

The molar absorptivities, Sandell sensitivities[11] and optimal concentration ranges of the determination of ruthenium and osmium are given in Table 2.

Accuracy and precision

The relative mean errors were $<0.5\%$ and the relative standard deviations $<1\%$ for 2–4 mg of ruthenium, and 6–12 mg of osmium (10 replicates at each level).

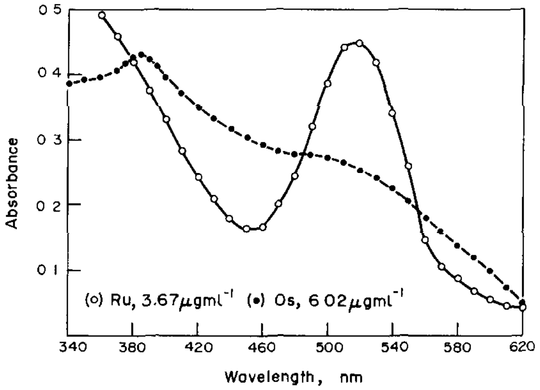

Fig. 1. Absorption spectra of thiobenzhydrazide complexes of rutheniun and osmium.

Interferences

The effect of a number of foreign ions was studied; the procedures involved appropriate acidity adjustment, use of EDTA as masking agent and sulphur dioxide as reducing agent. In some cases the extracts were centrifuged before the absorbance measurements. Osmium should be extracted as the thiobenzhydrazide complex before the determination of ruthenium. Table 3 shows the concentration of foreign ions that caused an error less than 2%.

Determination of ruthenium and osmium in a mixture

A mixture containing 91.7 μg of ruthenium and 150.5 μg of osmium was taken in a separatory funnel and 2 ml of 5% EDTA solution were added. The pH of the solution was adjusted to 4.5 and 2 ml of 0.01*M* thiobenzhydrazide were added The mixture was allowed to stand for 10 min, then was extracted with chloroform, and the osmium absorbance was measured at 480–490 nm. The acidity of the aqueous layer was then adjusted to be 3.0–4.0*M* in hydrochloric acid, 3 ml of 0.01*M* reagent solution were added and ruthenium was determined as described in the procedure. Errors in the determination of both metals were less than 2%.

DISCUSSION

Thiobenzhydrazide has been found to be a suitable reagent for the extraction and photometry of ruthenium and osmium. The method permits the determination of ruthenium selectively in the presence of diverse ions commonly

Table 2. Molar absorptivity, sensitivity and optimal concentration range for photometry of ruthenium and osmium

Wavelength *nm*	Molar absorptivity, *l. mole⁻¹. cm⁻¹*	Sensitivity, *μg/cm²*	Optimal concentration *μg/ml*
520	1.24×10^4	0.008	1.63–5.71
385	1.37×10^4	0.014	2.79–9.76
480–490	8.84×10^3	0.022	4.30–15.05

Table 3. Effect of foreign ions on the photometry of ruthenium and osmium

	Amount tolerated, *mg*, in the determination of	
Foreign ion	ruthenium [Ru(III) = 91.7 *μg*]	osmium [Os(VIII) = 150.5 *μg*]
Ti(IV)	2 00	2.00
V(V)	2.50	2.50
Cr(III)	1.50	1.50
Mn(II)	2.00	2.00
Fe(III)	1.50*	2.00
Co(II)	1.00	2.00
Ni	1.00	1 50
Cu(II)	0.90	1 35‡
Zn	5.00	5.00
Ga	3.00	2.00
Mo(VI)	1.00	1.00
Ru(III)	—	0.91
Rh(III)	2 00	1.50
Pd(II)	1.00‡	1.00‡
Cd	2.50	2.50
In	3 00	3.00
W(VI)	1 00	1.00
Re(VII)	1 66*	1.66
Os(VIII)	0.75†	—
Ir(III)	3.00	3.00
Pt(IV)	1.22‡	0.81
Au(III)	1.00‡	1.00‡
Hg(II)	2.00	2.00
Pb	2.50	2.50
Tl(III)	1.00	1.00
U(VI)	2 00	2.00

*Prior reduction with sulphur dioxide. †Prior separation by extraction with thiobenzhydrazide. ‡Centrifuged before absorption measurement.

Table 1. Effect of solvents on the extraction of thiobenzhydrazide complexes of ruthenium and osmium

Solvent	Extraction coefficient of ruthenium complex from 3.0*M* HCl	Ruthenium extracted, %	Extraction coefficient of osmium complex at pH = 4.0	Osmium extracted, %
Chloroform	24	96.0	33	97.1
Carbon tetrachloride	0.088	8.1	22	95.6
Methyl isobutyl ketone	1.78	64.0	10.7	91.5
Isoamyl alcohol	24	96.0	22	95.6
Benzene	0.17	14.6	9	90
Petroleum ether	—	—	1.24	55.6

associated with it, especially in the presence of other platinum metals. The sensitivity of the method for the determination of ruthenium is comparable to that of existing procedures for the metal. For osmium, the method is highly sensitive when the absorption measurements are made at 385 nm and rather less sensitive if the absorbances are measured at 480–490 nm. However, the longer wavelength is preferred because of the higher selectivity. Among other advantages of the reagent, ruthenium and osmium can be separated and subsequently determined spectrophotometrically.

Thiobenzhydrazide seems to be a potentially useful reagent for the determination of ruthenium and osmium in rocks and alloys. The metals may be brought into solution by $NaOH$–Na_2O_2 fusion[12] as ruthenium (VI) and osmium (VI) ions. The excess of peroxide should be destroyed before the metals are determined with thiobenzhydrazide as described above.

Acknowledgement—The authors thank the Director of Public Instruction, West Bengal, for financial assistance.

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SIMULTANEOUS TITRIMETRIC DETERMINATION OF POLYPHOSPHORIC AND SULPHURIC ACIDS IN A MIXTURE

REX W. SOUTER and RAFIK H. BISHARA
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(*Received* 21 *October* 1975. *Accepted* 11 *January* 1976)

Phosphoric acids with a high phosphorus pentoxide content are called "polyphosphoric acids."[1] Polyphosphoric and sulphuric acids both find use as dehydrating agents, especially in cyclodehydration—ring-closure reactions.[2–6] Analytical methods exist for analysis of concentrated phosphoric acids,[1] for titration of soluble phosphate compounds,[7] and for estimation of triphosphoric and pyrophosphoric acids in the presence of ortho- and metaphosphoric acids.[8] A complex procedure is available for titrimetric assay of nitric, phosphoric, sulphuric, and hydrochloric acids in the same sample.[9] Orthophosphoric acid may be titrated with sodium hydroxide but only two neutralization steps can be utilized.[10]

We report here an accurate, convenient method for assaying sulphuric–polyphosphoric acid mixtures used in the synthesis of 1,3,4-thiadiazoles.[11] Reaction yields are low if either concentrated sulphuric acid or polyphosphoric acid (PPA) alone is employed or they are mixed in other than a 1:3 (w/w) mixture. Calculation of percent by weight of each acid species is demonstrated.

EXPERIMENTAL

Titrations were done with a Brinkmann Metrohm E436 automatic titrator and a glass–calomel combination electrode. Standard 0.05*N* sodium hydroxide was used for all titrations

Before determining the percentages of sulphuric acid and PPA in the mixture, it is necessary to determine (*a*) the presence of hydrolysed PPA and (*b*) the experimental equivalent weights of PPA and sulphuric acid, using the same individual acids that were used to prepare the mixture.

Determination of hydrolysed PPA

Weigh 500 mg of the PPA into a 100-ml volumetric flask, dissolve it in water, dilute to volume, and mix. Pipette 5 ml into a suitable titration vessel, add 60 ml of water and titrate with 0.05*N* sodium hydroxide, with stirring to ensure only one sharp end-point.

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Determination of experimental equivalent weight of sulphuric acid

Accurately weigh in triplicate 500 mg of the sulphuric acid into each of three 100-ml volumetric flasks. Dissolve in water, dilute to volume and mix well. From each solution, pipette 5.0 ml into small boiling flasks and dilute with 60 ml of water. Reflux the samples for 3 hr and then cool to room temperature. Quantitatively transfer each sample to a titration vessel and titrate, while stirring, with 0.05*N* NaOH through the single end-point.

The sulphuric acid is refluxed like the samples in order to treat any impurities in the same manner.

Determination of experimental equivalent weight of polyphosphoric acid

Accurately weigh in triplicate 500 mg of the PPA sample into 100-ml volumetric flasks. Continue as described for sulphuric acid; the hydrolysed samples will show two end-points in the titration.

Determination of percentages of sulphuric and polyphosphoric acids in the mixture sample

Accurately weigh in triplicate 500 mg of the mixed acid sample into 100-ml volumetric flasks. Continue as described in the previous section; two end-points will be obtained.

Calculations

The first step in the procedure, performed only on the stock PPA used to make the mixtures, ensures that each PPA sample will only have one end-point. The presence of more than one sharp end-point indicates partial hydrolysis, and the stock of that PPA should be discarded since part of its dehydrating strength is already lost.

The experimental equivalent weight of sulphuric acid is calculated as follows from the volume of sodium hydroxide required for titration:

$$\text{eq. wt. } H_2SO_4 = \frac{(\text{mg } H_2SO_4 \text{ in } 100\text{ ml}) \times (5.0\text{ ml})}{(100\text{ ml}) \times (\text{ml NaOH}) \times (\text{normality NaOH})}$$

Calculation of the experimental equivalent weight of PPA is done by using the volume of base necessary to reach the first end-point for each hydrolysed PPA sample:

$$\text{eq. wt. PPA} = \frac{(\text{mg PPA in } 100\text{ ml}) \times (5.0\text{ ml})}{(100\text{ ml}) \times (\text{ml NaOH}) \times (\text{normality NaOH})}$$

The volume of base required to reach the second end-point is also calculated. Theoretically, titration to the first end-point and from the first to the second end-point should consume the same volume. However, experimental work has shown the latter volume to be larger than the former, perhaps because of slight titration towards the third equivalence point of phosphoric acid.[10] Thus, the difference between the first and second end-points is divided by the volume for the first end-point, and this ratio is used later as a "volume correction factor" for the base consumed in titration of the acid mixtures.

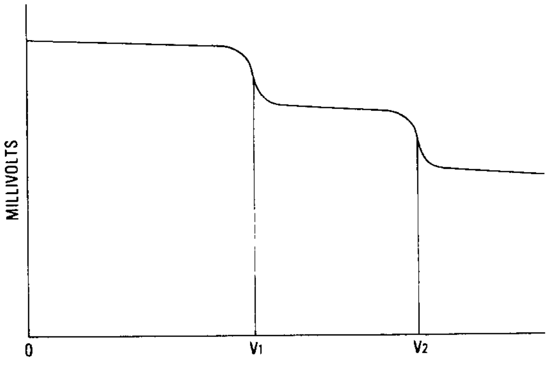

Fig. 1

For calculation of results of mixed-acid titrations refer to Figure 1.

For each such titration, the volume of base at each end-point V_1 and V_2 is calculated. V_1 is the volume of base required to titrate the sulphuric acid completely and the hydrolysed PPA to the first neutralization step. V_2 is V_1 plus the volume required to titrate to the second neutralization step of the hydrolysed PPA. The second neutralization step of hydrolysed PPA thus requires $V_2 - V_1 = V_3$. V_3 is divided by the volume correction factor calculated previously, to give the corrected volume of base necessary for titration of one equivalent of hydrolysed PPA, V_4. V_4 is subtracted from V_1 to give V_5, the volume of base equivalent to the sulphuric acid. The volumes V_4 and V_5 are used to calculate the amounts of PPA and sulphuric acid in the mixture:

$$\%\,\text{PPA} = \frac{(V_4, \text{ml}) \times (\text{normality NaOH}) \times (\text{eq. wt. PPA}) \times 10^4}{(\text{mg mixed acid}) \times 5}$$

$$\%\,H_2SO_4 = \frac{(V_5, \text{ml}) \times (\text{normality NaOH}) \times (\text{eq. wt. } H_2SO_4) \times 10^4}{(\text{mg mixed acid}) \times 5}$$

The orthophosphoric acid (H_3PO_4) equivalent to the stock PPA is calculated by using the volume of base needed to reach the first end-point for hydrolysed PPA:

$$\%\,H_3PO_4 = \frac{(\text{ml NaOH}) \times (\text{normality NaOH}) \times 98 \times 100 \times 100}{(\text{mg PPA}) \times 5}$$

The P_2O_5 equivalent to the PPA is then calculated from[10]

$$\%\,P_2O_5 = \%\,H_3PO_4 \times \frac{142}{196}$$

The amount of P_2O_5 in the mixed acid samples is calculated by.

$$\%\,P_2O_5 \text{ in mixture} = \frac{(\%\,P_2O_5 \text{ in PPA}) \times (\%\,\text{PPA in mixture})}{100}$$

RESULTS AND DISCUSSION

The equivalent weight of hydrolysed PPA must be experimentally determined for each lot used since the exact composition of PPA before and consequently after hydrolysis is unknown.[1] The equivalent weight of the sul-

Table 1. Assay results for synthetic acid mixtures

	Acid, %w/w taken	Acid, %w/w found	Relative error, %
PPA	77.3	78.3	+1.2
H_2SO_4	22 7	22.2	−2 2
PPA	57.5	57.6	+0.2
H_2SO_4	42.5	42.0	−1.2

Table 2. Typical assay results for PPA and H_2SO_4 in mixtures

Sample	H_2SO_4, %	Relative error	PPA, %	Relative error
1	24.2; 24.4	0.8	75.7; 76.1	0.5
2	25.0; 24.7	1.2	75.7; 75.6	0.1
3	24.2; 24.3	0.4	76.8; 77.1	0.4

phuric acid should also be experimentally determined in the manner used for sample assay. Typical equivalent weights found for hydrolysed PPA and sulphuric acid were 86.8 and 51.6, respectively. Typical values of the phosphorus pentoxide and orthophosphoric acid equivalents of the PPA were 83.4% (literature,[12] 83 0) and 115.3% (literature,[12] 115.0) respectively.

To test the accuracy of this method, synthetic mixtures were prepared and assayed. Results are presented in Table 1.

Precision of the determinations is good, as illustrated in Table 2 which presents duplicate assay results for both acids in several mixtures which were assayed.

A 3-hr reflux time was found adequate for complete hydrolysis of the PPA samples, although 8 hr has been used for ortho- and polyphosphate mixtures.[7] Some condensed phosphates have been shown to be completely hydrolysed in less than 4 hr.[13] In this work, 8 hr of reflux gave assay results essentially identical with those of 3 hr. Refluxing for 1.5 hr left the PPA incompletely hydrolysed.

This paper reports a convenient titrimetric method for determination of sulphuric and polyphosphoric acids in mixtures. Accuracy and precision are good and the method is useful to monitor the acid proportions, which are important to ensure correct dehydrating strength in chemical reactions.

Acknowledgements—The authors thank Mr. John D. Brunson for assistance in testing this method.

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Summary—Polyphosphoric and sulphuric acids in a mixture may be determined simultaneously by titration. Experimental equivalent weights of the separate individual acids are first determined and these values are used to calculate weight percents for each acid in the mixture. Hydrolysis of the polyphosphoric acid (PPA) for three hours is necessary for quantitative conversion into orthophosphoric acid.

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TOTAL SYSTEMATIC ERROR IN REDOX TITRATIONS WITH VISUAL INDICATORS—II EXPERIMENTAL VERIFICATION

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Equations were given in a previous paper,[1] describing the transition potential of an indicator (E), the end-point error (ΔV_T), the indicator consumption error (ΔV_I) and the total absolute titration error (ΔV). The transition potential depends on the formal redox potential of the indicator, its spectrophotometric characteristics and in most cases on the indicator concentration. The total systematic error is a function of the formal redox potentials of the titrant and titrand, and the transition potential of the indicator corresponding to the end-point potential of the titration.

In this study the calculated transition potentials and errors have been compared with the experimental values for some indicators. As model systems the following were chosen. Variamine Blue and 4-amino-4′-methyldiphenylamine as reversible one-colour indicators [titration of iron(II) with vanadium(V)]. Ferroin as a reversible two-colour indicator [titration of iron(II) with cerium(IV). Diphenylaminesulphonic acid as a pseudoreversible[2] one-colour indicator [titration of iron(II) with cerium(IV)].

EXPERIMENTAL

Evaluation of transition potential

The transition potentials were evaluated by the method proposed by Belcher *et al.*[3] with concentrations from 1×10^{-5} to $5 \times 10^{-4}M$, for the indicator in the titrated solution at the end-point.

All titrations were carried out in 200-ml beakers approximately 5 cm in diameter, with a magnetic stirrer, and a platinum–saturated calomel electrode pair for measurement of the potentials. The indicator was in most instances added as the $5 \times 10^{-3}M$ solution. The titrations were started with $0.1M$ titrant and the end-points were approached by adding a $0.01M$ solution for better evaluation of the colour-change and potential at the end-point.

In the case of Variamine Blue the colour changes from green to violet-red. The absorbance of solutions at the end-point was measured at $\lambda = 530$ nm where the oxidized form has an absorption maximum.[4] In several titrations the final absorbances were in the range 0.27–0.32.

For 4-amino-4′-methyldiphenylamine the colour change was similar, and the absorbances at 520 nm were in the range 0.26–0.33 at the end-point.

Ferroin changed from red to colourless at concentrations below $5 \times 10^{-5}M$, but above $1 \times 10^{-4}M$ a distinct two-colour change from red to blue-violet was observed. As the sensitivity of the eye to these two colours is different, the absorbance ratio at the end-point has been determined experimentally. Equal absorbances at 510 and 590 nm[5, 6] do not correspond to the point of visual colour change, but an absorbance ratio of 3:2, corresponding to a concentration ratio of 30:1, does. For this reason an M-value of 1.5 was used in the subsequent calculations.

Because diphenylaminesulphonic acid is a pseudoreversible indicator its apparent transition potential may change when some of the indicator has been destroyed by local excesses of the titrant. The amount lost depends on the rate of stirring and on the duration of the whole titration. Two sets of measurements were therefore made with this indicator—with total titration times 5 and 10 min. At the end-point the absorbance at 585 nm[7] was found to be in the range 0.3–0.7. At low concentrations of this indicator the solution changed from colourless to violet, but at higher concentrations, especially when the duration of the titration was longer, from green to violet. The experimental

Table 1. Conditions for titrations

Indicator	Titrand solution	E_x^0, V	Titrant	E_T^0, V
Variamine Blue	10 ml $0.1M$ Fe(II) 10 g $CH_3COONa.3H_2O$ 15 ml 85% H_3PO_4 80 ml H_2O pH 2.25	0.360	$0.1M$ V(V)	0.865
4-Amino-4′-methyldiphenyl amine	10 ml $0.1M$ Fe(II) 14 g $CH_3COONa.3H_2O$ 15 ml 85% H_3PO_4 80 ml H_2O pH 2.70	0.317	$0.1M$ V(V)	0.800
Ferroin	10 ml $0.1M$ Fe(II) 90 ml $1M$ H_2SO_4	0.683	$0.1M$ Ce(IV)	1.433
Diphenyl-aminesulphonic acid	10 ml $0.1M$ Fe(II) 85 ml $1M$ H_2SO_4 5 ml 85% H_3PO_4	0.610	$0.1M$ Ce(IV)	1.350
Diphenyl-aminesulphonic acid	10 ml $0.1M$ Fe(II) 90 ml $1M$ H_2SO_4	0.683	$0.1M$ Ce(IV)	1.433

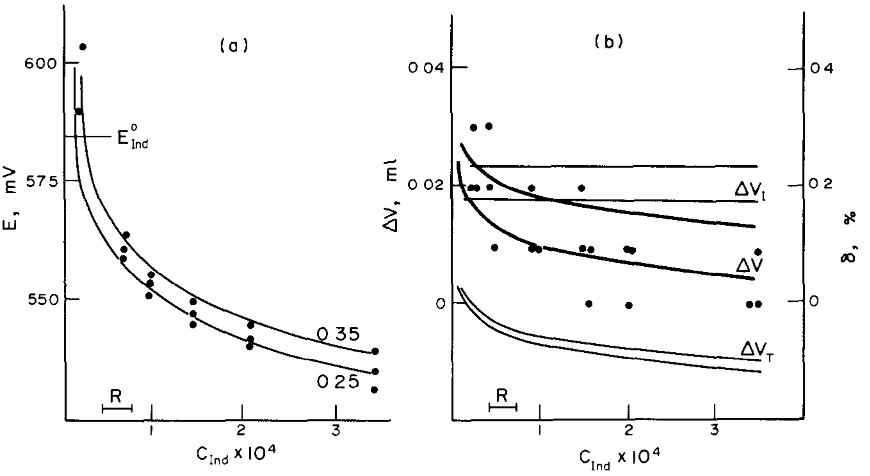

Fig 1 The change of transition potential (*a*) and titration error (*b*) as a function of indicator concentration for titration of iron (II) with vanadium (V), with Variamine Blue as indicator. Lines were calculated for $A = 0.25$ and 0.35. Points were obtained experimentally. ΔV_I—indicator consumption error, ΔV_T—end-point error, ΔV—total error R denotes usual concentration range of indicator.

transition potentials were not affected by the presence of phosphoric acid in the titrand solution.

Evaluation of total titration error

Titrations in the systems mentioned in Table 1 were carried out in parallel by using visual indicators and potentiometrically to the potential corresponding to the calculated equivalence point. The necessary formal potential values were estimated from the titration curves. The total experimental error was calculated as the difference between the results of the potentiometric and visual titrations, both performed under the same conditions and concentrations.

RESULTS AND DISCUSSION

Variamine Blue and 4-amino-4′-methyldiphenylamine are reversible one-colour indicators. However in titration of iron(II) with vanadium(V) the colour at the end-point changes from green to red-violet, because the vanadium(IV) is itself blue. This should not influence the validity of equations describing the transition potential and total error of titration. The formal redox potentials for these indicators are 0.585 V and 0.568 V respectively,[4, 7] under the titration conditions. The molar absorptivities of the oxidized forms are 7×10^3 and 6×10^3 $l.mole^{-1}.cm^{-1}$, respectively.[4, 7] The transition potential was calculated, assuming the absorbance at the end-point to be 0.25 or 0.35 (Figs. 1*a* and 2*a*). The agreement between calculated and experimental transition potentials for various indicator concentrations seems to support the assumptions.

The titration errors were also evaluated for the same experimental conditions (Figs. 1*b* and 2*b*). The precision of reading the volume of titrant (0.01 ml) results in some scatter in the experimental points around the calculated curve. The titration error was also calculated for the two values of absorbance at the end-point, *i.e.* 0.25 and 0.35, according to equation (13) and the appropriate equation in Table 3 in the previous paper.[1] Under the conditions of titration with the two indicators the following values of formal potentials were assumed: in titration with Variamine Blue: $E^0_x = 0.360$ V, $E^0_T = 0.865$ V; in titration with 4-amino-4′-methyldiphenylamine. $E^0_x = 0.317$ V, $E^0_T = 0.800$ V

With the reversible indicator ferroin, the situation is more complicated. At concentrations above $10^{-4}M$ it can

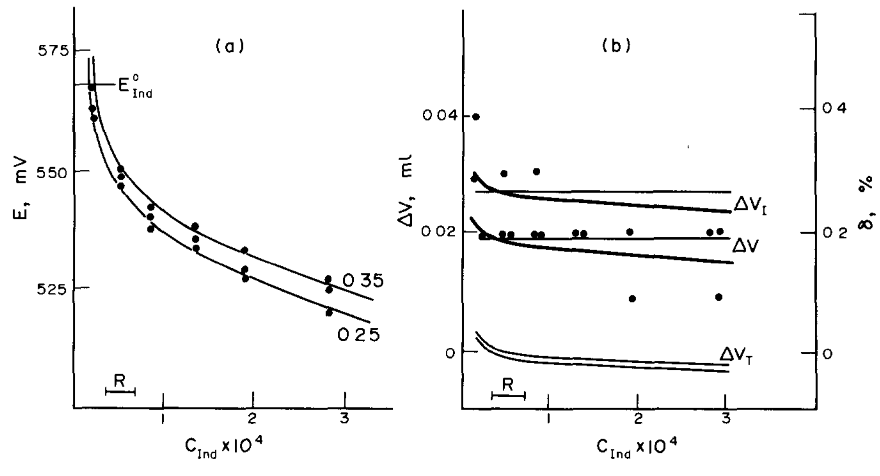

Fig. 2. The change of transition potential (*a*) and titration errors (*b*) as a function of indicator concentration for titration of iron (II) with vanadium (V), with 4-amino-4′-methyldiphenylamine as indicator. Symbols *etc.* as for Fig. 1.

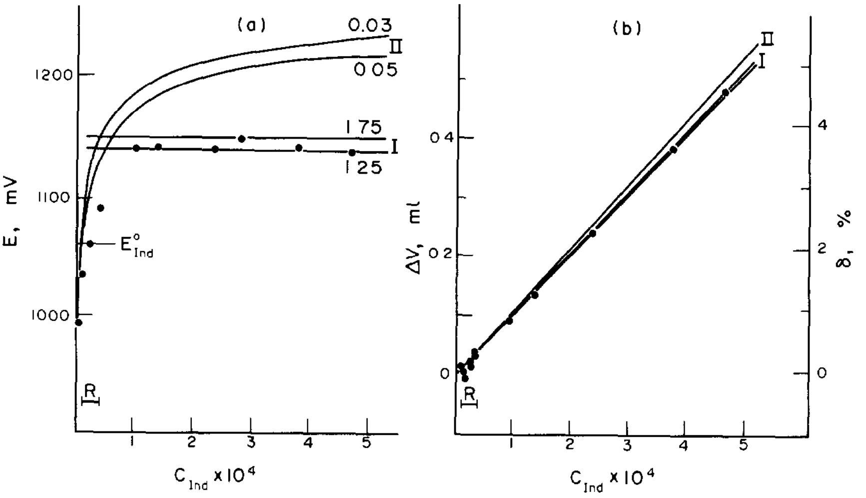

Fig. 3. The change of transition potential (*a*) and total titration errors (*b*) as a function of indicator concentration for titration of iron (II) with cerium (IV), with ferroin as indicator. Lines were calculated for a two-colour indicator (curves I) assuming $M = 1.25$ and 1.75, and a one-colour indicator (curves II) assuming $A' = 0.03$ and 0.05. Points were obtained experimentally. *R* denotes usual concentration range of indicator.

be considered as a two-colour indicator and its transition potential should therefore be independent of concentration (Fig 3*a* straight lines I). If ferroin is considered as a one-colour indicator then the transition potential would be expected to vary with concentration, as in the curves II, Fig. 3*a*. The measured potentials are in fact independent of concentration at higher indicator concentrations, whereas at lower concentrations they fit the predicted curve quite well. Because the indicator concentrations usually used in titrations do not exceed $5 \times 10^{-5}M$, ferroin should be treated in practice as a one-colour indicator. Two values of residual absorbance were used in the calculations for ferroin, namely 0.03 and 0.05, and for a two-colour indicator the ratio of absorbances at the end-point was accepted as $M = 1.25$ or 1.75. The value previously determined experimentally for this system is 1.5. The molar absorptivities for the reduced and oxidized forms of the indicator are 1.11×10^4 and 6×10^2 $\text{l mole}^{-1}.\text{cm}^{-1}$, and the formal redox potential is 1.06 V in 1*M* sulphuric acid.

The titration error in this system varies linearly with indicator concentration over a wide range, in spite of small differences in the slope depending on whether the system is considered as one- or two-colour (Fig. 3*b*) At higher indicator concentrations the two-colour relationship is in better agreement with the experimental data, and for the lowest concentrations either concept can be used. The linearity follows from the fact that the greater part of the error is due to titration of the indicator, since the large difference between the formal potentials of the titrand ($E^0_x = 0.683$ V) and the titrant ($E^0_T = 1.433$ V) leads one to expect that the end-point error would always be less than 0.01 ml.

In this example it is clear that the change from one- to two-colour indicator behaviour depends on the indicator concentration at which the observer can just perceive the colour of the oxidized form.

Diphenylaminesulphonic acid may be classified as a pseudoreversible indicator, because of the irreversibility of the chemical reaction, and also because of the instability of the oxidized form ($\tau_{1/2} = 13$ min in 1*M* sulphuric acid). The main assumption on which the equations for the transition potential and titration error are based is therefore not fulfilled, but it is interesting to see by how much the experimental values and those calculated for a reversible indicator differ.

The formal redox potential of the reaction

$$2\,\text{Ind}_{\text{red}} \rightarrow \text{Ind}_{\text{ox}} + 4e$$

may be determined from the half-oxidation potential ($E_{1/2} = 0.81$ V)[2] at a given concentration ($C_{\text{Ind}} = 8 \times 10^{-4}M$):

$$E^0_{\text{Ind}} = E_{1/2} + 0.059/4 \log C_{\text{Ind}} = 0.765 \text{ V}.$$

This value, and the molar absorptivity $\epsilon_{\text{ox}} = 1.4 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ enable us to calculate the transition potentials for $A = 0.2$ and $A = 0.9$ (Fig. 4) and hence to compare the calculated total error with experimental data (Fig 5). The calculated error in the absence of phosphoric acid is negative because the difference between the formal potentials of the titrand and indicator is small ($\Delta E^0 = 0.082$ V) but in the presence of phosphoric acid the decrease in potential of the Fe(III)/Fe(II) system ($\Delta E^0 = 0.160$ V) brings the theoretical error to a small positive value, mainly due to consumption of titrant by the indicator.

The experimental errors are always more positive than the calculated ones. Up to $5 \times 10^{-5}M$ indicator concen-

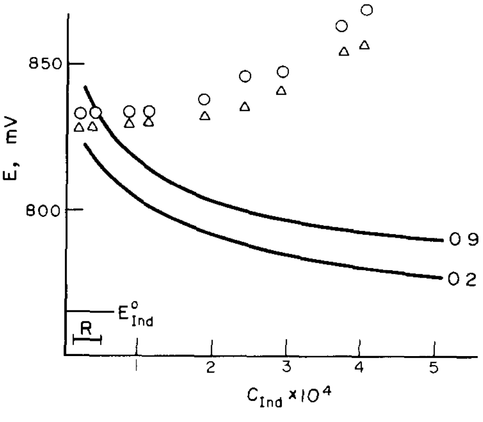

Fig. 4. The change of transition potential as a function of indicator concentration for titration of iron (II) with cerium (IV), with diphenylaminesulphonic acid as indicator. Lines were calculated for $A = 0.2$ and 0.9 Points were obtained experimentally for titration time 5 min (△) and 10 min (○).

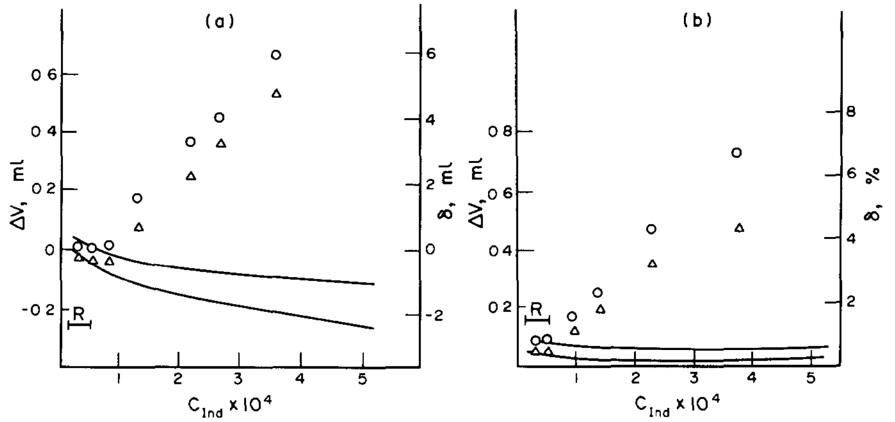

Fig. 5. The change of total titration errors as a function of indicator concentration for titration of iron (II) with cerium (IV), with diphenylamine sulphonic acid as indicator, in absence (*a*) and presence (*b*) of phosphoric acid. Symbols *etc.* as for Fig. 4.

tration the error is less than 0.05 ml (relative error 0.5%). For concentrations up to $1 \times 10^{-4}M$ in the absence of phosphoric acid the indicator consumption and end-point error compensate and the total error is still small. This is not the case when phosphoric acid is added, as is usually done in practice. At higher concentrations the error is always positive and too large to be acceptable in practice.

As decomposition of the indicator is time-dependent, the measurements were done for total titration times of 5 and 10 min. In the latter the error is significantly greater (more positive) indicating that the undesired process proceeds to a greater extent. Rapid titration is therefore advantageous, and the error can be further diminished by adding the indicator only shortly before the end-point. It must also be pointed out that effective stirring decreases local excesses of the titrant and therefore also decreases the total error.

This study clearly shows that for a reversible indicator the agreement between the calculated and experimental values of the titration error is quite good, and the equations presented may be used successfully for predicting the magnitude of the error. In the case of pseudoreversible indicators the equations give only the lowest possible value (in relative figures) of the error, whereas the real error is always more positive, and depends very much on the experimental conditions such as stirring, duration of titration etc.

Acknowledgement—The authors are greatly indebted to Professor R. Belcher, Chairman of the IUPAC Commission V-1, for stimulation of this study and his kind interest and discussion in the course of this work.

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Summary—The equations for calculating the transition potential of a redox indicator and the total titration error have been verified experimentally. Good agreement has been obtained for reversible indicators such as Variamine Blue, 4-methyl-4′-aminodiphenylamine and ferroin. In the latter case it was shown that at the usual concentrations the indicator acts as a one-colour indicator, whereas for higher concentrations its behaviour is typical of a two-colour indicator. In the case of a pseudoreversible indicator—diphenylaminosulphonic acid—the calculated values give only the minimum error. In real conditions the error is always more positive.

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DETERMINATION OF ORGANOTRITHIOCARBONATES WITH IODINE AND IODINE HALIDES IN NON-AQUEOUS MEDIA

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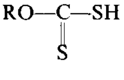
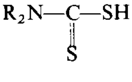
Xanthates, dithiocarbamates and organotrithiocarbonates are the salts of the corresponding xanthic (**I**), dithiocarbamic (**II**) and trithiocarbonic (**III**) acids respectively,



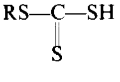
$\mathrm{RO{-}\underset{\Large S}{\overset{}{\underset{\|}{C}}}{-}SH}$

(**I**)



$\mathrm{R_2N{-}\underset{\Large S}{\underset{\|}{C}}{-}SH}$

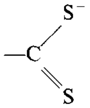
(**II**)

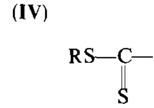


$\mathrm{RS{-}\underset{\Large S}{\underset{\|}{C}}{-}SH}$

(**III**)

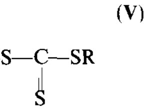
(R = alkyl or aryl groups)

and are characterized by the presence of the  $\mathrm{-C\langle^{S^-}_{S}}$ group. Because of their applications in analysis, industry, medicine and agriculture, their determination is of great interest and scope. Trithiocarbonates have found fewer applications than the other analogues. In spite of the tendency of these species to be easily oxidized to the corresponding dixanthogens (**IV**), thiuram disulphides (**V**) and bis[alkyl(aryl)mercapto thiocarbonyl] disulphides (**VI**) respectively, these compounds have not been widely studied by redox titrimetry. This is because of the tendency of these compounds to undergo decomposition with the acid media commonly used for redox titrations. Hence redox determination of these compounds in non-aqueous media is of value. Xanthates and dithiocarbamates have been determined in this way,[1–6] but the determination of trithiocarbonates by such methods does not appear to have attracted attention. This communication reports the use of iodine and iodine halides (monochloride, monobromide and trichloride) for the visual and potentiometric determination of trithiocarbonates in acetonitrile medium. The end-point in visual titrations is indicated by a sharp colour change from straw yellow to deep yellow (due to iodine) caused by the first drop of oxidant solution in excess. For potentiometric titration a platinum wire is used as an indicator electrode and an antimony or modified calomel electrode as reference



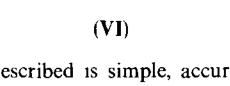
$\mathrm{RO{-}\underset{\Large S}{\underset{\|}{C}}{-}S{-}S{-}\underset{\Large S}{\underset{\|}{C}}{-}OR}$

(**IV**)



$\mathrm{R_2N{-}\underset{\Large S}{\underset{\|}{C}}{-}S{-}S{-}\underset{\Large S}{\underset{\|}{C}}{-}NR_2}$

(**V**)



$\mathrm{RS{-}\underset{\Large S}{\underset{\|}{C}}{-}S{-}S{-}\underset{\Large S}{\underset{\|}{C}}{-}SR}$

(**VI**)

The method described is simple, accurate, reliable and widely applicable.

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with an antimony or modified calomel (methanol saturated with potassium chloride was used instead of aqueous potassium chloride) reference electrode and a bright platinum wire indicator electrode.

Reagents

Acetonitrile. Distilled twice from phosphorus pentoxide.

Oxidants, 0.05N *in acetonitrile.* Iodine monobromide (solid) was prepared by the method of Popov and Skelly.[7] Commercially available iodine monochloride and trichloride were purified by reported methods.[8] Each oxidant solution was prepared by dissolving a little more than the calculated amount in the solvent. Iodine solution was standardized by titration against standard aqueous sodium thiosulphate. Iodine halides were standardized iodometrically in aqueous medium.

Trithiocarbonates. Prepared by shaking an equimolar mixture of the corresponding mercaptan, potassium hydroxide and carbon disulphide at a temperature below 10°. The compounds were recrystallized from suitable solvent mixtures and kept in a vacuum desiccator over phosphorus pentoxide.

Procedure

Aliquots of solutions of each compound in acetonitrile were taken in conical flasks (for visual titrations) or beakers (for potentiometric titrations) and diluted to 50–60 ml with the solvent. The solutions were cooled to room temperature and titrated visually or potentiometrically with standard (0.05*N*) iodine or iodine halide added from a microburette provided with a guard-tube for the protection from atmospheric moisture. In visual titrations, the end-point was marked by a sharp colour change from straw yellow to deep yellow.

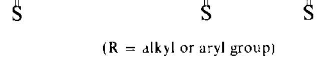
The solutions were magnetically stirred during potentiometric titrations. A sharp jump in potential was observed at the equivalence points. A series of potentiometric titrations was performed with different amounts of each compound and both electrode combinations.

The results of determinations with iodine monobromide (as a representative of these oxidants) are given in Table 1 Since the results obtained with both electrode assemblies agree closely, only one set (using platinum-modified calomel electrode assembly) is recorded in Table 1. The inflection points and potential jumps are also given.

RESULTS AND DISCUSSION

Johri and co-workers[9–11] have studied the oxidation of potassium trithiocarbonate, K_2CS_3, with various oxidants in acidic and alkaline media and have reported sulphate, carbon disulphide and/or elemental sulphur as the product(s) of oxidation, but no study seems to have been made of organic analogues.

The methods described here are based on oxidation with iodine in acetonitrile medium:



$$\mathrm{2RS{-}\underset{\Large S}{\underset{\|}{C}}{-}S^- + I_2 \rightarrow RS{-}\underset{\Large S}{\underset{\|}{C}}{-}S{-}S{-}\underset{\Large S}{\underset{\|}{C}}{-}SR + 2I^-}$$

(R = alkyl or aryl group)

Table 1. Titrations of organotrithiocarbonates with iodine monobromide in acetonitrile

Trithiocarbonate (potassium salt)	Amount found,*† *mg* Visual method	Amount found,*† *mg* Potentiometric method	Amount found,‡† *mg* Visual method	Amount found,‡† *mg* Potentiometric method	Inflection points,§ *mV*	Potential jump§ per 0.05 ml of IBr, *mV*
Ethyl	10.03, 0.038	10.02, 0.031	40.10, 0.074	40.05, 0.054	−80 ± 10	180–210
Isopropyl	10.02, 0.035	10.01, 0.024	40.06, 0.081	40.01, 0.052	−80 ± 10	180–210
n-Propyl	9.98, 0.031	9.99, 0.021	40.01, 0.077	39.98, 0.047	−90 ± 10	175–210
Isobutyl	9.96, 0.029	9.97, 0.024	39.89, 0.069	39.92, 0.051	−88 ± 12	185–220
n-Butyl	10.01, 0.035	9.98, 0.025	39.87, 0.077	39.90, 0.046	−85 ± 12	180–225
n-Amyl	9.98, 0.041	9.98, 0.030	40.00, 0.075	39.98, 0.054	−83 ± 12	180–215
Benzyl	10.03, 0.037	10.00, 0.027	40.08, 0.080	40.05, 0.055	−88 ± 12	170–210

* Amount taken, 10 mg.

† Mean of 10 determinations, with standard deviation (±).

‡ Amount taken, 40 mg.

§ Range of ten determinations.

In the titrations with iodine halides, iodine is formed as an intermediate which oxidizes the trithiocarbonates. The appearance and disappearance of the iodine colour (yellow) before the end-point can be readily seen. The end-point is indicated by the first permanent deep yellow colour.

Many trithiocarbonates (potassium salts of ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl and benzyl trithiocarbonic acids) have been successfully titrated with iodine and iodine halides. The overall standard deviations calculated from the pooled data for all the visual and potentiometric titrations performed with 10 mg of each trithiocarbonate were 0.035 and 0.026 respectively. For 40 mg of each trithiocarbonate the values were 0.076 and 0.051 respectively.

The effects of some possibly interfering compounds was studied. No interferences were found from alkyl isothiocyanates, isocyanates, carbon disulphide and urea even when present in up to fivefold amounts relative to trithiocarbonates.

Acknowledgement—The authors thank the Council of Scientific and Industrial Research (India) for the award of a research fellowship to one of them (S.K.).

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Summary—The determination of organotrithiocarbonates with iodine and iodine halides in acetonitrile medium by visual and potentiometric method is described. The visual end-point is indicated by a sharp colour change from straw yellow to deep yellow caused by the first drop of oxidant solution in excess. Potentiometric titrations are performed with antimony or modified calomel reference electrodes and a bright platinum wire as an indicator electrode. The proposed method is simple, requires very little time because of the rapidity of the reaction, and the minimum of apparatus.

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UNTERSUCHUNGEN ZUR BILDUNG VON *N*-NITROSO-NORNIKOTIN AUS NIKOTIN-*N*′-OXID

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(*Eingegangen am* 27. *Oktober* 1975. *Angenommen am* 12. *Januar* 1976)

Über das Vorkommen von *N*-Nitroso-Nornikotin (NNN) im Tabakrauch ist erstmals von Klus und Kuhn[1,2] und später von Hoffmann und Mitarbeitern[3] berichtet worden, wobei Werte bis zu 0,137 ppm im Tabakrauchkondensat gefunden wurden. Der Gehalt des Tabaks an NNN ist mit 0,3–90 ppm z.T. 10–100 mal höher als der des Kondensates.[3] Kürzlich wurde die biologische Aktivität des NNN als tumorerzeugende Substanz diskutiert.[4,5] Daher sind Untersuchungen zur Bildung des NNN von besonderem Interesse.

Für die Entstehung des NNN wurden bisher zwei Wege, nämlich die Bildung aus Nornikotin und aus Nikotin diskutiert,[1–3] wobei dem Nikotin aufgrund seiner höheren Konzentration größere Bedeutung zukommt. Eine Korrelation zwischen dem Nikotingehalt des Tabaks und dem NNN-Gehalt des Kondensates scheint gesichert zu sein;[2,3] ähnliches wird vom Nitratgehalt des Tabaks vermutet.[2] Dagegen lassen sich bisher keine eindeutigen Korrelationen des Alkaloid-, Nitrat- oder Nitritgehalts und des pH-Wertes im Tabak zum Gehalt an NNN im Tabak feststellen.[6] Bei *in vitro* Versuchen zur Bildung von NNN aus Nikotin und Nitrit lassen sich bei Raumtemperaturen nur geringe Mengen des Nitrosamins nachweisen. Bisher sind daher enzymatische oder bakteriologische Prozesse bei der Umwandlung von Nikotin zu NNN diskutiert worden

Von mehreren Autoren ist auf eine höhere Ausbeute an Nitrosaminen bei der Reaktion der tertiären Amine mit Nitrit, z.T unter dem Einfluß von Katalysatoren, hingewiesen worden.[7–9] In der vorliegenden Arbeit soll daher die *in vitro* Bildung von NNN aus Nitrit und Nikotin sowie Nikotin-*N*′-Oxid diskutiert werden.

MATERIAL UND METHODEN

Nikotin wurde unter Stickstoff im Vakuum über eine Vigreux Kolonne destilliert und wies nach dünnschichtchromatographischer Untersuchung keine nachweisbaren Verunreinigungen auf. Nikotin-*N*′-Oxid wurde nach einer Methode von Craig und Purushothaman[10] synthetisiert und als farblose Kristalle (Smp 151–153°) erhalten.

1. Umsetzung von Nikotin und Nitrit in wässriger Essigsaure

Ein g Nikotin wurde analog der Arbeitsvorschrift von Klus und Kuhn[2] unter Stickstoffbegasung in 25 ml 2,5*N* Essigsäure mit 1,725 g Natriumnitrit bei 20° bzw. 80° im thermostatisierten Wasserbad umgesetzt. Aliquote Proben wurden nach 15 Min, 60 Min und 240 Min entnommen, mit festem Na_2CO_3 alkalisiert, mit Benzol/Chloroform 8:2 ausgeschüttelt und auf 10 ml aufgefüllt. Die Komponenten wurden an einem dünnschichtchromatographischen System [DC-Fertigplatte Kieselgel 60 mit Fluoreszenzindikator F 254 (Merck AG); und Lösungsmittel Toluol:Isopropanol.10% wässriger Ammoniak (96:24:1)] getrennt und die Verbindungen mit Hilfe der König-Reaktion mit BrCN-Bedampfung sichtbar gemacht.

Halbquantitative Werte wurden über eine direkte Vermessung am Chromatogramm-Spektralphotometer (Zeiss AG) im Vergleich zu Eichkurven der jeweiligen Umsetzungsprodukte erhalten.

2. Umsetzung von Nikotin und Nitrit in Perchlorsäure

Wie vorher unter *1.* beschreiben wurde die Reaktion in 25 ml 10% wässriger Perchlorsäure [Methode von Lijinsky und Singer[9]] bei 20° bzw. 80° und 30 Min, 60 Min und 240 Min Einwirkungszeit durchgeführt und halbquantitative Werte des Unsetzungsproduktes NNN bestimmt.

3. Umsetzung von Nikotin-N′-Oxid und Nitrit in Perchlorsäure

Nikotin-*N*′-Oxid (0,2 g) wurde in einem 25 ml Kolben mit 5 ml 10% wässriger Perchlorsäure und 0,4 g Natriumnitrit bei 20° bzw. 80° umgesetzt. Aliquote Proben wurden nach 30 Min, 60 Min und 240 Min Umsetzungszeit entnommen, mit 2*N* Natriumhydroxid alkalisiert und mehrmals mit Methylenchlorid ausgeschüttelt. Aliquote Teile wurden an zwei dunnschichtchromatographischen Systemen getrennt:

(*a*) DC-Kieselgel 60/F 254 Platte (Merck AG); Fließmittel Chloroform:Methanol:Essigsäure (60:20:1)

(*b*) Fertigfolie Polyamid 11 (Macherey, Nagel & Co.), Fließmittel Benzol:Methanol.Dimethylformamid (93:5:2) Vom Umsetzungsprodukt NNN wurden halbquantitative Werte bestimmt

4. Umsetzung von Nikotin mit Nitrit in wässriger Perchlorsäure in Gegenwart von Formaldehyd

Reaktionen wie unter *2.* beschrieben, aber unter Zusatz von 1 ml 37% wässrige Formaldehydlösung.

5. Umsetzung von Nikotin-N′-Oxid mit Nitrit in wassriger Perchlorsaure in Gegenwart von Formaldehyd

Reaktionen wie unter *3.* beschrieben unter Zusatz von 1 ml 37% wässrige Formaldehydlösung.

6. Umsetzung von Nikotin-N′-Oxid mit Nitrit in wassriger Perchlorsäure in Gegenwart von Chlorogensaure

Reaktionen wie unter *3.* beschrieben, aber nur bei 23° und unter Zusatz von 50 mg Chlorogensäure.

ERGEBNISSE UND DISKUSSION

Die Umsetzungen des tertiären Amins Nikotin mit Nitrit sind, wie die Tabelle 1 zeigt, deutlich Zeit- und pH-abhängig. Damit bestätigen sich Befunde verschiedener Arbeitsgruppen,[2,3,11] deren Ausbeute an *N*-Nitroso-Nornikotin z.T. allerdings deutlich höher liegen. Es kann hier nicht endgültig entschieden werden, ob die Reinheit des eingesetzten Nikotins, die Stickstoffbegasung und damit der Ausschluß von Sauerstoff oder die selektivere Bestimmung des NNN nach dünnschichtchromatographischer Tren-

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Tabelle 1. Ausbeute an NNN bei der Umsetzung von Nikotin und Nitrit bei verschiedenem pH-Wert. Konzentration von Nikotin = 100%

Zeit	NNN-Ausbeute, %			
	in Essigsäure		in $HClO_4$	
Min	20°C	80°C	20°C	80°C
15	Spuren	4,3	Spuren	5,2
60	0,15	6,2	0,33	8,3
240	0,37	8,6	0,82	12,4

Tabelle 2. Ausbeute an NNN bei der Umsetzung von Nikotin und Nitrit in wässriger $HClO_4$ in Gegenwart von Formaldehyd. Konzentration von Nikotin = 100%

Zeit,	NNN-Ausbeute (%)	
Min	20°C	80°C
30	Spuren	Spuren
60	Spuren	0,15
240	0,12	0,10

Tabelle 3. Ausbeute an NNN bei der Umsetzung von Nikotin-*N*'-Oxid und Nitrit in $HClO_4$ z.T. in Gegenwart von Katalysatoren. Konzentration von Nikotin = 100%

	NNN-Ausbeute, %				
Zeit,	ohne Katalysator		+ Formaldehyd		+ Chlorogensäure
Min	20°C	80°C	20°C	80°C	23°C
30	0,15	4,8	0,42	8,35	1,38
60	0,53	9,7	1,35	—	3,43
240	1,15	15,1	5,22	24,5	9,37

nung zu einer niedrigeren Ausbeute an NNN führen. Auf der Kieselgelplatte lassen sich neben Nikotin (R_f = 0,55) und *N*-Nitroso-Nornikotin (R_f = 0,67) zwei weitere nicht identifizierte Flecken mit R_f = 0,23 und R_f = 0,75 erkennen, so daß mit dem Auftreten anderer Umsetzungsprodukte[2] gerechnet werden muß.

Von mehreren Autoren[7,8,9] ist beobachtet worden, daß eine Nitrosierung tertiärer Amin-*N*-Oxide im Sinne einer Polonovski-Reaktion[12] zu einer höheren Ausbeute an Nitrosaminen führt. Wie ein Vergleich der NNN-Ausbeute der Tabellen 1 und 3 zeigt, liegt auch die Ausbeute bei der Umsetzung mit Nikotin-*N*-Oxid bis zu dreifach höher als beim Einsatz von Nikotin.

Sowohl im Trennsystem auf der Kieselgelplatte als auch auf der etwas schärfer trennenden Polyamidfolie lassen sich aus dem Reaktionsgemisch neben Nikotin-*N*'-Oxid (R_f-Polyamid = 0,13) und *N*-Nitroso-Nornikotin (R_f-Polyamid = 0,63) zwei weitere nicht identifizierte Umsetzungsprodukte (R_f-Polyamid = 0,58 und 0,71) und Nikotin (R_f-Polyamid = 0,24) nachweisen, so daß auch bei diesen Reaktionen mit dem Auftreten weiterer Produkte zu rechnen ist. Da sich bei der Reaktion z.T. beträchtliche Mengen an Nikotin bilden, können Anteile des NNN auch aus der Reaktion zwischen Nikotin und Nitrit entstehen. Die Ausbeuten an NNN liegen bei der Reaktion des Nikotin-*N*'-Oxids aber deutlich höher, so daß eine Bildung des NNN im Sinne einer Polonovsky-Reaktion als sehr wahrscheinlich anzusehen ist.

In letzter Zeit werden verstärkt die katalytischen Einflüsse von Carbonylverbindungen[13] und Polyphenol-Körpern[14] bei der Bildung von Nitrosaminen aus tertiären Aminen und Nitrit diskutiert. Dabei wurden sowohl reaktionsbeschleunigende als auch reaktionshemmende Effekte beobachtet.

Bei der Umsetzung eines tertiären Amins mit Nitrit in Gegenwart von Formaldehyd wird am Beispiel des Nikotins eine Reaktion zum Nitrosamin deutlich gehemmt (Tabelle 2). Im Gegensatz hierzu (Tabelle 3) wird durch Formaldehyd die Umsetzung eines tertiären Amin-*N*-Oxids mit Nitrit zum Nitrosamin katalytisch so beschleunigt, daß selbst bei Raumtemperaturen bereits bemerkenswerte Mengen *N*-Nitroso-Nornikotin nachweisbar sind. Der gleiche Effekt läßt sich bei der Umsetzung in Gegenwart von Chlorogensäure feststellen (Tabelle 3).

Damit kann gezeigt werden, daß eine Entstehung von *N*-Nitroso-Nornikotin in Gegenwart verschiedener Katalysatoren, wie sie auch in der Tabakpflanze in reiner oder derivatisierter Form vorkommen, aus Nikotin-*N*'-Oxid selbst bei niedriger Temperaturen möglich ist. Ob Nikotin-*N*'-Oxid damit als ein Präkursor für *N*-Nitroso-Nornikotin im Tabak anzusehen ist, muß durch weitere Untersuchungen im Tabak wie etwa der Bestimmung des Nikotin-*N*'-Oxid-Gehaltes in Korrelation zum *N*-Nitroso-Nornikotin bei gleichzeitiger Bestimmung ähnlicher Katalysatoren, wie in dieser Arbeit verwendet, geklärt werden.

Wie Klus und Kuhn[1] durch Bestimmung des *N*-Nitroso-Nornikotingehaltes im tabakfreien Filter einer Zigarette diskutieren,[2] sollte NNN zumindest anteilsmäßig ein nativer Rauchbestandteil sein. Ob damit NNN nicht zumindest anteilweise aus dem Tabak in den Rauch übergeht, sollte durch Messungen der Transferrate mit ^{14}C-*N*-Nitroso-Nornikotin bestimmt werden. Hecht und Mitarb.[5] vermerken immerhin eine Rauchübergangsrate um 10%.

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Zusammenfassung—Die Umsetzung von Nikotin-*N'*-Oxid mit Nitrit zu *N*-Nitroso-Nornikotin (NNN) führt zu höheren Ausbeuten als ähnliche Reaktionen zwischen Nikotin und Nitrit. Es werden dunnschichtchromatographische Systeme zur Trennung und *in-situ* Analyse entwickelt und der Einfluß von Katalysatoren auf die Bildung von NNN untersucht.

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ANALYTICAL DATA

EXTRACTION AND PHOTOMETRIC DETERMINATION OF MICROAMOUNTS OF Zn^{2+}, Cd^{2+} AND Hg^{2+} WITH 1-(2-QUINOLYLAZO)-2-ACENAPHTHYLENOL

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The analytical potentialities of 1-(2-quinolylazo)-2-acenaphthylenol (QAAc), already synthesized,[1] for the spectrophotometric determination of Zn^{2+}, Cd^{2+} and Hg^{2+} are reported. They may be compared with those of other heterocyclic azo dyes used for this purpose[2–8]

EXPERIMENTAL

Reagents

Stock solutions of zinc, cadmium and mercury were prepared by dissolving appropriate amounts of analytical-reagent grade ZnO in perchloric acid, $Cd(CH_3COO)_2 \cdot 2H_2O$ in water, and metallic mercury in perchloric acid and were standardized by conventional methods if necessary. A stock solution of QAAc was obtained by dissolving the requisite quantity in pure methanol In no case reagent solutions used were over a week old. The pH was adjusted in the Zn^{2+} and Cd^{2+} systems with a 2*M* solution of sodium acetate, and with 0.5*M* sodium carbonate and 1*M* sodium perchlorate in the Hg^{2+} system. All other reagents used were of the highest purity.

RESULTS AND DISCUSSION

Solvent effect and stability

Red metal–QAAc species precipitate from 50% methanol They are soluble in various organic solvents Carbon tetrachloride, in which the coloured chelates are stable for at least 8 hr, was found to be the most suitable.

The physicochemical characteristics of the metal complexes of QAAc are summarized in Table 1.

Recommended procedures

Zn(II) and Cd(II). To a suitable aliquot containing 2–7 μg of Zn(II) or 4–23 μg of Cd(II) add 5 ml of 10^{-3} *M* QAAc (in methanol), followed by 4 ml of 2 *M* sodium acetate to give the appropriate pH (Table 1). Dilute to 10 ml and extract the complex into 10 ml of carbon tetrachloride.

Hg(II). To a suitable aliquot of solution containing 5–20 μg of Hg(II), add 5 ml of 10^{-3} *M* QAAc (in methanol), followed by the addition of 0.1 ml of 0.5 *M* sodium carbonate and 1 ml of 1 *M* sodium perchlorate (necessary

Table 1. Physicochemical characteristics of the metal complexes of QAAc

Characteristics	Zn–QAAc complex	Cd–QAAc complex	Hg–QAAc complex
λ_{max}, *nm*	540	550	540
Workable pH range	7.0–11 3	8.5–11 8	8 5–10.7
Molar ratio of QAAc needed for complete complexation	25	12.5	10
Validity of Beer's law, *ppm*	0–1.36	0–3.36	0–2.5
Molar composition (metal:ligand)	1:2	1:2	1:2
Sandell's sensitivity, *μg/cm²*	8.8×10^{-4}	2.4×10^{-3}	3.3×10^{-3}
Optimum range, *ppm*	0 2–0 7	0.4–2.3	0 5–2.0

Table 2. Tolerance limits of various foreign ions, *ppm*

Foreign ion	Zn–QAAc complex	Cd–QAAc complex	Hg–QAAc complex	Masking agent if any
F^-	150	200	100	
Cl^-	1000	1000	250	
Br^-	1000	1000	250	
I^-	2000	500	100	
SCN^-	500	500	250	
CN^-	Interferes	Interferes	Interferes	
NO_2^-	1000	1000	1000	
NO_3^-	1000	1000	1000	
ClO_4^-	1000	1000	1000	
SO_3^{2-}	1000	1000	250	

Continued on next page

Table 2 *continued*

Foreign ion	Zn–QAAc complex	Cd–QAAc complex	Hg–QAAc complex	Masking agent if any
$S_2O_3^{2-}$	1000	Interferes	Interferes	
SO_4^{2-}	1000	1000	500	
$C_2O_4^{2-}$	100	500	250	
Tartrate	200	200	500	
Thiourea	1000	1000	Interferes	
PO_4^{3-}	Interferes	Interferes	100	
BO_3^{3-}	200	500	1000	
Citrate	500	250	500	
EDTA	Interferes	Interferes	Interferes	
Cu(II)	3	Interferes	Interferes	Thiourea
Ag(I)	5	5	5	Halides
Au(III)	10	5	—	I^-
Ba(II)	20	20	20	
Sr(II)	20	20	20	
U(VI)	20	20	20	F^-
Zn(II)	—	Interferes	Interferes	
Cd(II)	3	—	Interferes	I^-
Hg(II)	6	4	—	I^-
Al(III)	10	10	10	
V(V)	5	5	5	
Mn(II)	10	10	10	
Fe(II)	5	5	5	F^-
Co(II)	Interferes	Interferes	Interferes	
Ni(II)	5	5	5	Citrate
Pd(II)	5	5	5	NO_2^-
Ir(III)	10	10	10	
Os(VIII)	10	10	10	
Pt(IV)	10	10	10	
Ru(III)	5	5	5	
Mo(VI)	7	5	5	
Pb(II)	5	5	5	Citrate and tartrate

for complete extraction), dilute to 10 ml and extract the complex into 10 ml of carbon tetrachloride.

Measure the absorbance against a reagent blank.

Effect of foreign ions

The effect of other ions was studied by taking 6.5 μg of Zn^{2+}, 22.4 μg of Cd^{2+} or 20.1 μg of Hg^{2+}, adding different amounts of the ion to be investigated and following the recommended procedure. Table 2 records the results; the tolerance limits are the concentrations which do not cause a deviation of more than ±2% in the absorbance.

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Summary—1-(2-Quinolylazo)-2-acenaphthylenol (QAAc) combines with Zn(II), Cd(II) and Hg(II), giving deep red 1:2 complexes which are extractable in CCl_4 and other organic solvents. Spectrophotometric methods based on the reactions are sensitive and fairly selective, the Sandell's sensitivities being 8.8×10^{-4}, 2.4×10^{-3} and 3.3×10^{-3} μg/cm² for Zn(II), Cd(II) and Hg(II) respectively.

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ANNOTATIONS

THE RELATIONSHIP BETWEEN THE INFLECTION POINT AND EQUIVALENCE POINT OF A POTENTIOMETRIC TITRATION

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Although the principles of potentiometric titrations are described in some detail in almost every modern textbook of analytical chemistry, it appears that the treatment given in most of these books is incorrect on one particular point, namely the relationship between the equivalence point and the inflection point of the titration curve. In the following discussion a brief outline of this question will be given.

The end-point of a potentiometric titration is usually defined as the inflection point of the titration curve. Moreover, it is usually stated quite categorically that the inflection point will coincide with the equivalence point of the titration, provided that the titration curve is "symmetrical", whereas the inflection point of an "unsymmetrical" curve is said to differ somewhat from the equivalence point. The term "symmetrical" is used to indicate that the reactants combine in a one-to-one stoichiometric ratio. In contrast to these statements a rigorous mathematical treatment reveals that the inflection point and equivalence point of potentiometric titrations will *never* coincide for so-called symmetrical titration curves.[1-3] Only for unsymmetrical reactions may there be conditions under which the inflection point and equivalence point will coincide.[2]

Fortunately, the difference between the inflection point and the equivalence point is usually negligible. However, the categorical form of the statements found in most textbooks could easily lead the reader to the erroneous conclusion that the inflection point of a symmetrical curve coincides with the equivalence point also in a mathematical sense. In this connection it is particularly misleading that attention is frequently drawn to the lack of coincidence for unsymmetrical curves, while at the same time claiming coincidence for symmetrical curves. As already mentioned, the opposite statement is more correct.

The somewhat misleading treatment found in many textbooks concerning this topic may be due to the early results of Roller[4] and Butler.[5] As pointed out by Meites[1] their incorrect results were due to the neglect of dilution in the mathematical treatment of the titration curves. For ion-combination titrations, such as acid–base and precipitation titrations, this neglect results in the coincidence of the inflection point and equivalence point provided that the titration curve is symmetrical. However, for complexometric titration curves the two points in question will never fully coincide, even if volume changes are neglected. This is rather surprising, as complex formation is in some ways the simplest of the common titration reactions. To illustrate this point the difference between the equivalence point and inflection point is calculated below for the complexometric titration of A with B according to the reaction $A + B \rightleftharpoons AB$.

Three equations must be taken into consideration:

$$C_A = [A] + [AB] \tag{1}$$

$$C_B = [B] + [AB] \tag{2}$$

$$[AB] = K[A][B] \tag{3}$$

where C_A and C_B are the total concentrations of A and B respectively, and K is the formation constant for the complex AB. If volume changes are neglected, the equation for the potentiometric titration curve can be obtained by eliminating [B] and [AB] from equations (1), (2) and (3).

$$K[A]^2 + (KC_B - KC_A + 1)[A] - C_A = 0 \tag{4}$$

or written in an explicit form

$$pA = \log(2K) - \log\{[\sqrt{(KC_B - KC_A + 1)^2 + 4KC_A}] - [KC_B - KC_A + 1]\} \tag{5}$$

where pA ($= -\log[A]$) is a function of C_B, the concentration of titrant. The concentration of C_B at the inflection point of the titration curve is calculated by differentiating equation (5) twice with respect to C_B:

$$\frac{d^2(pA)}{dC_B^2} = -(\log e)K^2(KC_B - KC_A + 1) \times \{(KC_B - KC_A + 1)^2 + 4\,KC_A\}^{-3/2} \tag{6}$$

At the inflection point the second derivative is zero, giving

$$C_B = C_A - K^{-1} \tag{7}$$

From equation (7) it is seen that the inflection point does not coincide with the equivalence point ($C_B = C_A$), even though the titration curve is symmetrical, and volume changes are neglected. However, the difference between the inflection point and equivalence point is only K^{-1}, which implies that the difference is quite insignificant. It turns out that the same holds for systems in which volume changes are taken into consideration.

As a conclusion of the discussion above the author would like to point out that it would be wise to avoid too categorical statements when discussing the inflection point of titration curves. In introductory textbooks it seems most appropriate to explain in general terms that the inflection point is usually very close to the equivalence point of the titration, although the two points do not coincide in a mathematical sense.

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Summary—Attention is drawn to a common textbook error concerning the coincidence of the end-point and equivalence point of potentiometric titration curves

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DETERMINATION OF 14 TRACE ELEMENTS IN COBALT BY PROTON-ACTIVATION ANALYSIS

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Summary—Proton-activation analysis has been applied to the determination of 14 trace impurities in cobalt. The method consists of a short (~10 min) and a longer (~2 hr) irradiation of the sample with 13-MeV and 12-MeV protons, respectively, followed by high-resolution γ-ray spectrometry. The elements Ti, Cr, Fe, Ni, Cu, Zn, Nb, Mo, Ru and W have been determined in VP-purity cobalt. In the case of V, Cu, Zr, Pd and Sn, the amounts present were below the limit of detection. In the case of Fe, Ni, and Mo, the results are compared with those obtained by a second independent method. Data on reproducibility, limits of detection and possible interferences are given.

Relatively few trace analytical studies have been performed on cobalt matrices of good and high-purity grades. Optical emission spectrography has been used to determine Si, Mn, Fe, Ni, Cu and Zn,[1] and in addition Al[2] and also As and Sb[3] in cobalt. A spectrographic technique used for the determination of all the above-mentioned elements and, in addition, the alkali metals, Ca, Ti, V, Cr, Nb, Mo, Rh, Pd, Cd, Ag, W and Tl, in cobalt of 99.999% purity has been described by Tombu[4] together with a listing of the different chemical methods for the determination of H, C, N, O, Na, Mg, Al, Si, P, S, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Se, Sn, Sb, W, Tl, Pb and Bi. Unfortunately, neither the concentration intervals to which the individual methods have been applied nor the limits of detection were given. Activation analytical techniques have rarely been applied to the analysis of cobalt matrices.[5,6] In activation analysis with reactor neutrons, there are difficulties with the very high matrix activity due to the high thermal neutron cross-section and the resonance integral for the $^{59}Co(n,\gamma)^{60}Co$ reaction and the long half-life of ^{60}Co. Radiochemical neutron activation analysis has been used for the determination of Cu,[7,8] Mn and Zn.[8]

Recently an article by Benaben, Barrandon and Debrun has appeared[9] in which the application of an instrumental proton-activation technique to multielement analysis of cobalt has been described. However, the experimental conditions and sample types used by these authors differ from those used in the present work. While they irradiated the cobalt samples with 10-MeV protons for 1 hr, in our case the cobalt samples were activated with 13-MeV protons to produce short-lived indicator radionuclides in short irradiations (~10 min), and with 12-MeV protons to produce long-lived indicator radionuclides in longer irradiations (~2 hr). To check the accuracy of the proton-activation technique described here, analytical results for iron, nickel and molybdenum are compared with results obtained by atomic-absorption spectrometry and by X-ray fluorescence spectrometry.

EXPERIMENTAL

Sample and standards

A cobalt sample of VP grade supplied by Material Research, GmbH, Eching bei München, West Germany, was analysed. From the cobalt metal, targets with a thickness of ~0.6 mm were cut. To remove possible surface contamination, a pre-irradiation chemical etch was accomplished with dilute nitric acid (1:1 ultrapure water and nitric acid). Thick metal targets of pure elements, their alloys or pressed powder mixtures were used for the standardization. For the etching of the standards, different solutions were used according to the character of the metal For the measurements of the activation curve of the $^{59}Co(p,pn)^{58}Co$ reaction, stacked foils of VP-purity cobalt were used

Irradiation

Irradiations were performed with 12-MeV and 13-MeV protons at the Karlsruhe isochronous cyclotron. For standardization, the average beam currents were 5–200 nA and the irradiation times were 20–60 sec Cobalt samples were irradiated in a water-cooled target holder for 5–120 min with beam intensities of 3–5 MeV. The activation curve was measured for proton energies up to 25 MeV.

Data acquisition

Gamma-rays were counted with a 55-cm^3 Ge(Li) detector having an energy resolution of 2.1 keV FWHM for the 1.332-MeV γ-ray of ^{60}Co and a peak-to-Compton ratio of 29:1. The detector was coupled with a 4096-channel pulse-height analyser. Computer programs[10] were used to list and plot the spectra and to determine the energies and intensities of the photopeaks. Data on the reaction studied and on the properties of the indicator radionuclides were obtained from recent compilations and tables[11–14]

RESULTS AND DISCUSSION

Selection of activation reactions

Inspection of the nuclear data and preliminary experiments indicated proton-activation analysis to be

Table 1. Proton-induced cobalt reactions producing radionuclides

Reaction	Q-value, MeV	Half-life	γ-Rays, MeV	Intensity, %
^{59}Co(p,n)^{59}Ni	- 1.9	7.5 x 10^{4} yr	-	-
^{59}Co(p,pn)^{58m}Co	-10.5	8.94 hr	0.0249	0.03
^{59}Co(p,pn)^{58}Co	-10.5	70.78 d	0.5110 0.8106 0.8636 1.6748	30.0 99.4 0.7 0.5
^{59}Co(p,p2n)^{57}Co	-19.0	270.0 d	0.0144 0.1221 0.1364 0.5703 0.6921	9.5 85.6 10.6 0.01 0.15
^{59}Co(p,αn)^{55}Fe	- 8.0	2.7 yr	-	-

the most suitable with respect to the instrumental performance and the multi-element character of the cobalt analysis. In activation with thermal neutrons, the matrix is strongly activated through the ^{59}Co(n,γ)^{60}Co reaction, with fast neutrons through the ^{59}Co(n,2n)^{58}Co, ^{59}Co(n,p)^{59}Fe and ^{59}Co(n,α)^{56}Mn reactions, with photons through the ^{59}Co(γ,n)^{58}Co reaction, with deuterons through the ^{59}Co(d,p)^{60}Co reaction, and with ^{3}He and α-particles mainly through ^{59}Co(α,xn) reactions yielding copper nuclides with different half-lives.

Table 1 lists nuclear reactions which can be induced in cobalt when it is bombarded with protons of energy up to 20 MeV. As is evident from the data, the instrumental performance of analysis requires that the ^{59}Co(p,pn)^{58}Co reaction be eliminated or reduced. The activation curve of this reaction is shown in Fig. 1. This activation curve is in good agreement with that obtained by Benaben *et al.*[9] and with the published excitation function.[15] More detailed experiments on this problem showed that a proton energy of 12 MeV can be used even over long irradiation times, *i.e.*, the reaction occurs only to an insignificant extent. Short irradiation times can be used with protons up to an energy of 13 MeV. With use of these proton energies, good sensitivities are obtained as the position of the maximum cross-sections is located in this energy region for most of the analytical reactions. Nuclear data on the analytical reactions used and on the properties of the indicator radionuclides are given in Table 2.

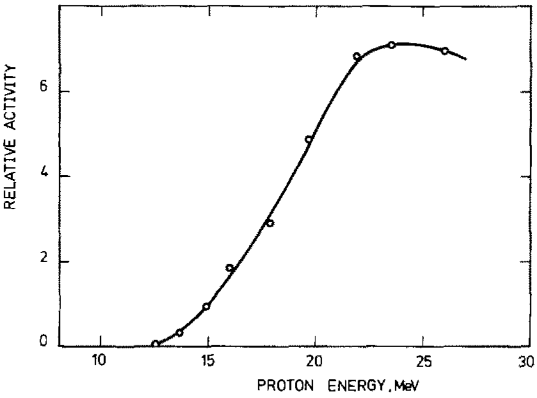

Fig. 1. Activation curve for the ^{59}Co(p,pn)^{58}Co reaction.

Interferences

Primary interference reactions which are energetically possible at the proton energies used are listed in Table 3. No primary interference reactions can occur in the determination of Ti and Cr. By experiment it has already been shown that no measurable interferences occur in the determination of Zr and Nb,[16] V, Fe, Mo and W,[17] and of Ni and Cu,[18] even if the concentrations of the interfering elements are many times those of the elements to be determined. A detailed analysis of the experimental results obtained in the irradiation of cobalt samples has shown that no measurable interferences occurred in the determination of Zn, Ru, Pd and Sn where Ge, Pd, Cd and Te could interfere through nuclear reactions of (p,α) and (p,αn) types. The presence of these interfering elements and the possible extent of their interferences were checked through the corresponding (p,n) reactions, which could yield, at the given proton energy, radioactivities higher by one or two orders of magnitude than those formed in the interfering reactions.

By bombardment of thick targets with protons of medium energy, neutrons can be produced by (p, xn) reactions. The neutron fluxes are considerably lower than the original proton-beam intensities, so the secondary interference reactions induced by neutrons, do not normally occur to a detectable extent if they are induced on the trace elements. However, if such reactions are induced on the main constituents of the sample they must be considered. Secondary interference reactions which can be induced in cobalt are listed in Table 4 together with cross-section data and energies of the γ-rays emitted by the radionuclides produced. None of the radionuclides produced in these reactions is used as an indicator radionuclide

Table 2. Data on production and properties of the indicator radionuclides

Element to be determined	Principal reactions	Isotopic abundance, %	Q-value, MeV	Half-life	Major γ-rays, MeV	Intensity, %
Ti	$^{48}\text{Ti}(p,n)^{48}\text{V}$	73.7	- 4.8	15.97 d	0.9443	8.0
					0.9835	100.0
					1.3116	98.0
V	$^{51}\text{V}(p,n)^{51}\text{Cr}$	99.75	- 1.5	27.7 d	0.3201	9.8
Cr	$^{52}\text{Cr}(p,n)^{52m}\text{Mn}$	83.79	- 5.5	21.0 min	1.4343	100.0
	$^{52}\text{Cr}(p,n)^{52}\text{Mn}$	83.79	- 5.5	5.7 d	0.7442	85.0
					0.9356	93.0
					1.4343	100.0
Fe	$^{56}\text{Fe}(p,n)^{56}\text{Co}$	91.7	- 5.4	77.3 d	0.8467	99.99
					1.0378	14.0
					1.2383	67.6
					1.7715	15.7
					2.5986	16.9
Ni	$^{60}\text{Ni}(p,n)^{60}\text{Cu}$	26.42	- 6.9	23.0 min	0.8260	19.2
					1.3325	87.3
					1.7920	44.9
Cu	$^{63}\text{Cu}(p,n)^{63}\text{Zn}$	69.1	- 4.1	38.4 min	0.6696	8.5
					0.9619	6.7
Zn	$^{66}\text{Zn}(p,n)^{66}\text{Ga}$	27.8	- 6.0	9.3 hr	1.0393	37.3
					2.7523	22.8
Zr	$^{90}\text{Zr}(p,n)^{90}\text{Nb}$	51.4	- 6.9	14.6 hr	0.1412	67.0
					1.1291	92.0
					2.1860	18.0
					2.3190	82.0
Nb	$^{93}\text{Nb}(p,n)^{93m}\text{Mo}$	100.0	- 1.2	6.9 hr	0.2632	61.2
					0.6846	91.9
					1.4772	99.4
Mo	$^{94}\text{Mo}(p,n)^{94m}\text{Tc}$	9.1	- 5.0	53.0 min	0.8709	91.0
					1.5220	5.4
					1.8688	5.3
	$^{94}\text{Mo}(p,n)^{94}\text{Tc}$	9.1	- 5.0	4.9 hr	0.7026	100.0
					0.8497	100.0
					0.8709	100.0
					0.9162	6.8
	$^{95}\text{Mo}(p,n)^{95}\text{Tc}$	15.9	- 2.5	20.0 hr	0.7658	94.0
	$^{96}\text{Mo}(p,n)^{96}\text{Tc}$	16.7	- 3.7	4.3 d	0.7783	100.0
					0.8128	82.0
					0.8503	99.0
					1.1272	15.0
Ru	$^{100}\text{Ru}(p,n)^{100}\text{Rh}$	12.6	- 4.4	20.0 hr	0.4462	11.5
					0.5396	80.0
					0.8225	20.6
					1.1071	13.5
					1.3621	15.3
					1.5534	21.0
					1.9297	12.4
					2.3761	35.7
	$^{101}\text{Ru}(p,n)^{101m}\text{Rh}$	17.1	- 1.3	4.4 d	0.3068	94.0
Pd	$^{104}\text{Pd}(p,n)^{104m}\text{Ag}$	11.0	- 4.9	33.5 m	0.5558	91.0
	$^{104}\text{Pd}(p,n)^{104}\text{Ag}$	11.0	- 4.9	69.2 min	0.5558	92.5
					0.7674	66.3
					0.9232	16.3
					0.9259	12.5
					0.9416	25.0
					1.5261	6.2
Sn	$^{116}\text{Sn}(p,n)^{116}\text{Sb}$	14.4	- 5.3	16.0 m	0.9330	23.0
					1.2937	88.0
					2.2298	11.5
	$^{120}\text{Sn}(p,n)^{120m}\text{Sb}$	32.8	- 3.5	5.76 d	0.0898	77.0
					0.1972	89.0
					1.0230	99.0
					1.1713	100.0
W	$^{182}\text{W}(p,n)^{182m}\text{Re}$	26.3	- 3.6	13.0 hr	0.1001	17.4
					1.1213	38.5
					1.1890	18.4
					1.2214	30.5
	$^{182}\text{W}(p,n)^{182}\text{Re}$	26.3	- 3.6	64.0 hr	0.1001	15.0
					0.1489	15.0
					0.1784	18.0
					0.2292	25.0
					0.2564	13.0
					1.1220	20.0
					1.1895	7.9
					1.2218	15.0

Table 3. Possible primary interference reactions

Element to be determined	Activation reaction used	Interfering reaction	Q-value, MeV	Isotopic abundance, %
Ti	^{48}Ti(p,n)^{48}V	^{52}Cr(p,αn)^{48}V	-14.2	83.79
V	^{51}V(p,n)^{51}Cr	^{55}Mn(p,αn)^{51}Cr	- 9.0	100.00
		^{52}Cr(p,pn)^{51}Cr	-12.0	83.79
Cr	^{52}Cr(p,n)^{52}Mn	^{56}Fe(p,αn)^{52}Mn	-13.1	91.7
Fe	^{56}Fe(p,n)^{56}Co	^{60}Ni(p,αn)^{56}Co	-11.6	26.23
Ni	^{60}Ni(p,n)^{60}Cu	^{64}Zn(p,αn)^{60}Cu	-10.9	48.9
Cu	^{63}Cu(p,n)^{63}Zn	^{64}Zn(p,pn)^{63}Zn	-11.9	48.9
Zn	^{66}Zn(p,n)^{66}Ga	^{70}Ge(p,αn)^{66}Ga	-10.0	20.7
Zr	^{90}Zr(p,n)^{90}Nb	^{94}Mo(p,αn)^{95}Nb	-9.0	9.1
Nb	^{93}Nb(p,n)^{93m}Mo	^{94}Mo(p,pn)^{93m}Mo	-9.7	9.1
Mo	^{94}Mo(p,n)^{94}Tc	^{98}Ru(p,αn)^{94}Tc	-7.3	1.9
	^{95}Mo(p,n)^{95}Tc	^{96}Ru(p,2p)^{95}Tc	-7.4	5.5
		^{98}Ru(p,α)^{95}Tc	+2.7	1.9
		^{99}Ru(p,αn)^{95}Tc	-7.3	12.7
	^{96}Mo(p,n)^{96}Tc	^{99}Ru(p,α)^{96}Tc	+3.1	12.7
		^{100}Ru(p,αn)^{96}Tc	-6.6	12.6
Ru	^{100}Ru(p,n)^{100}Rh	^{104}Pd(p,αn)^{100}Rh	-7.0	11.0
	^{101}Ru(p,n)^{101m}Rh	^{104}Pd(p,α)^{101m}Rh	+2.9	11.0
		^{105}Pd(p,αn)^{101m}Rh	-4.2	22.2
Pd	^{104}Pd(p,n)^{104}Ag	^{108}Cd(p,αn)^{104}Ag	-7.1	0.9
	^{106}Pd(p,n)^{106m}Ag	^{107}Ag(p,pn)^{106m}Ag	-9.5	51.83
		^{110}Cd(p,αn)^{106m}Ag	-6.6	12.4
Sn	^{116}Sn(p,n)^{116}Sb	^{120}Te(p,αn)^{116}Sb	-5.6	0.09
	^{120}Sn(p,n)^{120m}Sb	^{121}Sb(p,pn)^{120m}Sb	-9.2	57.3
		^{123}Te(p,α)^{120m}Te	+4.1	0.87
		^{124}Te(p,αn)^{120m}Te	-5.3	4.6
W	^{182}W(p,n)^{182}Re	^{186}Os(p,αn)^{182}Re	-0.8	1.6
		^{187}Os(p,α2n)^{182}Re	-7.1	1.6

in the analysis, so these reactions cannot act as secondary interference reactions, but the γ-rays of the radionuclides produced in this way have to be considered as instrumental interferences. Possible instrumental interferences which can occur in γ-ray spectrometry using up-to-date Ge(Li) detectors have already been summarized in detail for the analytically relevant γ-ray energies of the indicator radionuclides in the determination of Ti, V, Cr, Fe, Ni, Cu, Zr, Mo and W.[17,18] All instrumental interferences which could occur in the determination of Zn, Nb, Ru, Pd and Sn were also considered. From the many theoretically possible instrumental interferences only those given in Table 5 were actually observed. Also given in this Table are the assumed nuclear reactions yielding radionuclides with the interfering γ-rays. In cases where instrumental interferences occurred, either other lines without interferences (see Tables 2 and 6) were used, or it was possible to count the activated sample after the interferences had decayed, or to eliminate the interferences by analysing the complex decay curves.

Analytical results and their comparison

Typical γ-ray spectra for a proton-irradiated cobalt sample of VP-purity grade, measured after two different irradiation times, are shown in Figs. 2 and 3. Concentrations of trace elements determined in cobalt of VP-purity grade are summarized in Table 6. The results represent averages of three separate determinations, for which average deviations are also given.

Table 4. Possible secondary neutron-induced reactions of cobalt

Reaction	Threshold energy, MeV	E_m, MeV	σ_m, mb	Half-life	Major γ-rays, keV	Intensity, %
^{59}Co(n,α)^{56}Mn	0.0	14.5	30	2.58 hr	846.6	99.0
					1811.2	30.0
					2112.6	15.5
^{59}Co(n,p)^{59}Fe	0.8	12.9	56	44.6 d	192.2	2.8
					1099.3	56.0
					1291.6	44.0
^{59}Co(n,2n)^{58m}Co	10.7	16-18	500	8.94 hr	7.0	22.0
^{59}Co(n,2n)^{58}Co	10.7	17.3	740	70.78 d	511.0	30.0
					810.6	99.4
^{59}Co(n,γ)^{60m}Co	0.0	-	$< 10^{a)}$	10.5 min	58.6	99.75
^{59}Co(n,γ)^{60}Co	0.0	-	$< 10^{a)}$	5.27 yr	1173.2	99.9
					1332.5	100.0

E_m is the position of the maximum cross-section and σ_m is the maximum cross section of the excitation function, a) for neutron energy > 0.5 MeV.

Table 5. Observed γ-ray interferences in the analysis of VP-purity cobalt by instrumental proton-activation analysis

Element to be determined	Indicator radionuclide	Half-life	γ-Ray measured, MeV	Interferences				
				γ-Ray, MeV	Intensity, %	Nuclide	Half-life	Mode of formation
Ti	^{48}V	15.97 d	1.3116	1.3164	7.2	^{55}Co	18.0 hr	^{58}Ni(p,α)
Cr	^{52g}Mn	5.7 d	0.9356	0.9311	73.3	^{55}Co	18.0 hr	^{58}Ni(p,α)
Fe	^{56}Co	77.3 d	0.8467	0.8466	99.0	^{56}Mn	2.58 hr	^{59}Co(n,α)
				0.8503	99.0	^{96}Tc	4.35 d	^{96}Mo(p,n)
			1.0378	1.0393	37.3	^{66}Ga	9.3 hr	^{66}Zn(p,n)
				1.0393	4.0	^{95m}Tc	61.0 d	^{95}Mo(p,n)
Ni	^{60}Cu	23.0 min	1.3325	1.3325	100.0	^{60}Co	5.27 yr	^{59}Co(n,γ)
Zn	^{66}Ga	9.3 hr	1.0393	1.0370	3.3	^{60}Cu	23.0 min	^{60}Ni(p,n)
				1.0378	14.0	^{56}Co	77.3 d	^{56}Fe(p,n)
				1.0393	4.0	^{95m}Tc	61.0 d	^{95}Mo(p,n)
Nb	^{93m}Mo	6.9 h.	1.4772	1.4749	17.0	^{82}Br	35.4 h	^{82}Se(p,n)
Mo	^{94}Tc	4.9 hr	0.8497	0.8466	99.0	^{56}Mn	2.58 hr	^{59}Co(n,α)
				0.8467	100.0	^{56}Co	77.3 d	^{56}Fe(p,n)
	^{96g}Tc	4.3 d	0.8503	- " -	- " -	- " -	- " -	- " -
	^{96g}Tc	4.3 d	0.8128	0.8106	99.4	^{58}Co	70.78 d	^{59}Co(p,pn)
Ru	^{100}Rh	20.0 hr	1.7621	1.3602	4.3	^{56}Co	77.7 d	^{56}Fe(p,n)
				1.2916	44.0	^{59}Fe	44.6 d	^{59}Co(n,p)
Sn	^{116}Sb	16.0 min	1.2937	1.2916	44.0	^{59}Fe	44.6 d	^{59}Co(n,p)
				1.2920	1.5	^{60}Cu	23.4 min	^{60}Ni(p,n)
	^{120}Sb	5.76 d	1.1713	1.1732	99.9	^{60g}Co	5.27 yr	^{59}Co(n,γ)
				1.1741	?	^{184m}Re	160.0 d	^{184}W (p,n)
				1.1750	1.2	^{56}Co	77.3 d	^{56}Fe(p,n)
Zr	^{90}Nb	14.6 hr	1.1291	1.1272	15.0	^{96g}Tc	4.3 d	^{96}Mo(p,n)

Table 6. Concentrations of trace elements determined in VP-purity grade cobalt

Trace element	Indicator radionuclide	Counted γ-rays, keV	Concentration found by proton AA, ppm	Concentration by other methods, ppm
Ti	^{48}V	983 1312	0.6 ± 0.1	
V	^{51}Cr	320	$\lesssim$ 1.4	
Cr	^{52m}Mn	1434	4.6 ± 0.6	
	^{52g}Mn	1434	4.7 ± 0.5	
Fe	^{56}Co	1238 1771 2598	15.4 ± 2.3	17 [a]
Ni	^{60}Cu	826 1332 1792	568.4 ± 61	524 [a]
Cu	^{63}Zn	670	38.2 ± 5.8	
Zn	^{66}Ga	2752	0.4 ± 0.1	
Zr	^{90}Nb	2319	$\lesssim$ 0.05	
Nb	^{93m}Mo	1477	0.9 ± 0.7	
Mo	^{94g}Tc	703 871	87.0 ± 4.2	124 ± 12 [b]
	^{95g}Tc	766	93.4 ± 3.8	
	^{96g}Tc	778	89.1 ± 3.9	
Ru	^{100}Rh	1553	0.4 ± 0.3	
Pd	^{104,m,g}Ag	556	$\lesssim$ 0.6	
Sn	^{120m}Sb	1023	$\lesssim$ 0.6	
W	^{182}Re	1121 1189 1221	23.7 ± 3.7	

[a] average from two determinations by atomic absorption spectrometry

[b] determined by X-ray fluorescence spectrometry

In spite of the fact that attention was paid to the possible nuclear and instrumental interferences, reliable information about the accuracy of the results can be obtained only by checking the accuracy directly on a real sample. The best way of checking the accuracy would be by applying the method to the analysis of Standard Reference Materials, but unfortunately there are no cobalt reference standards available. Therefore, use was made of the opportunity to obtain comparative data for some of the elements determined, *i.e.*, iron, nickel and molybdenum, by two different techniques. Iron and nickel could be determined by atomic-absorption spectrometry and molybdenum by X-ray fluorescence spectrometry performed destructively. The results for the determination of iron and nickel showed that, with both proton-activation analysis and atomic-absorption spectrometry, good agreements were obtained. In the case of molybdenum, the results of proton-activation analysis are on avarage 27% lower than those obtained by X-ray fluorescence spectrometry. Taking into account the deviations of both methods, the lower value differs from the upper by 13%. The agreement is good enough to provide an acceptable measure of certainty about the concentration of these three elements found in cobalt. For information about trace impurities in pure materials, needed by producers and users, this degree of accuracy should be sufficient.

Unfortunately, a similar comparison for other trace elements could not be carried out as the methods still have to be developed, optimized or checked. Because of the need to save costly irradiation time, the reproducibility of the results was obtained in terms of the average deviations for three adjacent samples from the original cobalt material. It varied from element to element and depended mainly on the concentration level above the limit of detection. The reproducibility was poor in the determination of niobium and ruthenium, as these two elements were present at concentrations only slightly above the limits of detection. The average deviation obtained for cop-

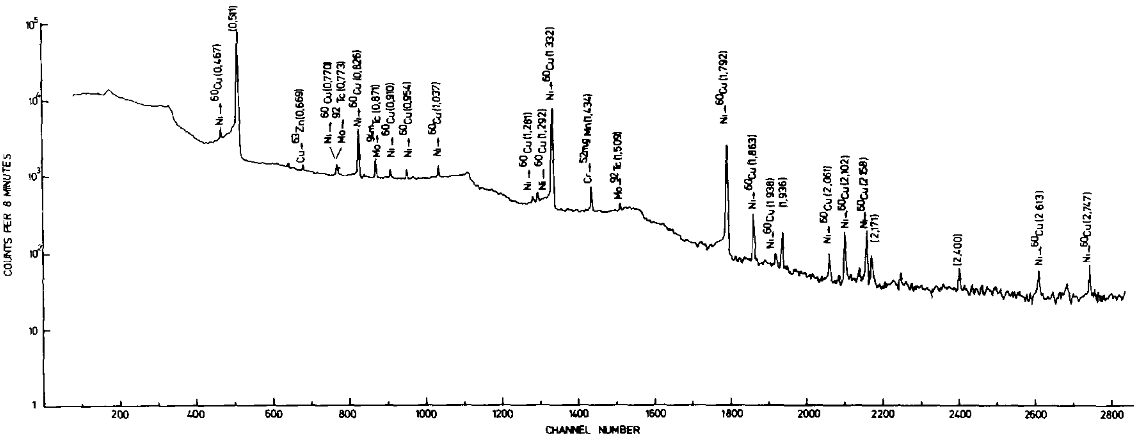

Fig. 2. Gamma-ray spectrum of a proton-irradiated cobalt sample observed 16 min after a 10-min irradiation.

per seems to have been *too* good in view of the high limit of detection. On the other hand, the average deviation for nickel should have been better. The average deviation includes the contribution of any lack of uniformity in the distribution of the trace elements in the sample material.

An irradiation time of 5–10 min is sufficient to determine elements giving rise to short-lived indicator radionuclides, such as Cr, Ni, Cu, Mo, Pd and Sn with ^{52m}Mn, ^{60}Cu, ^{63}Zn, ^{94m}Tc, ^{104m}Ag and ^{116g}Sb, respectively, as indicator radionuclides. In a previous paper,[18] it was shown that the determination of Cr, Ni and Cu by proton-activation analysis is extremely sensitive. However, nickel is present in the sample at higher concentration than all the other impurities. At the same time, the corresponding indicator radionuclide for nickel, ^{60}Cu, emits many high-energy γ-rays, giving a high background affecting the limits of detection for other elements. In addition to Ni, Cr and Cu, Mo can be determined by counting indicator radionuclides with $t_{1/2} < 1$ hr. However, ^{104m,g}Ag and ^{116g}Sb, being indicator radionuclides for the determination of Pd and Sn, respectively, could not be observed, so the limit of detection was taken as the upper concentration limit for these. For counting other than the above-mentioned indicator radionuclides, longer irradiation times, decay times and counting times are more suitable.

Table 7 lists the experimental limits of detection estimated on the basis of the spectral data of the VP-purity grade cobalt. The limits of detection are peak intensities corresponding to three standard deviations of the background at the peak of interest under the given experimental conditions, *i.e.*, irradiation, cooling and counting times. The data given represent the best observed limits of detection. The elements V, Zr, Pd and Sn are present in the sample at such low concentrations that the appropriate indicator radionuclides could not be observed. In these cases, the limits of detection have been estimated from spectra obtained by simultaneous measurement of both the cobalt sample and the pure elements irradiated

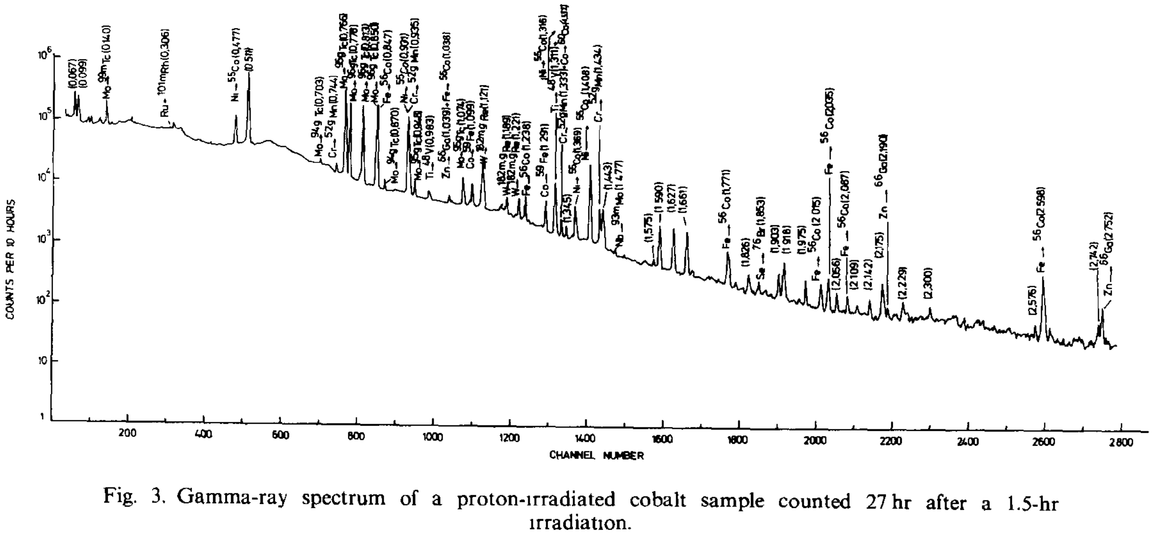

Fig. 3. Gamma-ray spectrum of a proton-irradiated cobalt sample counted 27 hr after a 1.5-hr irradiation.

Table 7. Limits of detection achieved in the analysis of VP-purity grade cobalt, and the appropriate experimental conditions

Element	Indicator radionuclide	Counted γ-rays, keV	Cooling time	Counting time	LD, ppm
Ti	^{48}V	1312	178 hr	14 hr	0.04 a)
V	^{51}Cr	320	178 hr	14 hr	1.4 a)
Cr	^{52m}Mn	1434	8 min	10 min	0.4 b)
	^{52g}Mn	1434	50 hr	14 hr	0.15 a)
Fe	^{56}Co	1238	178 hr	14 hr	0.3 a)
Ni	^{60}Cu	1332	8 min	10 min	3.9 b)
Cu	^{63}Cu	669	1 hr	20 min	12.8 b)
Zn	^{66}Ga	2752	10 hr	5 hr	0.05 a)
Zr	^{90}Nb	2319	7 hr	3 hr	0.05 a)
Nb	^{93m}Mo	1477	7 hr	3 hr	0.4 a)
Mo	^{94g}Tc	871	5 hr	3 hr	1.1 a)
	^{95g}Tc	766	20 hr	14 hr	0.09 a)
	^{96g}Tc	778	50 hr	14 hr	0.1 a)
Ru	^{100}Rh	1553	7 hr	3 hr	0.15 a)
Pd	^{104m,g}Ag	556	50 min	20 min	0.6 b)
Sn	^{120m}Sb	1023	50 hr	14 hr	0.6 a)
W	^{182m,g}Re	1221	10 hr	5 hr	0.8 a)

a) Irradiation conditions assumed: proton energy of 12 MeV, beam intensity of ∼ 4 μA, irradiation time of ∼2 hr

b) proton energy of 13 MeV, beam intensity of ∼4.5 μA, irradiation time of ∼10 min.

separately for shorter irradiation times and at lower beam intensities. After making the appropriate normalization for the different experimental conditions used in processing the cobalt sample and the given element, the limits of detection were estimated by using the same criterion as described above. The limits of detection of the instrumental proton-activation analysis, given in Table 6, are referred to the composition of the cobalt sample analysed and are not generally valid, Since the background may depend on the composition of the cobalt sample. One can assume that the limits of detection listed become better with decreasing concentrations of trace impurities, *i.e.*, with higher purity of the cobalt matrix. A considerable improvement in the limits of detection can be achieved by using high-efficiency γ-ray or β-ray counting. For instance, a measurable radioactivity of 0.5 nCi (1110 dpm) is produced in an activation of a cobalt sample with 12-MeV protons, with a beam intensity of 5 μA and an irradiation time of one half-life (or a maximum of 2 hr) from 3.5 ppM (parts per milliard) chromium, 16 ppM nickel, 3 ppM copper and 90 ppM molybdenum through the reactions ^{52}Cr(p,n)^{52m}Mn, ^{60}Ni(p,n)^{60}Cu, ^{63}Cu(p,n)^{63}Zn and ^{95}Mo(p,n)^{95g}Tc, respectively.

It is possible to compare our technique with that of Benaben *et al.*[9] and from the γ-ray spectra it is evident that, upon activation with 10-MeV protons, much higher relative radioactivities of ^{56}Mn, ^{59}Fe and ^{60}Co in comparison with the indicator radionuclides are produced than with 12-MeV or 13-MeV protons. These radionuclides can be produced only through reactions induced by secondary neutrons on the cobalt matrix. For example, the ratio of the radioactivity of ^{59}Fe produced by the ^{59}Co(n,p)^{59}Fe reaction from the matrix, to the radioactivity of ^{56}Co produced as indicator radionuclide for the determination of iron through the ^{56}Fe(p,n)^{56}Co reaction, is more than twice as high for 10-MeV protons as for 12-MeV protons at the same iron concentration. This is caused by the fact that the activation yield of the ^{56}Fe(p,n)^{56}Co reaction is increased more than the neutron yield by the proton energy, but it may also depend on the thickness of the sample. A similar picture can be expected for all principal reactions for which the maximum cross-section of the excitation function lies above 10 MeV. This is the case with most of the analytical reactions considered. In counting of a number of indicator radionuclides, the radionuclides ^{56}Mn, ^{59}Fe and ^{60}Fe, which emit γ-rays of relatively high energy, contribute to the background.

A direct comparison of the limits of detection for both techniques is unfortunately not possible as the composition of the cobalt samples and the detection conditions were different. A comparison of results obtained for the two samples closest in their composition, indicates that better limits of detection can be obtained by using 12-MeV or 13-MeV proton energy than by using 10-MeV proton energy. For example, the sensitivity (dpm/μA/ppm) in the determination of Cr, Ni and Cu increases by factors of 2, 3 and 4, on increasing the proton energy from 10 MeV to

13 MeV. On increasing the proton energy from 10 MeV to 12 MeV, the sensitivity in the determination of Mo by the reactions Mo + p→ ^{96g}Tc and Mo + p→ ^{95g}Tc is improved by factors of 10 and 15 respectively. Another aspect which should be considered is the range of the protons in cobalt, which is 208 mg/cm^2 at 10 MeV, 284 mg/cm^2 at 12 MeV and 325 mg/cm^2 at 13 MeV. In the case of 12-MeV and 13-MeV proton energies, a larger volume of the cobalt sample is activated and this is of advantage with respect to possible inhomogeneities in the distribution of the trace elements in the sample.

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DETERMINATION OF 14 TRACE ELEMENTS IN COBALT BY PROTON-ACTIVATION ANALYSIS

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Summary—Proton-activation analysis has been applied to the determination of 14 trace impurities in cobalt. The method consists of a short (~10 min) and a longer (~2 hr) irradiation of the sample with 13-MeV and 12-MeV protons, respectively, followed by high-resolution γ-ray spectrometry. The elements Ti, Cr, Fe, Ni, Cu, Zn, Nb, Mo, Ru and W have been determined in VP-purity cobalt. In the case of V, Cu, Zr, Pd and Sn, the amounts present were below the limit of detection. In the case of Fe, Ni, and Mo, the results are compared with those obtained by a second independent method. Data on reproducibility, limits of detection and possible interferences are given.

Relatively few trace analytical studies have been performed on cobalt matrices of good and high-purity grades. Optical emission spectrography has been used to determine Si, Mn, Fe, Ni, Cu and Zn,[1] and in addition Al[2] and also As and Sb[3] in cobalt. A spectrographic technique used for the determination of all the above-mentioned elements and, in addition, the alkali metals, Ca, Ti, V, Cr, Nb, Mo, Rh, Pd, Cd, Ag, W and Tl, in cobalt of 99.999% purity has been described by Tombu[4] together with a listing of the different chemical methods for the determination of H, C, N, O, Na, Mg, Al, Si, P, S, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Se, Sn, Sb, W, Tl, Pb and Bi. Unfortunately, neither the concentration intervals to which the individual methods have been applied nor the limits of detection were given. Activation analytical techniques have rarely been applied to the analysis of cobalt matrices.[5,6] In activation analysis with reactor neutrons, there are difficulties with the very high matrix activity due to the high thermal neutron cross-section and the resonance integral for the ^{59}Co(n,γ)^{60}Co reaction and the long half-life of ^{60}Co. Radiochemical neutron activation analysis has been used for the determination of Cu,[7,8] Mn and Zn.[8]

Recently an article by Benaben, Barrandon and Debrun has appeared[9] in which the application of an instrumental proton-activation technique to multi-element analysis of cobalt has been described. However, the experimental conditions and sample types used by these authors differ from those used in the present work. While they irradiated the cobalt samples with 10-MeV protons for 1 hr, in our case the cobalt samples were activated with 13-MeV protons to produce short-lived indicator radionuclides in short irradiations (~10 min), and with 12-MeV protons to produce long-lived indicator radionuclides in longer irradiations (~2 hr). To check the accuracy of the proton-activation technique described here, analytical results for iron, nickel and molybdenum are compared with results obtained by atomic-absorption spectrometry and by X-ray fluorescence spectrometry.

EXPERIMENTAL

Sample and standards

A cobalt sample of VP grade supplied by Material Research, GmbH, Eching bei München, West Germany, was analysed. From the cobalt metal, targets with a thickness of ~0.6 mm were cut. To remove possible surface contamination, a pre-irradiation chemical etch was accomplished with dilute nitric acid (1:1 ultrapure water and nitric acid). Thick metal targets of pure elements, their alloys or pressed powder mixtures were used for the standardization. For the etching of the standards, different solutions were used according to the character of the metal For the measurements of the activation curve of the ^{59}Co(p,pn)^{58}Co reaction, stacked foils of VP-purity cobalt were used

Irradiation

Irradiations were performed with 12-MeV and 13-MeV protons at the Karlsruhe isochronous cyclotron. For standardization, the average beam currents were 5–200 nA and the irradiation times were 20–60 sec Cobalt samples were irradiated in a water-cooled target holder for 5–120 min with beam intensities of 3–5 MeV. The activation curve was measured for proton energies up to 25 MeV.

Data acquisition

Gamma-rays were counted with a 55-cm^3 Ge(Li) detector having an energy resolution of 2.1 keV FWHM for the 1.332-MeV γ-ray of ^{60}Co and a peak-to-Compton ratio of 29:1. The detector was coupled with a 4096-channel pulse-height analyser. Computer programs[10] were used to list and plot the spectra and to determine the energies and intensities of the photopeaks. Data on the reaction studied and on the properties of the indicator radionuclides were obtained from recent compilations and tables[11–14]

RESULTS AND DISCUSSION

Selection of activation reactions

Inspection of the nuclear data and preliminary experiments indicated proton-activation analysis to be

Table 1. Proton-induced cobalt reactions producing radionuclides

Reaction	Q-value, MeV	Half-life	γ-Rays, MeV	Intensity, %
$^{59}Co(p,n)^{59}Ni$	- 1.9	7.5 x 10^4 yr	-	-
$^{59}Co(p,pn)^{58m}Co$	-10.5	8.94 hr	0.0249	0.03
$^{59}Co(p,pn)^{58}Co$	-10.5	70.78 d	0.5110 0.8106 0.8636 1.6748	30.0 99.4 0.7 0.5
$^{59}Co(p,p2n)^{57}Co$	-19.0	270.0 d	0.0144 0.1221 0.1364 0.5703 0.6921	9.5 85.6 10.6 0.01 0.15
$^{59}Co(p,\alpha n)^{55}Fe$	- 8.0	2.7 yr	-	-

the most suitable with respect to the instrumental performance and the multi-element character of the cobalt analysis. In activation with thermal neutrons, the matrix is strongly activated through the $^{59}Co(n,\gamma)^{60}Co$ reaction, with fast neutrons through the $^{59}Co(n,2n)^{58}Co$, $^{59}Co(n,p)^{59}Fe$ and $^{59}Co(n,\alpha)^{56}Mn$ reactions, with photons through the $^{59}Co(\gamma,n)^{58}Co$ reaction, with deuterons through the $^{59}Co(d,p)^{60}Co$ reaction, and with ^3He and α-particles mainly through $^{59}Co(\alpha,xn)$ reactions yielding copper nuclides with different half-lives.

Table 1 lists nuclear reactions which can be induced in cobalt when it is bombarded with protons of energy up to 20 MeV. As is evident from the data, the instrumental performance of analysis requires that the $^{59}Co(p,pn)^{58}Co$ reaction be eliminated or reduced. The activation curve of this reaction is shown in Fig. 1. This activation curve is in good agreement with that obtained by Benaben *et al.*[9] and with the published excitation function.[15] More detailed experiments on this problem showed that a proton energy of 12 MeV can be used even over long irradiation times, *i.e.*, the reaction occurs only to an insignificant extent. Short irradiation times can be used with protons up to an energy of 13 MeV. With use of these proton energies, good sensitivities are obtained as the position of the maximum cross-sections is located in this energy region for most of the analytical reactions. Nuclear data on the analytical reactions used and on the properties of the indicator radionuclides are given in Table 2.

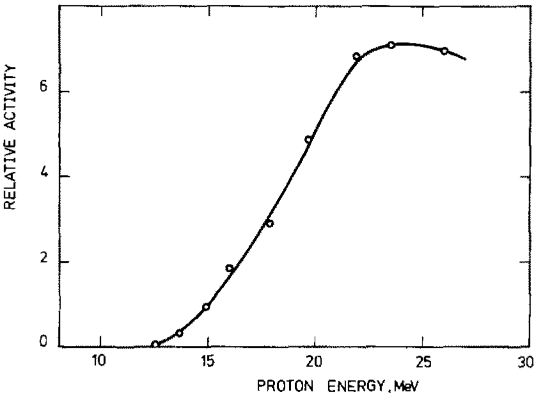

Fig. 1. Activation curve for the $^{59}Co(p,pn)^{58}Co$ reaction.

Interferences

Primary interference reactions which are energetically possible at the proton energies used are listed in Table 3. No primary interference reactions can occur in the determination of Ti and Cr. By experiment it has already been shown that no measurable interferences occur in the determination of Zr and Nb,[16] V, Fe, Mo and W,[17] and of Ni and Cu,[18] even if the concentrations of the interfering elements are many times those of the elements to be determined. A detailed analysis of the experimental results obtained in the irradiation of cobalt samples has shown that no measurable interferences occurred in the determination of Zn, Ru, Pd and Sn where Ge, Pd, Cd and Te could interfere through nuclear reactions of (p,α) and (p,αn) types. The presence of these interfering elements and the possible extent of their interferences were checked through the corresponding (p,n) reactions, which could yield, at the given proton energy, radioactivities higher by one or two orders of magnitude than those formed in the interfering reactions.

By bombardment of thick targets with protons of medium energy, neutrons can be produced by (p, xn) reactions. The neutron fluxes are considerably lower than the original proton-beam intensities, so the secondary interference reactions induced by neutrons, do not normally occur to a detectable extent if they are induced on the trace elements. However, if such reactions are induced on the main constituents of the sample they must be considered. Secondary interference reactions which can be induced in cobalt are listed in Table 4 together with cross-section data and energies of the γ-rays emitted by the radionuclides produced. None of the radionuclides produced in these reactions is used as an indicator radionuclide

Table 2. Data on production and properties of the indicator radionuclides

Element to be determined	Principal reactions	Isotopic abundance, %	Q-value, MeV	Half-life	Major γ-rays, MeV	Intensity, %
Ti	^{48}Ti(p,n)^{48}V	73.7	- 4.8	15.97 d	0.9443	8.0
					0.9835	100.0
					1.3116	98.0
V	^{51}V(p,n)^{51}Cr	99.75	- 1.5	27.7 d	0.3201	9.8
Cr	^{52}Cr(p,n)^{52m}Mn	83.79	- 5.5	21.0 min	1.4343	100.0
	^{52}Cr(p,n)^{52}Mn	83.79	- 5.5	5.7 d	0.7442	85.0
					0.9356	93.0
					1.4343	100.0
Fe	^{56}Fe(p,n)^{56}Co	91.7	- 5.4	77.3 d	0.8467	99.99
					1.0378	14.0
					1.2383	67.6
					1.7715	15.7
					2.5986	16.9
Ni	^{60}Ni(p,n)^{60}Cu	26.42	- 6.9	23.0 min	0.8260	19.2
					1.3325	87.3
					1.7920	44.9
Cu	^{63}Cu(p,n)^{63}Zn	69.1	- 4.1	38.4 min	0.6696	8.5
					0.9619	6.7
Zn	^{66}Zn(p,n)^{66}Ga	27.8	- 6.0	9.3 hr	1.0393	37.3
					2.7523	22.8
Zr	^{90}Zr(p,n)^{90}Nb	51.4	- 6.9	14.6 hr	0.1412	67.0
					1.1291	92.0
					2.1860	18.0
					2.3190	82.0
Nb	^{93}Nb(p,n)^{93m}Mo	100.0	- 1.2	6.9 hr	0.2632	61.2
					0.6846	91.9
					1.4772	99.4
Mo	^{94}Mo(p,n)^{94m}Tc	9.1	- 5.0	53.0 min	0.8709	91.0
					1.5220	5.4
					1.8688	5.3
	^{94}Mo(p,n)^{94}Tc	9.1	- 5.0	4.9 hr	0.7026	100.0
					0.8497	100.0
					0.8709	100.0
					0.9162	6.8
	^{95}Mo(p,n)^{95}Tc	15.9	- 2.5	20.0 hr	0.7658	94.0
	^{96}Mo(p,n)^{96}Tc	16.7	- 3.7	4.3 d	0.7783	100.0
					0.8128	82.0
					0.8503	99.0
					1.1272	15.0
Ru	^{100}Ru(p,n)^{100}Rh	12.6	- 4.4	20.0 hr	0.4462	11.5
					0.5396	80.0
					0.8225	20.6
					1.1071	13.5
					1.3621	15.3
					1.5534	21.0
					1.9297	12.4
					2.3761	35.7
	^{101}Ru(p,n)^{101m}Rh	17.1	- 1.3	4.4 d	0.3068	94.0
Pd	^{104}Pd(p,n)^{104m}Ag	11.0	- 4.9	33.5 m	0.5558	91.0
	^{104}Pd(p,n)^{104}Ag	11.0	- 4.9	69.2 min	0.5558	92.5
					0.7674	66.3
					0.9232	16.3
					0.9259	12.5
					0.9416	25.0
					1.5261	6.2
Sn	^{116}Sn(p,n)^{116}Sb	14.4	- 5.3	16.0 m	0.9330	23.0
					1.2937	88.0
					2.2298	11.5
	^{120}Sn(p,n)^{120m}Sb	32.8	- 3.5	5.76 d	0.0898	77.0
					0.1972	89.0
					1.0230	99.0
					1.1713	100.0
W	^{182}W(p,n)^{182m}Re	26.3	- 3.6	13.0 hr	0.1001	17.4
					1.1213	38.5
					1.1890	18.4
					1.2214	30.5
	^{182}W(p,n)^{182}Re	26.3	- 3.6	64.0 hr	0.1001	15.0
					0.1489	15.0
					0.1784	18.0
					0.2292	25.0
					0.2564	13.0
					1.1220	20.0
					1.1895	7.9
					1.2218	15.0

Table 3. Possible primary interference reactions

Element to be determined	Activation reaction used	Interfering reaction	Q-value, MeV	Isotopic abundance, %
Ti	^{48}Ti(p,n)^{48}V	^{52}Cr(p,αn)^{48}V	-14.2	83.79
V	^{51}V(p,n)^{51}Cr	^{55}Mn(p,αn)^{51}Cr	- 9.0	100.00
		^{52}Cr(p,pn)^{51}Cr	-12.0	83.79
Cr	^{52}Cr(p,n)^{52}Mn	^{56}Fe(p,αn)^{52}Mn	-13.1	91.7
Fe	^{56}Fe(p,n)^{56}Co	^{60}Ni(p,αn)^{56}Co	-11.6	26.23
Ni	^{60}Ni(p,n)^{60}Cu	^{64}Zn(p,αn)^{60}Cu	-10.9	48.9
Cu	^{63}Cu(p,n)^{63}Zn	^{64}Zn(p,pn)^{63}Zn	-11.9	48.9
Zn	^{66}Zn(p,n)^{66}Ga	^{70}Ge(p,αn)^{66}Ga	-10.0	20.7
Zr	^{90}Zr(p,n)^{90}Nb	^{94}Mo(p,αn)^{95}Nb	-9.0	9.1
Nb	^{93}Nb(p,n)^{93m}Mo	^{94}Mo(p,pn)^{93m}Mo	-9.7	9.1
Mo	^{94}Mo(p,n)^{94}Tc	^{98}Ru(p,αn)^{94}Tc	-7.3	1.9
	^{95}Mo(p,n)^{95}Tc	^{96}Ru(p,2p)^{95}Tc	-7.4	5.5
		^{98}Ru(p,α)^{95}Tc	+2.7	1.9
		^{99}Ru(p,αn)^{95}Tc	-7.3	12.7
	^{96}Mo(p,n)^{96}Tc	^{99}Ru(p,α)^{96}Tc	+3.1	12.7
		^{100}Ru(p,αn)^{96}Tc	-6.6	12.6
Ru	^{100}Ru(p,n)^{100}Rh	^{104}Pd(p,αn)^{100}Rh	-7.0	11.0
	^{101}Ru(p,n)^{101m}Rh	^{104}Pd(p,α)^{101m}Rh	+2.9	11.0
		^{105}Pd(p,αn)^{101m}Rh	-4.2	22.2
Pd	^{104}Pd(p,n)^{104}Ag	^{108}Cd(p,αn)^{104}Ag	-7.1	0.9
	^{106}Pd(p,n)^{106m}Ag	^{107}Ag(p,pn)^{106m}Ag	-9.5	51.83
		^{110}Cd(p,αn)^{106m}Ag	-6.6	12.4
Sn	^{116}Sn(p,n)^{116}Sb	^{120}Te(p,αn)^{116}Sb	-5.6	0.09
	^{120}Sn(p,n)^{120m}Sb	^{121}Sb(p,pn)^{120m}Sb	-9.2	57.3
		^{123}Te(p,α)^{120m}Te	+4.1	0.87
		^{124}Te(p,αn)^{120m}Te	-5.3	4.6
W	^{182}W(p,n)^{182}Re	^{186}Os(p,αn)^{182}Re	-0.8	1.6
		^{187}Os(p,α2n)^{182}Re	-7.1	1.6

in the analysis, so these reactions cannot act as secondary interference reactions, but the γ-rays of the radionuclides produced in this way have to be considered as instrumental interferences. Possible instrumental interferences which can occur in γ-ray spectrometry using up-to-date Ge(Li) detectors have already been summarized in detail for the analytically relevant γ-ray energies of the indicator radionuclides in the determination of Ti, V, Cr, Fe, Ni, Cu, Zr, Mo and W.[17,18] All instrumental interferences which could occur in the determination of Zn, Nb, Ru, Pd and Sn were also considered. From the many theoretically possible instrumental interferences only those given in Table 5 were actually observed. Also given in this Table are the assumed nuclear reactions yielding radionuclides with the interfering γ-rays. In cases where instrumental interferences occurred, either other lines without interferences (see Tables 2 and 6) were used, or it was possible to count the activated sample after the interferences had decayed, or to eliminate the interferences by analysing the complex decay curves.

Analytical results and their comparison

Typical γ-ray spectra for a proton-irradiated cobalt sample of VP-purity grade, measured after two different irradiation times, are shown in Figs. 2 and 3. Concentrations of trace elements determined in cobalt of VP-purity grade are summarized in Table 6. The results represent averages of three separate determinations, for which average deviations are also given.

Table 4. Possible secondary neutron-induced reactions of cobalt

Reaction	Threshold energy, MeV	E_m, MeV	σ_m, mb	Half-life	Major γ-rays, keV	Intensity, %
^{59}Co(n,α)^{56}Mn	0.0	14.5	30	2.58 hr	846.6 1811.2 2112.6	99.0 30.0 15.5
^{59}Co(n,p)^{59}Fe	0.8	12.9	56	44.6 d	192.2 1099.3 1291.6	2.8 56.0 44.0
^{59}Co(n,2n)^{58m}Co	10.7	16-18	500	8.94 hr	7.0	22.0
^{59}Co(n,2n)^{58}Co	10.7	17.3	740	70.78 d	511.0 810.6	30.0 99.4
^{59}Co(n,γ)^{60m}Co	0.0	-	$< 10^{a)}$	10.5 min	58.6	99.75
^{59}Co(n,γ)^{60}Co	0.0	-	$< 10^{a)}$	5.27 yr	1173.2 1332.5	99.9 100.0

E_m is the position of the maximum cross-section and σ_m is the maximum cross section of the excitation function, $^{a)}$for neutron energy > 0.5 MeV.

Table 5. Observed γ-ray interferences in the analysis of VP-purity cobalt by instrumental proton-activation analysis

Element to be determined	Indicator radionuclide	Half-life	γ-Ray measured, MeV	Interferences				
				γ-Ray, MeV	Intensity, %	Nuclide	Half-life	Mode of formation
Ti	^{48}V	15.97 d	1.3116	1.3164	7.2	^{55}Co	18.0 hr	^{58}Ni(p,α)
Cr	^{52g}Mn	5.7 d	0.9356	0.9311	73.3	^{55}Co	18.0 hr	^{58}Ni(p,α)
Fe	^{56}Co	77.3 d	0.8467	0.8466 0.8503	99.0 99.0	^{56}Mn ^{96}Tc	2.58 hr 4.35 d	^{59}Co(n,α) ^{96}Mo(p,n)
			1.0378	1.0393 1.0393	37.3 4.0	^{66}Ga ^{95m}Tc	9.3 hr 61.0 d	^{66}Zn(p,n) ^{95}Mo(p,n)
Ni	^{60}Cu	23.0 min	1.3325	1.3325	100.0	^{60}Co	5.27 yr	^{59}Co(n,γ)
Zn	^{66}Ga	9.3 hr	1.0393	1.0370 1.0378 1.0393	3.3 14.0 4.0	^{60}Cu ^{56}Co ^{95m}Tc	23.0 min 77.3 d 61.0 d	^{60}Ni(p,n) ^{56}Fe(p,n) ^{95}Mo(p,n)
Nb	^{93m}Mo	6.9 h.	1.4772	1.4749	17.0	^{82}Br	35.4 h	^{82}Se(p,n)
Mo	^{94}Tc	4.9 hr	0.8497	0.8466 0.8467	99.0 100.0	^{56}Mn ^{56}Co	2.58 hr 77.3 d	^{59}Co(n,α) ^{56}Fe(p,n)
	^{96g}Tc	4.3 d	0.8503	- " -	- " -	- " -	- " -	- " -
	^{96g}Tc	4.3 d	0.8128	0.8106	99.4	^{58}Co	70.78 d	^{59}Co(p,pn)
Ru	^{100}Rh	20.0 hr	1.7621	1.3602 1.2916	4.3 44.0	^{56}Co ^{59}Fe	77.7 d 44.6 d	^{56}Fe(p,n) ^{59}Co(n,p)
Sn	^{116}Sb	16.0 min	1.2937	1.2916 1.2920	44.0 1.5	^{59}Fe ^{60}Cu	44.6 d 23.4 min	^{59}Co(n,p) ^{60}Ni(p,n)
	^{120}Sb	5.76 d	1.1713	1.1732 1.1741 1.1750	99.9 ? 1.2	^{60g}Co ^{184m}Re ^{56}Co	5.27 yr 160.0 d 77.3 d	^{59}Co(n,γ) ^{184}W (p,n) ^{56}Fe(p,n)
Zr	^{90}Nb	14.6 hr	1.1291	1.1272	15.0	^{96g}Tc	4.3 d	^{96}Mo(p,n)

Table 6. Concentrations of trace elements determined in VP-purity grade cobalt

Trace element	Indicator radionuclide	Counted γ-rays, keV	Concentration found by proton AA, ppm	Concentration by other methods, ppm
Ti	^{48}V	983 1312	0.6 ± 0.1	
V	^{51}Cr	320	$\lesssim$ 1.4	
Cr	^{52m}Mn	1434	4.6 ± 0.6	
	^{52g}Mn	1434	4.7 ± 0.5	
Fe	^{56}Co	1238 1771 2598	15.4 ± 2.3	17 [a]
Ni	^{60}Cu	826 1332 1792	568.4 ± 61	524 [a]
Cu	^{63}Zn	670	38.2 ± 5.8	
Zn	^{66}Ga	2752	0.4 ± 0.1	
Zr	^{90}Nb	2319	$\lesssim$ 0.05	
Nb	^{93m}Mo	1477	0.9 ± 0.7	
Mo	^{94g}Tc	703 871	87.0 ± 4.2	124 ± 12 [b]
	^{95g}Tc	766	93.4 ± 3.8	
	^{96g}Tc	778	89.1 ± 3.9	
Ru	^{100}Rh	1553	0.4 ± 0.3	
Pd	^{104,m,g}Ag	556	$\lesssim$ 0.6	
Sn	^{120m}Sb	1023	$\lesssim$ 0.6	
W	^{182}Re	1121 1189 1221	23.7 ± 3.7	

[a] average from two determinations by atomic absorption spectrometry

[b] determined by X-ray fluorescence spectrometry

In spite of the fact that attention was paid to the possible nuclear and instrumental interferences, reliable information about the accuracy of the results can be obtained only by checking the accuracy directly on a real sample. The best way of checking the accuracy would be by applying the method to the analysis of Standard Reference Materials, but unfortunately there are no cobalt reference standards available. Therefore, use was made of the opportunity to obtain comparative data for some of the elements determined, *i.e.*, iron, nickel and molybdenum, by two different techniques. Iron and nickel could be determined by atomic-absorption spectrometry and molybdenum by X-ray fluorescence spectrometry performed destructively. The results for the determination of iron and nickel showed that, with both proton-activation analysis and atomic-absorption spectrometry, good agreements were obtained. In the case of molybdenum, the results of proton-activation analysis are on avarage 27% lower than those obtained by X-ray fluorescence spectrometry. Taking into account the deviations of both methods, the lower value differs from the upper by 13%. The agreement is good enough to provide an acceptable measure of certainty about the concentration of these three elements found in cobalt. For information about trace impurities in pure materials, needed by producers and users, this degree of accuracy should be sufficient.

Unfortunately, a similar comparison for other trace elements could not be carried out as the methods still have to be developed, optimized or checked. Because of the need to save costly irradiation time, the reproducibility of the results was obtained in terms of the average deviations for three adjacent samples from the original cobalt material. It varied from element to element and depended mainly on the concentration level above the limit of detection. The reproducibility was poor in the determination of niobium and ruthenium, as these two elements were present at concentrations only slightly above the limits of detection. The average deviation obtained for cop-

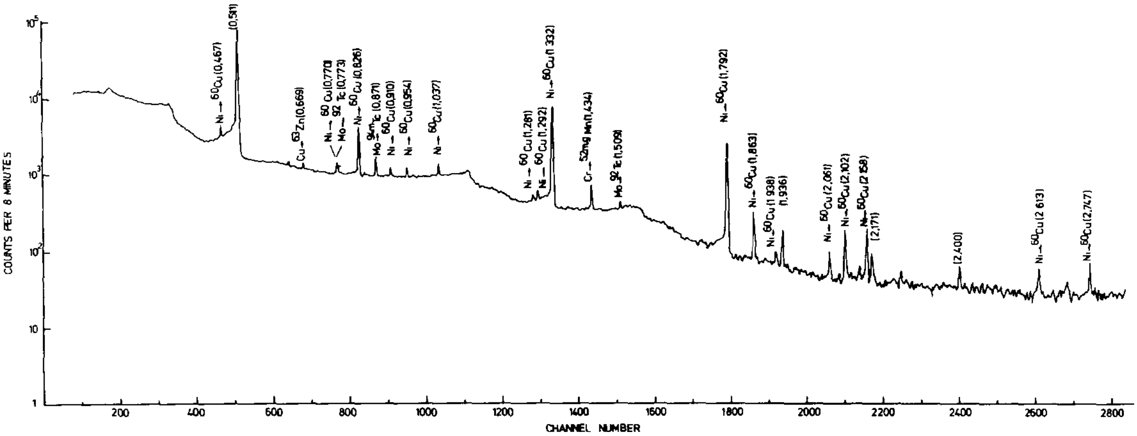

Fig. 2. Gamma-ray spectrum of a proton-irradiated cobalt sample observed 16 min after a 10-min irradiation.

per seems to have been *too* good in view of the high limit of detection. On the other hand, the average deviation for nickel should have been better. The average deviation includes the contribution of any lack of uniformity in the distribution of the trace elements in the sample material.

An irradiation time of 5–10 min is sufficient to determine elements giving rise to short-lived indicator radionuclides, such as Cr, Ni, Cu, Mo, Pd and Sn with ^{52m}Mn, ^{60}Cu, ^{63}Zn, ^{94m}Tc, ^{104m}Ag and ^{116g}Sb, respectively, as indicator radionuclides. In a previous paper,[18] it was shown that the determination of Cr, Ni and Cu by proton-activation analysis is extremely sensitive. However, nickel is present in the sample at higher concentration than all the other impurities. At the same time, the corresponding indicator radionuclide for nickel, ^{60}Cu, emits many high-energy γ-rays, giving a high background affecting the limits of detection for other elements. In addition to Ni, Cr and Cu, Mo can be determined by counting indicator radionuclides with $t_{1/2} < 1$ hr. However, ^{104m,g}Ag and ^{116g}Sb, being indicator radionuclides for the determination of Pd and Sn, respectively, could not be observed, so the limit of detection was taken as the upper concentration limit for these. For counting other than the above-mentioned indicator radionuclides, longer irradiation times, decay times and counting times are more suitable.

Table 7 lists the experimental limits of detection estimated on the basis of the spectral data of the VP-purity grade cobalt. The limits of detection are peak intensities corresponding to three standard deviations of the background at the peak of interest under the given experimental conditions, *i.e.*, irradiation, cooling and counting times. The data given represent the best observed limits of detection. The elements V, Zr, Pd and Sn are present in the sample at such low concentrations that the appropriate indicator radionuclides could not be observed. In these cases, the limits of detection have been estimated from spectra obtained by simultaneous measurement of both the cobalt sample and the pure elements irradiated

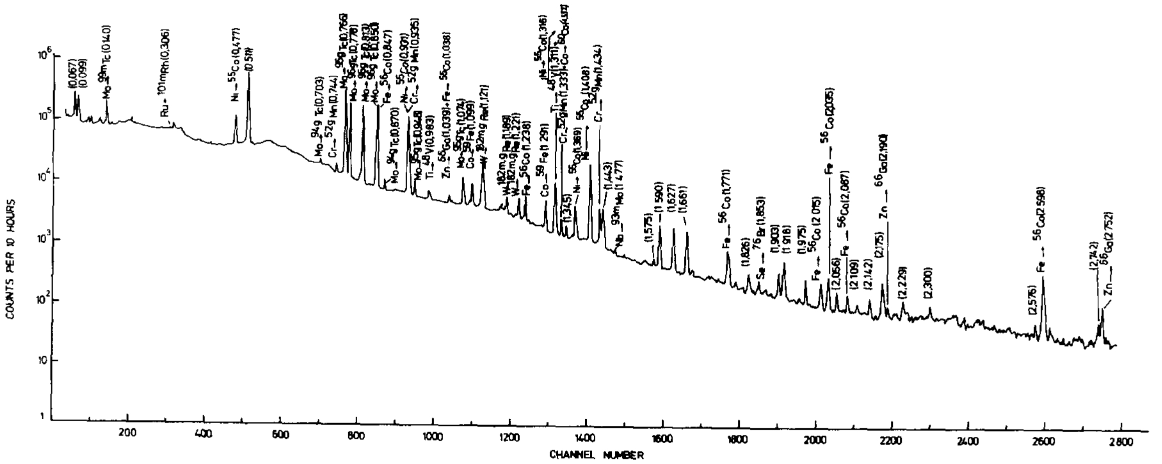

Fig. 3. Gamma-ray spectrum of a proton-irradiated cobalt sample counted 27 hr after a 1.5-hr irradiation.

Table 7. Limits of detection achieved in the analysis of VP-purity grade cobalt, and the appropriate experimental conditions

Element	Indicator radionuclide	Counted γ-rays, keV	Cooling time	Counting time	LD, ppm
Ti	^{48}V	1312	178 hr	14 hr	0.04 a)
V	^{51}Cr	320	178 hr	14 hr	1.4 a)
Cr	^{52m}Mn	1434	8 min	10 min	0.4 b)
	^{52g}Mn	1434	50 hr	14 hr	0.15 a)
Fe	^{56}Co	1238	178 hr	14 hr	0.3 a)
Ni	^{60}Cu	1332	8 min	10 min	3.9 b)
Cu	^{63}Cu	669	1 hr	20 min	12.8 b)
Zn	^{66}Ga	2752	10 hr	5 hr	0.05 a)
Zr	^{90}Nb	2319	7 hr	3 hr	0.05 a)
Nb	^{93m}Mo	1477	7 hr	3 hr	0.4 a)
Mo	^{94g}Tc	871	5 hr	3 hr	1.1 a)
	^{95g}Tc	766	20 hr	14 hr	0.09 a)
	^{96g}Tc	778	50 hr	14 hr	0.1 a)
Ru	^{100}Rh	1553	7 hr	3 hr	0.15 a)
Pd	^{104m,g}Ag	556	50 min	20 min	0.6 b)
Sn	^{120m}Sb	1023	50 hr	14 hr	0.6 a)
W	^{182m,g}Re	1221	10 hr	5 hr	0.8 a)

a) Irradiation conditions assumed: proton energy of 12 MeV, beam intensity of ∿ 4 μA, irradiation time of ∿2 hr

b) proton energy of 13 MeV, beam intensity of ∿4.5 μA, irradiation time of ∿10 min.

separately for shorter irradiation times and at lower beam intensities. After making the appropriate normalization for the different experimental conditions used in processing the cobalt sample and the given element, the limits of detection were estimated by using the same criterion as described above. The limits of detection of the instrumental proton-activation analysis, given in Table 6, are referred to the composition of the cobalt sample analysed and are not generally valid, Since the background may depend on the composition of the cobalt sample. One can assume that the limits of detection listed become better with decreasing concentrations of trace impurities, *i.e.*, with higher purity of the cobalt matrix. A considerable improvement in the limits of detection can be achieved by using high-efficiency γ-ray or β-ray counting. For instance, a measurable radioactivity of 0.5 nCi (1110 dpm) is produced in an activation of a cobalt sample with 12-MeV protons, with a beam intensity of 5 μA and an irradiation time of one half-life (or a maximum of 2 hr) from 3.5 ppM (parts per milliard) chromium, 16 ppM nickel, 3 ppM copper and 90 ppM molybdenum through the reactions ^{52}Cr(p,n)^{52m}Mn, ^{60}Ni(p,n)^{60}Cu, ^{63}Cu(p,n)^{63}Zn and ^{95}Mo(p,n)^{95g}Tc, respectively.

It is possible to compare our technique with that of Benaben *et al.*[9] and from the γ-ray spectra it is evident that, upon activation with 10-MeV protons, much higher relative radioactivities of ^{56}Mn, ^{59}Fe and ^{60}Co in comparison with the indicator radionuclides are produced than with 12-MeV or 13-MeV protons. These radionuclides can be produced only through reactions induced by secondary neutrons on the cobalt matrix. For example, the ratio of the radioactivity of ^{59}Fe produced by the ^{59}Co(n,p)^{59}Fe reaction from the matrix, to the radioactivity of ^{56}Co produced as indicator radionuclide for the determination of iron through the ^{56}Fe(p,n)^{56}Co reaction, is more than twice as high for 10-MeV protons as for 12-MeV protons at the same iron concentration. This is caused by the fact that the activation yield of the ^{56}Fe(p,n)^{56}Co reaction is increased more than the neutron yield by the proton energy, but it may also depend on the thickness of the sample. A similar picture can be expected for all principal reactions for which the maximum cross-section of the excitation function lies above 10 MeV. This is the case with most of the analytical reactions considered. In counting of a number of indicator radionuclides, the radionuclides ^{56}Mn, ^{59}Fe and ^{60}Fe, which emit γ-rays of relatively high energy, contribute to the background.

A direct comparison of the limits of detection for both techniques is unfortunately not possible as the composition of the cobalt samples and the detection conditions were different. A comparison of results obtained for the two samples closest in their composition, indicates that better limits of detection can be obtained by using 12-MeV or 13-MeV proton energy than by using 10-MeV proton energy. For example, the sensitivity (dpm/μA/ppm) in the determination of Cr, Ni and Cu increases by factors of 2, 3 and 4, on increasing the proton energy from 10 MeV to

13 MeV. On increasing the proton energy from 10 MeV to 12 MeV, the sensitivity in the determination of Mo by the reactions Mo + p → ^{96g}Tc and Mo + p → ^{95g}Tc is improved by factors of 10 and 15 respectively. Another aspect which should be considered is the range of the protons in cobalt, which is 208 mg/cm^2 at 10 MeV, 284 mg/cm^2 at 12 MeV and 325 mg/cm^2 at 13 MeV. In the case of 12-MeV and 13-MeV proton energies, a larger volume of the cobalt sample is activated and this is of advantage with respect to possible inhomogeneities in the distribution of the trace elements in the sample.

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CANDOLUMINESCENCE—A NEW FLAME TECHNIQUE FOR TRACE ANALYSIS—II

DETERMINATION OF NANOGRAM AMOUNTS OF MANGANESE

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Summary—The yellow candoluminescence of manganese stimulated in a 8:1 w/w calcium oxide–calcium sulphate matrix at the edge of a hydrogen–nitrogen–air flame is used to determine 0.1–3.0 ng of manganese in 1-μl samples. Large amounts of chloride ions enhance the emission, and many transition metals suppress it.

In a previous paper,[1] the candoluminescence spectra of bismuth, manganese, antimony, lead, and a number of lanthanides in a calcium hydroxide–calcium sulphate matrix were reported. A quantitative relationship was established between luminescence emission intensity and the concentration of bismuth activator introduced into the matrix by co-precipitation. In a later paper,[2] the determination of bismuth down to the sub-nanogram level was described. This was made possible by introducing the activator sample directly onto the surface of a matrix, instead of using co-precipitation; with the latter method, most of the activator used is inside the body of the matrix, and is not available for luminescence. The candoluminescence of manganese was first studied by Donau,[3] who found that a bead of calcium carbonate on a platinum wire could be activated by manganese ions to give a yellow emission at the edge of a hydrogen flame. This paper describes the use of the surface-application technique to determine down to sub-ng amounts of manganese, based on this yellow candoluminescence. The lower limit of determination is 0.1 ng, but it could be an order of magnitude lower, except that traces of manganese in the calcium carbonate used as matrix precursor set a practical lower limit.

EXPERIMENTAL

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The candoluminescence emission intensity of manganese was measured at 580 nm by using a Unicam SP 900 flame-emission spectrometer, a Servoscribe chart recorder, and sample holder as described previously.[2] The matrix was inlaid into the hexagonal aperture (2 mm deep, 5 mm maximum diagonal) in the head of an Allen screw.[2] The apparatus was used in a dimly illuminated laboratory to eliminate interference from extraneous light sources.

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Determination of manganese

A 1000-ppm manganese(II) solution was prepared by dissolving the appropriate quantity of analytical reagent grade manganese(II) sulphate in water. Calibration solutions down to 0.1 ppm were prepared from this solution by dilution in volumetric flasks.

The candoluminescence spectrum of manganese was obtained by scanning a steady emission, the latter being obtained by lowering the flame temperature so that it was only just above the temperature of maximum emission for the activator.[2] In these circumstances a bright steady luminescence can be obtained.

To measure the emission intensities from a prepared set of matrices, the optimal horizontal positioning of the matrix was first determined by carefully adjusting the position of one matrix at the edge of the flame so that the luminescence intensity was maximal. The matrix holder was then kept fixed at this position for the measurement of the succeeding matrices. Graphs of peak luminescence intensity *vs.* quantity of manganese added were obtained.

RESULTS

The candoluminescence spectrum of manganese is shown in Fig. 1. The peak emission intensity is at 580 nm, and all further measurements were made at this wavelength.

Effect of flame conditions and matrix position

The three gases admitted to the pre-mix burner were hydrogen, nitrogen, and air. Under optimal conditions, the part of the flame that stimulated luminescence at the matrix surface was a narrow region at the "edge". Because of this, the lateral positioning of the matrix holder was very critical. Once the optimal position had been found, the holder was left in this position so that the matrices could be positioned reproducibly in the flame by simply rotating the socket.[2] Each matrix–activator pair has a temperature at which maximal luminescence occurs. Thus, if the flame temperature is greater than this, the emission intensity from a matrix at the edge of the flame rises to a maximum, then decreases as the temperature of the surface increases. The emission-time profile of manganese-activated calcium oxide under optimal flame conditions is shown in Fig. 2. The luminescence begins 10 sec after the flame is entered by the matrix and reaches a maximum after 30 sec. The term "optimal flame conditions" implies not only that the emission intensity reached is maximal, but that the, noise, from the flame (principally from dust particles and sodium impurities) is minimal.

Apart from the horizontal distance of the matrix from the flame axis, the four principal flame variables involved are the hydrogen, nitrogen and air flow-rates, and the height of the matrix in the flame above the burner. Each of these was investigated separately. For each study, three of the parameters were fixed at about their optimal value (determined approximately in experiments beforehand), while the fourth was varied. The results are shown in Figs. 3 and 4. The nitrogen flow-rate appeared not to be very critical as far as luminescence intensity was concerned, but was critical for reducing the flame noise, the noise decreasing markedly as the nitrogen flow increased. Variations in hydrogen and air flows were more critical, both with respect to emission intensity and flame noise. This is to be expected, as it is the hydrogen–oxygen interaction in the flame which produces the radicals which stimulate candoluminescence. On the basis of these experiments the optimal gas flow-rates were considered to be: nitrogen 8.0 l./min, hydrogen 2.0 l./min and air 2.5 l./min. The variation of the height of the centre of the matrix above the burner head was not very critical, and 3.0 cm was chosen as suitable.

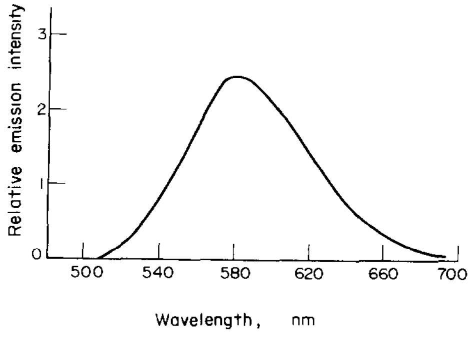

Fig. 1. Candoluminescence spectrum of manganese

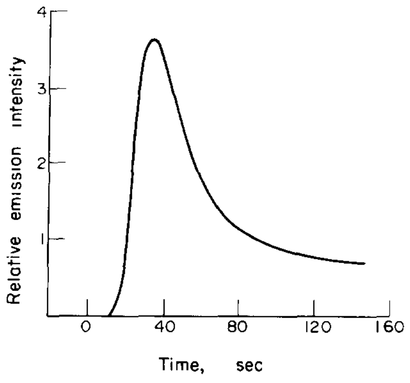

Fig. 2. Change in manganese candoluminescence intensity at 580 nm with time. Matrix inserted into flame at 0 sec

Calibration and reproducibility

Figure 5 shows the calibration curves obtained for 0.1–1.0 and 1.0–5.0 ng of manganese. It was found that, as with other activators,[2,4] there is an upper calibration limit above which the curve levels off or falls. For manganese, this occurs at about 3 ng; for bismuth[2] it had been found to be 2 ng. Below 0.1 ng of manganese the emission becomes difficult to measure because the emission is mainly that of manganese impurity in the matrix. However, it is expected that by utilizing ultrapure calcium carbonate as a matrix material, the calibration range could be extended to well below 0.1 ng.

Good reproducibility in candoluminescence is obtained by exercising precise control over a large number of parameters, including the flame conditions, the sample introduction technique, and above all the

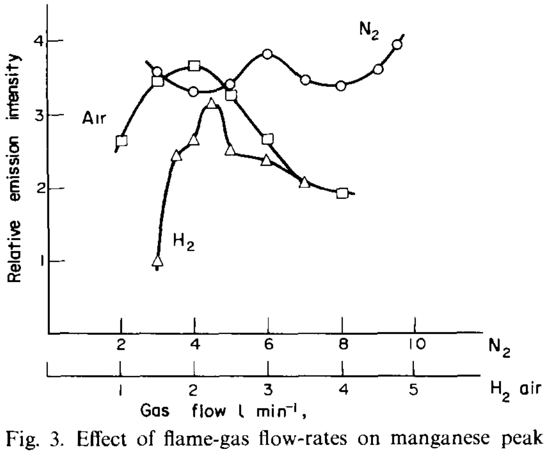

Fig. 3. Effect of flame-gas flow-rates on manganese peak candoluminescence intensity.

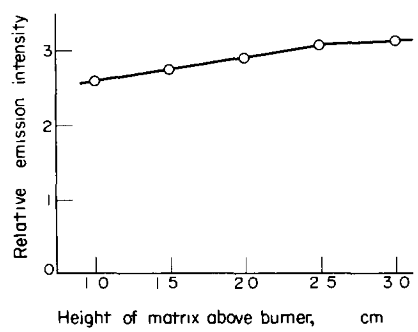

Fig. 4. Effect of height of matrix in flame on manganese peak candoluminescence intensity

matrix preparation technique. With manganese, the reproducibility was ±5%, but could be ±10% or more if the experimental technique was inadequate.

Interferences

Interferences were investigated by preparing solutions containing a standard quantity of manganese together with various quantities of another cation (usually as the sulphate) or of another anion (as its potassium salt). The activator and interferent were applied together in a 1-μl drop of solution.

Cations. Transition metal cations interfered markedly with the luminescence of 10 ng of manganese, causing a gradual decrease in emission intensity, an example of which is shown in Fig. 6. Table 1 shows the degree of interference from various metal ions, when present in a 1:1 and 10:1 w:w ratio to the activator. In most instances, a deposit was visible on the matrix surface after removing it from the flame, and its colour corresponded to that of transition metal oxide. Such a deposit would shield the calcium oxide surface from the flame and thus reduce the luminescence. Zinc, aluminium, bismuth, lead and potassium ions were found to have little effect on the luminescence when present in up to ten times the weight

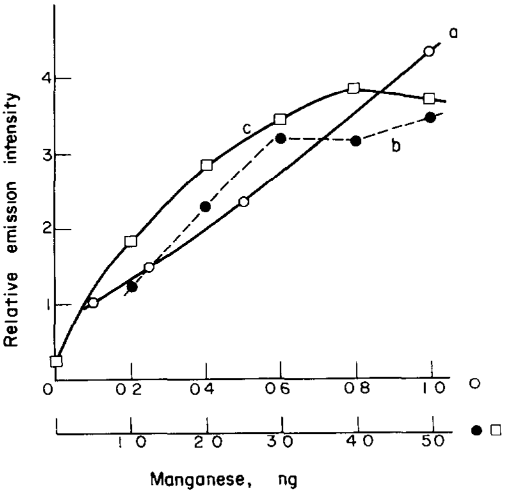

Fig 5. Calibration graphs for (*a*) 0–1.0 ng of Mn; (*b*) 1.0–5.0 ng of Mn; (*c*) 0–5.0 ng of Mn in the presence of 10 μg of Cl⁻.

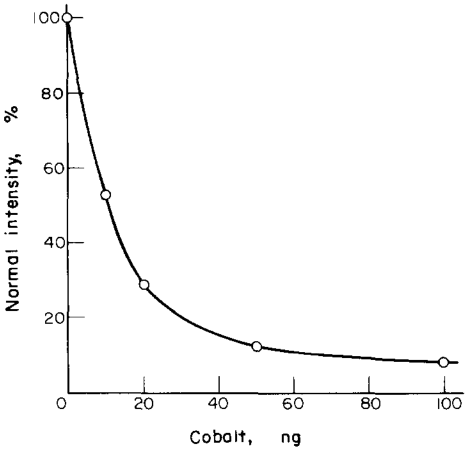

Fig. 6 Effect of cobalt(II) on the peak candoluminescence intensity from 10 ng of manganese.

Table 1. Effect of metal ions on manganese candoluminescence intensity

Metal ion added†	Emission intensity* Amount of metal ion added 10 ng	 100 ng
V(IV)	30	4
V(V) (as NH_4VO_3)	13	3
Cr(III)	31	11
Cr(VI) (as K_2CrO_4)	70	35
Fe(II)	35	5
Co(II)	53	8
Ni(II)	51	11
Cu(II) (as chloride)	83	33
Pb(II) (as nitrate)	97	100
Bi(III) (as nitrate)	98	84
Al(III)	100	98
Zn(II)	83	100
K(I)	96	88

* Luminescence emission intensity from 10 ng of Mn(II); value = 100 if no interference.

† As sulphate, unless otherwise stated.

of manganese. Of these, bismuth and lead are themselves activators in CaO. Manganese and bismuth have a similar optimal candoluminescence temperature, and thus emit simultaneously in the flame, but the spectra of manganese (peak at 580 nm) and bismuth (400 nm) do not overlap, and the manganese emission can be measured without interference from bismuth. The same considerations apply to lead, with a peak at 390 nm. Moreover, the lead emission occurs at a much lower temperature than that of manganese, and fades to zero before the manganese luminescence starts. The non-luminescing interferents mentioned have white oxides, and so no surface deposit was visible.

Anions. Common anions such as SO_4^{2-}, NO_3^-, NO_2^-, SCN^-, IO_3^- and some organic anions (formate, oxalate) were found to have no effect on the manganese candoluminescence at any concentration. Chloride ions, however, enhanced the luminescence, as shown in Fig. 7. The emission from 10 ng of manganese was found to be twice as intense in the presence of 1 μg of chloride, and was increased 4.2 times by 10 μg of chloride. Bromide had a slight enhancing effect (1.7 times the original intensity, with 10 μg of bromide); fluoride enhanced the emission by about 100% only when present in low concentrations (500 ppm), and had no effect at high concentrations (Fig. 7). Iodide had no effect. The phenomenon of an anion or an acid enhancing the emission from a matrix–activator pair has been termed co-activation, and has been found to occur quite frequently in candoluminescence [4,5] Chloride, for example, co-activates the emissions from lead and antimony in calcium oxide, and from indium in magnesium oxide.[5] Sulphuric acid co-activates cerium and europium candoluminescence in calcium oxide.[4] The emission from co-activated manganese has the same spectrum as that from manganese that has not been co-activated. The presence of a co-activator gives greater sensitivity, as is shown in Fig. 5. However, the calibration range is not extended in the presence of the co-activator, nor is the reproducibility improved.

The only anions that reduced the luminescent intensity were those that contained a transition metal, *viz.* VO_3^- and CrO_4^{2-}.

Acids. As the matrix is mainly calcium oxide, the presence of acids in the sample solution would be expected to interfere chemically with its composition, and thus with the luminescence produced. Increasing concentrations of nitric and sulphuric acids were found to produce a gradual decrease of emission intensity as shown in Fig. 8, the sulphuric acid interference being the greater. Hydrochloric acid was found to cause an initial sharp enhancement of emission, because of chloride co-activation, but with increasing acid concentration, the enhancement fell steadily. However, as shown in Fig. 8, even in the presence of 5 *M* acid, the emission intensity did not fall below that in the absence of co-activation.

Repeated emissions

If, after emission had been obtained from an activated matrix, the matrix was removed from the flame for about a minute to let it cool, and then re-introduced into the flame, the emission intensity obtained was up to three times the initial intensity. Further small enhancements occurred each time the process was repeated, as is shown in Fig. 9. Such a phenomenon does not seem to be exhibited by bismuth, for which repetition of heating gives the same emission from a single matrix.[2]

DISCUSSION

The phenomenon of candoluminescence has been shown to be the basis for a method for the determination of nanogram and sub-nanogram quantities of manganese in aqueous solution. The method is rapid, very sensitive and requires fairly simple apparatus. Co-activation increases the sensitivity of the method.

In the initial quantitative candoluminescence studies of bismuth,[1] the activator was introduced into the matrix by co-precipitating it with the matrix in solution. This gave a calibration range in the microgram region. Much greater sensitivity could be

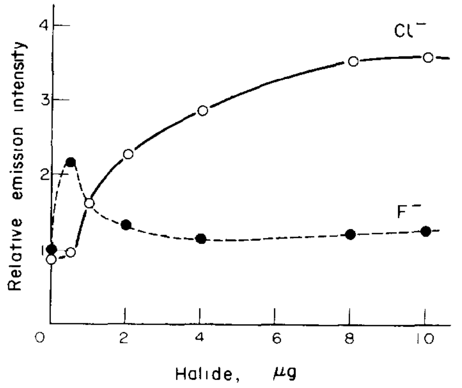

Fig. 7 Effect of chloride and fluoride ions on the peak candoluminescence intensity from 10 ng of manganese.

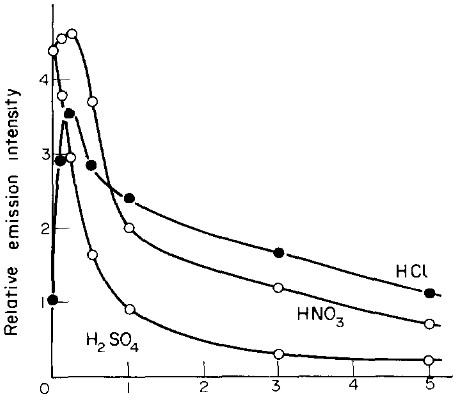

Fig. 8. Effect of some acids on the peak candoluminescence intensity from 10 ng of manganese

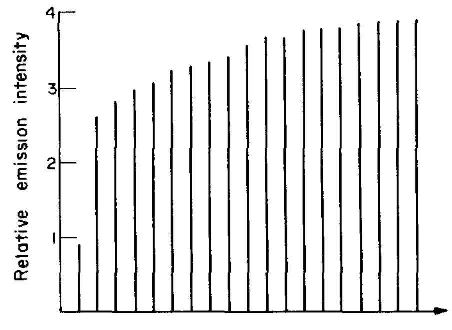

Fig. 9. Peak emission intensities obtained by sequential restimulation of manganese candoluminescence.

obtained by directly adding the activator in solution to the pure matrix surface. With improving techniques, it has been possible to apply a direct-injection method for all activators, including manganese. However, in order to have reasonably reproducible results, it is necessary to have a standardized, reproducible procedure for the preparation of each matrix. This is because the variation of compactness and porosity between matrices is a major cause of poor reproducibility of luminescence emission.

Certain metal ions are found to interfere with the manganese luminescence; thus it is necessary to ensure that these ions are not present in solution with the activator, either by chemically removing them, or by selectively extracting the manganese before determining it.

More matrix–activator pairs are being discovered, and analytical applications of these will be the subject of future papers. With such developments it is apparent that candoluminescence has much potential as a general quantitative trace analytical technique.

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The candoluminescence spectrum of manganese is shown in Fig. 1. The peak emission intensity is at 580 nm, and all further measurements were made at this wavelength.

Effect of flame conditions and matrix position

The three gases admitted to the pre-mix burner were hydrogen, nitrogen, and air. Under optimal conditions, the part of the flame that stimulated luminescence at the matrix surface was a narrow region at the "edge". Because of this, the lateral positioning of the matrix holder was very critical. Once the optimal position had been found, the holder was left in this position so that the matrices could be positioned reproducibly in the flame by simply rotating the socket.[2] Each matrix–activator pair has a temperature at which maximal luminescence occurs. Thus, if the flame temperature is greater than this, the emission intensity from a matrix at the edge of the flame rises to a maximum, then decreases as the temperature of the surface increases. The emission-time profile of manganese-activated calcium oxide under optimal flame conditions is shown in Fig. 2. The luminescence begins 10 sec after the flame is entered by the matrix and reaches a maximum after 30 sec. The term "optimal flame conditions" implies not only that the emission intensity reached is maximal, but that the, noise, from the flame (principally from dust particles and sodium impurities) is minimal.

Apart from the horizontal distance of the matrix from the flame axis, the four principal flame variables involved are the hydrogen, nitrogen and air flow-rates, and the height of the matrix in the flame above the burner. Each of these was investigated separately. For each study, three of the parameters were fixed at about their optimal value (determined approximately in experiments beforehand), while the fourth was varied. The results are shown in Figs. 3 and 4. The nitrogen flow-rate appeared not to be very critical as far as luminescence intensity was concerned, but was critical for reducing the flame noise, the noise decreasing markedly as the nitrogen flow increased. Variations in hydrogen and air flows were more critical, both with respect to emission intensity and flame noise. This is to be expected, as it is the hydrogen–oxygen interaction in the flame which produces the radicals which stimulate candoluminescence. On the basis of these experiments the optimal gas flow-rates were considered to be: nitrogen 8.0 l./min, hydrogen 2.0 l./min and air 2.5 l./min. The variation of the height of the centre of the matrix above the burner head was not very critical, and 3.0 cm was chosen as suitable.

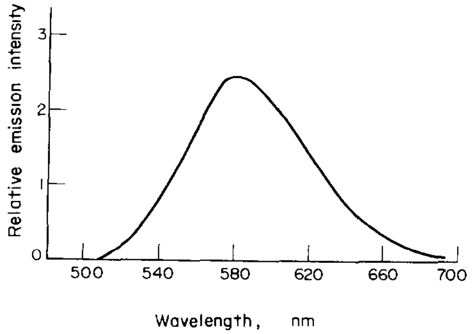

Fig. 1. Candoluminescence spectrum of manganese

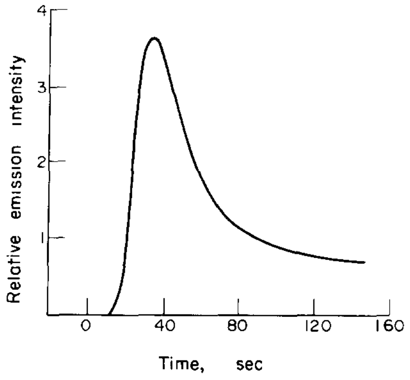

Fig. 2. Change in manganese candoluminescence intensity at 580 nm with time. Matrix inserted into flame at 0 sec

Calibration and reproducibility

Figure 5 shows the calibration curves obtained for 0.1–1.0 and 1.0–5.0 ng of manganese. It was found that, as with other activators,[2,4] there is an upper calibration limit above which the curve levels off or falls. For manganese, this occurs at about 3 ng; for bismuth[2] it had been found to be 2 ng. Below 0.1 ng of manganese the emission becomes difficult to measure because the emission is mainly that of manganese impurity in the matrix. However, it is expected that by utilizing ultrapure calcium carbonate as a matrix material, the calibration range could be extended to well below 0.1 ng.

Good reproducibility in candoluminescence is obtained by exercising precise control over a large number of parameters, including the flame conditions, the sample introduction technique, and above all the

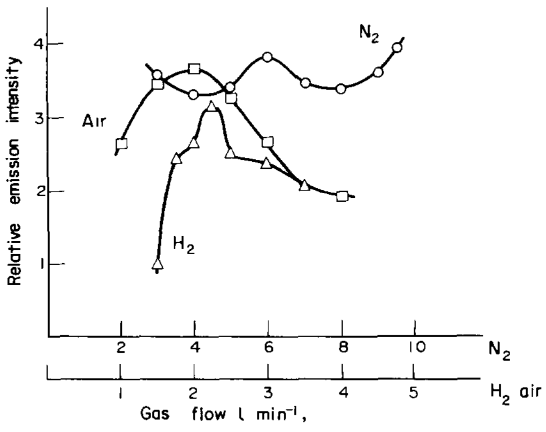

Fig. 3. Effect of flame-gas flow-rates on manganese peak candoluminescence intensity.

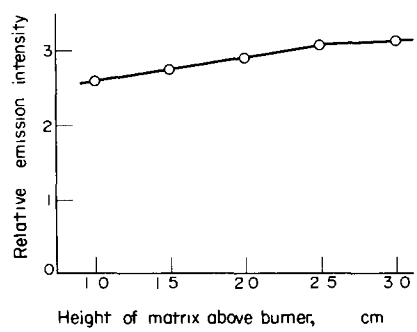

Fig. 4. Effect of height of matrix in flame on manganese peak candoluminescence intensity

matrix preparation technique. With manganese, the reproducibility was ±5%, but could be ±10% or more if the experimental technique was inadequate.

Interferences

Interferences were investigated by preparing solutions containing a standard quantity of manganese together with various quantities of another cation (usually as the sulphate) or of another anion (as its potassium salt). The activator and interferent were applied together in a 1-μl drop of solution.

Cations. Transition metal cations interfered markedly with the luminescence of 10 ng of manganese, causing a gradual decrease in emission intensity, an example of which is shown in Fig. 6. Table 1 shows the degree of interference from various metal ions, when present in a 1:1 and 10:1 w:w ratio to the activator. In most instances, a deposit was visible on the matrix surface after removing it from the flame, and its colour corresponded to that of transition metal oxide. Such a deposit would shield the calcium oxide surface from the flame and thus reduce the luminescence. Zinc, aluminium, bismuth, lead and potassium ions were found to have little effect on the luminescence when present in up to ten times the weight

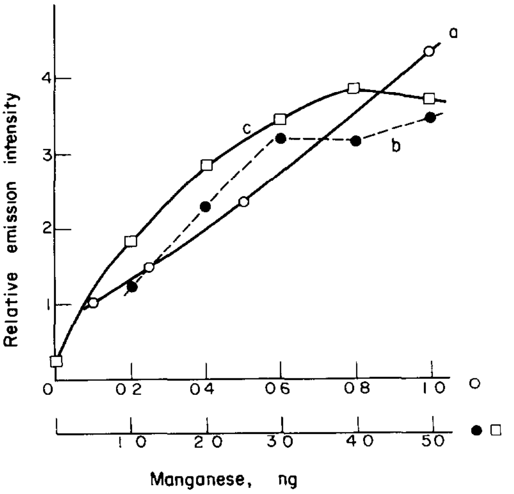

Fig 5. Calibration graphs for (*a*) 0–1.0 ng of Mn; (*b*) 1.0–5.0 ng of Mn; (*c*) 0–5.0 ng of Mn in the presence of 10 μg of Cl$^-$.

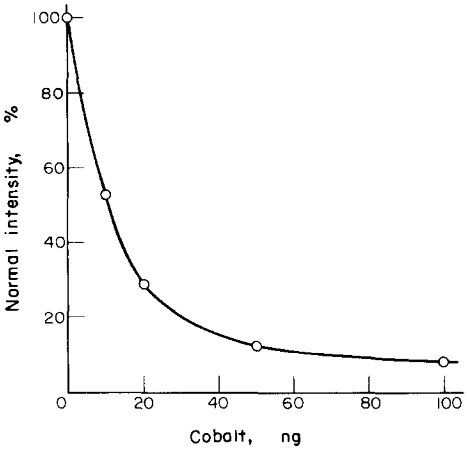

Fig. 6 Effect of cobalt(II) on the peak candoluminescence intensity from 10 ng of manganese.

Table 1. Effect of metal ions on manganese candoluminescence intensity

Metal ion added†	Emission intensity* Amount of metal ion added 10 ng	 100 ng
V(IV)	30	4
V(V) (as NH_4VO_3)	13	3
Cr(III)	31	11
Cr(VI) (as K_2CrO_4)	70	35
Fe(II)	35	5
Co(II)	53	8
Ni(II)	51	11
Cu(II) (as chloride)	83	33
Pb(II) (as nitrate)	97	100
Bi(III) (as nitrate)	98	84
Al(III)	100	98
Zn(II)	83	100
K(I)	96	88

* Luminescence emission intensity from 10 ng of Mn(II); value = 100 if no interference.

† As sulphate, unless otherwise stated.

of manganese. Of these, bismuth and lead are themselves activators in CaO. Manganese and bismuth have a similar optimal candoluminescence temperature, and thus emit simultaneously in the flame, but the spectra of manganese (peak at 580 nm) and bismuth (400 nm) do not overlap, and the manganese emission can be measured without interference from bismuth. The same considerations apply to lead, with a peak at 390 nm. Moreover, the lead emission occurs at a much lower temperature than that of manganese, and fades to zero before the manganese luminescence starts. The non-luminescing interferents mentioned have white oxides, and so no surface deposit was visible.

Anions. Common anions such as SO_4^{2-}, NO_3^-, NO_2^-, SCN^-, IO_3^- and some organic anions (formate, oxalate) were found to have no effect on the manganese candoluminescence at any concentration. Chloride ions, however, enhanced the luminescence, as shown in Fig. 7. The emission from 10 ng of manganese was found to be twice as intense in the presence of 1 μg of chloride, and was increased 4.2 times by 10 μg of chloride. Bromide had a slight enhancing effect (1.7 times the original intensity, with 10 μg of bromide); fluoride enhanced the emission by about 100% only when present in low concentrations (500 ppm), and had no effect at high concentrations (Fig. 7). Iodide had no effect. The phenomenon of an anion or an acid enhancing the emission from a matrix–activator pair has been termed co-activation, and has been found to occur quite frequently in candoluminescence [4,5] Chloride, for example, co-activates the emissions from lead and antimony in calcium oxide, and from indium in magnesium oxide.[5] Sulphuric acid co-activates cerium and europium candoluminescence in calcium oxide.[4] The emission from co-activated manganese has the same spectrum as that from manganese that has not been co-activated. The presence of a co-activator gives greater sensitivity, as is shown in Fig. 5. However, the calibration range is not extended in the presence of the co-activator, nor is the reproducibility improved.

The only anions that reduced the luminescent intensity were those that contained a transition metal, *viz.* VO_3^- and CrO_4^{2-}.

Acids. As the matrix is mainly calcium oxide, the presence of acids in the sample solution would be expected to interfere chemically with its composition, and thus with the luminescence produced. Increasing concentrations of nitric and sulphuric acids were found to produce a gradual decrease of emission intensity as shown in Fig. 8, the sulphuric acid interference being the greater. Hydrochloric acid was found to cause an initial sharp enhancement of emission, because of chloride co-activation, but with increasing acid concentration, the enhancement fell steadily. However, as shown in Fig. 8, even in the presence of 5 *M* acid, the emission intensity did not fall below that in the absence of co-activation.

Repeated emissions

If, after emission had been obtained from an activated matrix, the matrix was removed from the flame for about a minute to let it cool, and then re-introduced into the flame, the emission intensity obtained was up to three times the initial intensity. Further small enhancements occurred each time the process was repeated, as is shown in Fig. 9. Such a phenomenon does not seem to be exhibited by bismuth, for which repetition of heating gives the same emission from a single matrix.[2]

DISCUSSION

The phenomenon of candoluminescence has been shown to be the basis for a method for the determination of nanogram and sub-nanogram quantities of manganese in aqueous solution. The method is rapid, very sensitive and requires fairly simple apparatus. Co-activation increases the sensitivity of the method.

In the initial quantitative candoluminescence studies of bismuth,[1] the activator was introduced into the matrix by co-precipitating it with the matrix in solution. This gave a calibration range in the microgram region. Much greater sensitivity could be

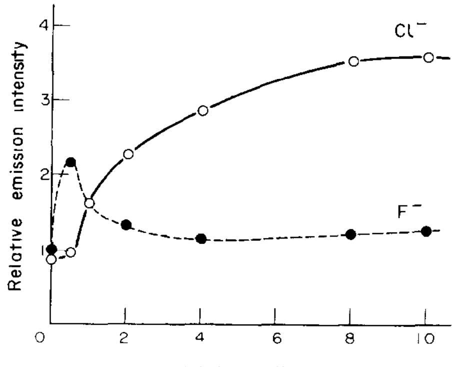

Fig. 7 Effect of chloride and fluoride ions on the peak candoluminescence intensity from 10 ng of manganese.

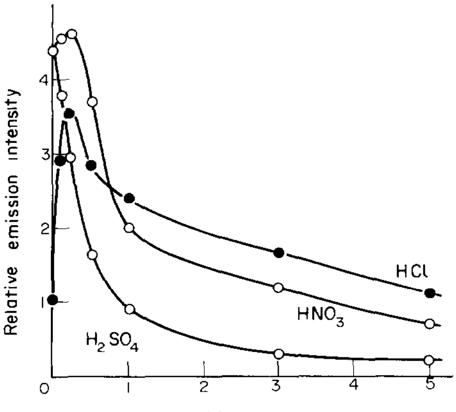

Fig. 8. Effect of some acids on the peak candoluminescence intensity from 10 ng of manganese

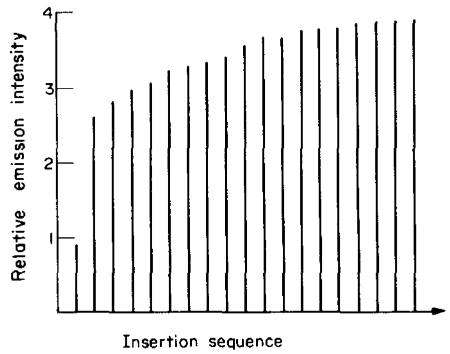

Fig. 9. Peak emission intensities obtained by sequential restimulation of manganese candoluminescence.

obtained by directly adding the activator in solution to the pure matrix surface. With improving techniques, it has been possible to apply a direct-injection method for all activators, including manganese. However, in order to have reasonably reproducible results, it is necessary to have a standardized, reproducible procedure for the preparation of each matrix. This is because the variation of compactness and porosity between matrices is a major cause of poor reproducibility of luminescence emission.

Certain metal ions are found to interfere with the manganese luminescence; thus it is necessary to ensure that these ions are not present in solution with the activator, either by chemically removing them, or by selectively extracting the manganese before determining it.

More matrix–activator pairs are being discovered, and analytical applications of these will be the subject of future papers. With such developments it is apparent that candoluminescence has much potential as a general quantitative trace analytical technique.

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A SENSOR FOR HYDROGEN SULPHIDE

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Summary—A sensor for hydrogen sulphide is described. It is based on the catalytic effect of the gas on the iodine–azide reaction. An iodine–azide solution is exuded from a sintered-glass ball (10 mm diameter) at a flow-rate of 3.30 ml/min whilst its potential is monitored by two platinum electrodes, one inside and the other outside the ball. Sample is carried in a gas at a flow-rate of 350 ml/min. Carbon disulphide, methyl mercaptan or sulphur dioxide in amounts up to a hundred times that of the hydrogen sulphide do not interfere. The detection limit is 5 ng and the determination limit is 8 ng, with a relative standard deviation of 10%.

The flame photometric detector has been widely used to monitor sulphur compounds in the atmosphere.[1–4] This detector is selective and sensitive for sulphur, but it does not differentiate one compound of sulphur from another.

The object of this work was to construct a sensor for the sensitive and selective determination of hydrogen sulphide. To achieve this we took advantage of the catalytic effect of hydrogen sulphide. It is well known that the iodine–azide reaction is catalysed by sulphides, thiosulphates, thiocyanates, mercaptans, and thioketones,[5] and this has been used as a basis for the determination of these compounds. For example, metallic sulphides, thiosulphates and thiocyanates have been determined arsenimetrically,[6–11] manometrically,[12–15] amperometrically,[16–20] and photometrically.[21,22] Carbon disulphide has been determined by the chronometric method[23] and arsenimetry.[24] Hydrogen sulphide in the atmosphere was determined manometrically as metallic sulphide,[25] but the direct determination of hydrogen sulphide based on the catalytic reaction has not been reported previously.

Although many sulphur compounds exert a catalytic effect on the reaction, the only gaseous substances able to do so at room temperature are hydrogen sulphide, carbon disulphide, and lower alkyl mercaptans. Further, the mercaptans dissolve in water and react much more slowly than hydrogen sulphide. In our procedure, iodine–azide solution is exuded from a sintered-glass ball at constant flow-rate and the difference in potential between two platinum wire electrodes, one of which is placed in the solution inside the sintered-glass ball and the other outside the ball, is measured. Hydrogen sulphide, which is transported by a carrier gas at constant flow-rate, reacts only with the solution outside the ball. The catalysed reaction results in a variation in composition of the solutions inside and outside the ball and consequently a measurable potential difference across the electrodes.

A device having a sintered-glass ball was devised first by Araki *et al.*,[26] who determined sulphur dioxide at the 0.5–20 ppm level by using an iodine concentration cell.

EXPERIMENTAL

Apparatus

The essential features of the device are shown in Fig. 1. The sintered-glass ball was a glass filter ball 10 mm in diameter. The iodine–azide solution was pumped peristaltically. Potentials were measured with a TOA potentiometer HM-5A connected to a TOA recorder EPR-10A. The platinum wire electrodes were 0.5 mm in diameter and

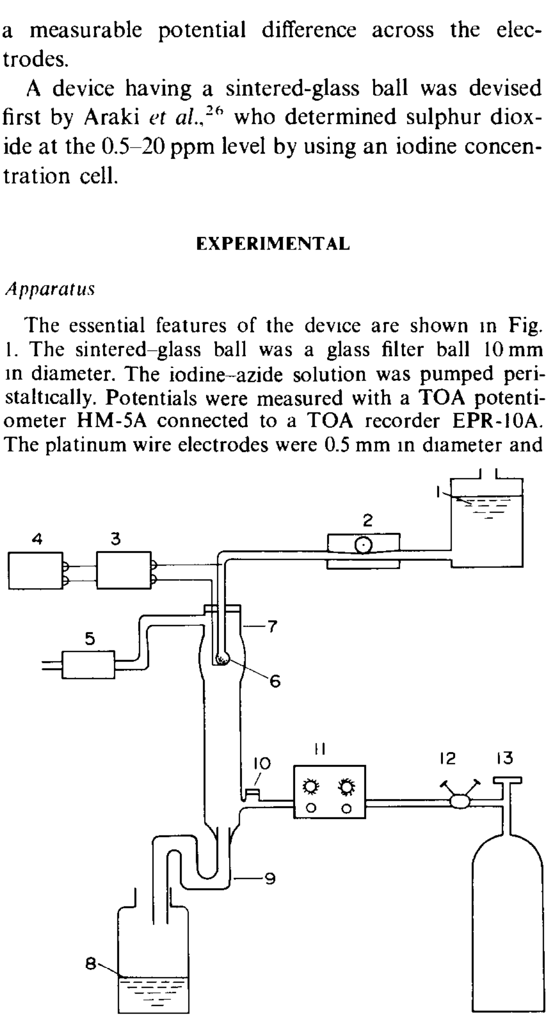

Fig. 1. Schematic diagram of apparatus. 1, Iodine–azide solution; 2, peristaltic pump; 3, potentiometer; 4, recorder; 5, gas flowmeter; 6, sintered-glass ball; 7, glass tube; 8, drain; 9, rubber tube; 10, injection port; 11, pressure controller; 12, pressure gauge; 13, nitrogen cylinder.

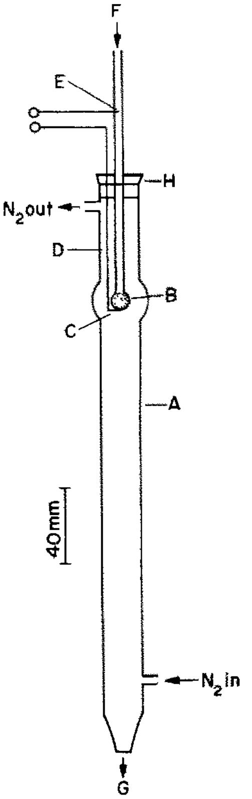

Fig. 2 Sensor. A, Glass tube; B, sintered-glass ball; C, counter-electrode; D, electric lead; E, working electrode; F, iodine–azide solution; G, solution drain; H, rubber stopper.

5 mm long. The electrode outside the ball was placed in contact with the ball as shown in Fig. 2, and the platinum wire (0.5 mm diameter and 100 mm long) was insulated with poly(vinyl chloride). The electrodes were cleaned by electrolysis in 0.2 M sodium acetate for 30 min at 0.0 V *vs.* S.C.E. and stored in 7.0 M nitric acid. This treatment allowed the electrodes to function continuously for about 200 hr

Reagents

A $10^{-3}M$ stock solution of iodine in 0.1M potassium iodide was prepared and standardized by titration with thiosulphate. The sodium azide was checked iodometrically by the method of Feigl *et al.*[27] Solutions were buffered with mixtures of potassium dihydrogen phosphate and sodium hydroxide.

All reagents were analytical-reagent grade and used without further purification.

Procedure

Nitrogen was used as carrier gas, at a constant flow-rate of 350 ml/min. The iodine–azide solution ($3 \times 10^{-5}M$ iodine, 0.02 M sodium azide, 0.02 M potassium iodide, buffered at pH 7.0) was exuded from the sintered-glass ball at a constant flow-rate of 3.3 ml/min by means of the peristaltic pump. When a recorder gave a steady trace, 100 μl of sample were injected with a gas-syringe. A suitable sensitivity was chosen by trial. The recorder was run at a speed of 10 mm/min. All experiments were carried out at room temperature, 25°.

Calibration was made by injecting 5 ml of hydrogen sulphide into a 2250-ml flask, equipped with a rubber stopper coated with silicone grease, and extracting sample from the flask through the rubber stopper with a 500-μl gas-syringe. The amount of hydrogen sulphide injected was determined iodometrically. When the total volume of sample extracted amounted to 2 ml, a fresh sample was prepared.

RESULTS AND DISCUSSION

The pH and flow-rate of the iodine–azide solution

The iodine–azide solution was buffered at pH 5.0, 6.0, 7.0, and 8.0 and the solutions were exuded from the ball at different flow-rates. Typical potential *vs* time (E–t) curves and the results, together with relative standard deviation, are shown in Figs. 3 and 4, respectively. In Fig. 3, the curves rise rapidly and then tail off. The tailing is considerable at the lower flow-rates but, the shapes of the curves do not vary with pH. At the lower flow-rates the base-lines of the curves are very unstable and the curves show several sharp peaks (A, B, E and F in Fig. 3). At higher flow-rates, the base-lines are stable, the curves show a single peak, and the values of the relative standard deviations are more reproducible than those for lower flow-rates. Figure 4 shows that the potential difference is highly dependent on both the pH and the flow-rate of the solution. A slight change of the flow-rate in the range 1.65–4.40 ml/min has a remarkable

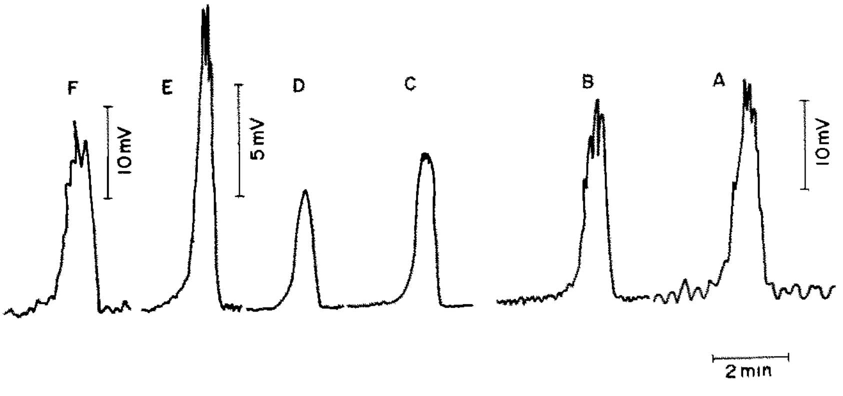

Fig. 3. Potential–time curves. pH and flow-rate of solution, ml/min: A, 7.0, 0.62; B, 7.0, 1.65; C, 7.0, 2.25; D, 7.0, 3.30; E, 8.0, 1.65; F, 6.0, 1.65. Iodine $6.30 \times 10^{-5}M$, sodium azide $1.85 \times 10^{-2}M$, potassium iodide $8.45 \times 10^{-2}M$, gas flow-rate 110 ml/min, hydrogen sulphide 190 ng.

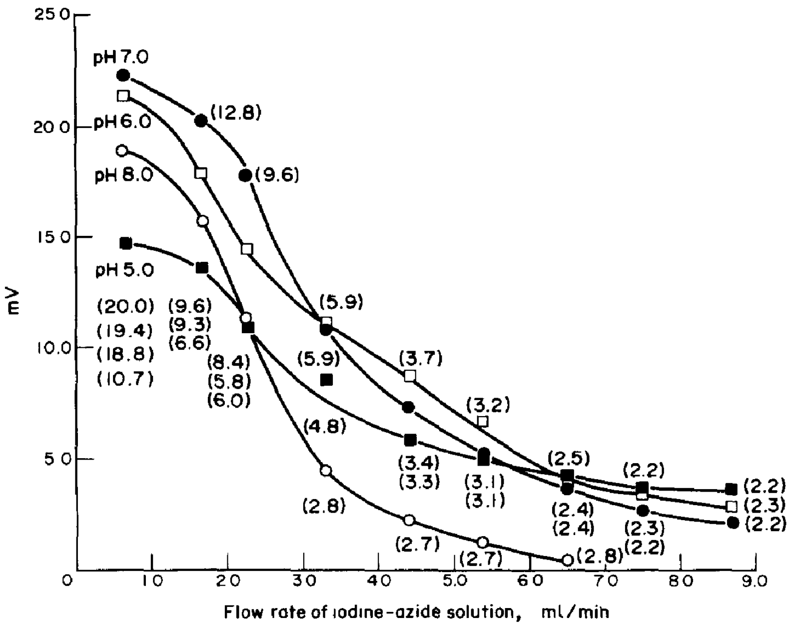

Fig. 4. Relationship between flow-rate of iodine–azide solution and potentials in solutions of different pH. Figures in parentheses represent the relative standard deviations. Each value is the average of 7 runs. Experimental conditions as for Fig. 3.

effect on the potential difference, especially at pH 8.0. When the exudation of the solution from the ball was stopped and four separate samples were successively injected at intervals (Fig. 5), a sloping base-line was obtained because of the evaporation of iodine. The curves show that the catalyst is not fully active until a while after the reaction begins. The maximum potentials were obtained at the third injection for all solutions (Fig. 6). The results (Figs. 4 and 6) show that the best compromise between sensitivity and reproducibility is given by using a pH of 7.0 and a flow-rate of about 3.3 ml/min were chosen.

Concentration of the iodine–azide solution

Measurements made on solutions with varied concentrations of iodine, of sodium azide and potassium iodide are shown in Tables 1–3. Plots of potential *vs.* log iodine or azide concentration were linear, whereas the potential was independent of iodide concentration. The results show that the sensitivity of the reaction towards hydrogen sulphide is determined mainly by the azide:iodine ratio. Babko *et al.*,[21] using a photometric method, reported that the sensitivity of the reaction increased with concentration of potassium iodide over the range 0.1–2.8 *M*, concentrations

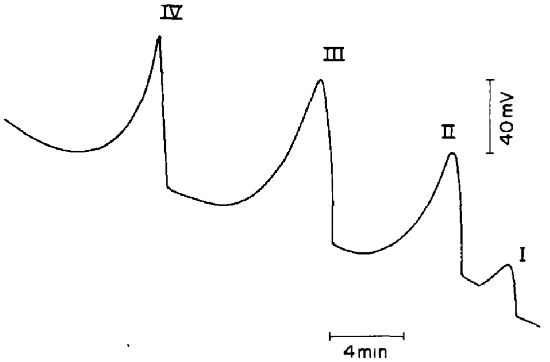

Fig. 5. Potential–time curves when the exudation of solution is stopped. I, First injection; II, second injection; III, third injection, IV, fourth injection; pH 7.0, other experimental conditions as for Fig. 3.

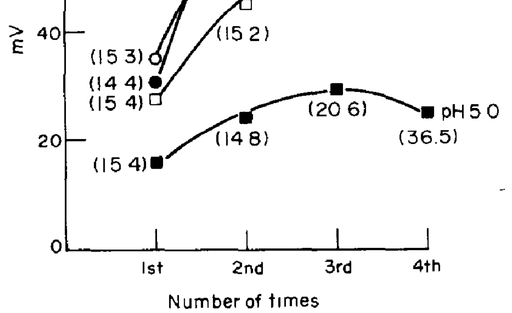

Fig. 6. Relationship between number of injections of sample and potential in solutions of different pH. Figures in parentheses represent the relative standard deviations. Each value is the average of 7 runs. Other experimental conditions as for Fig. 3.

Table 1. Effect of concentration of iodine on the iodine-azide reaction*

	Concentration of iodine, $10^{-5}M$						
	9.47	6.77	5.60	4.17	2.71	1.36	0.677
Potential, mV	4.0 (4.3)	8.2 (4.4)	10.8 (4.4)	13.7 (4.8)	18.3 (6.3)	26.0 (8.6)	33.5 (14.7)

*Each value is the average of 7 runs and figures in parentheses represent the relative standard deviations. Experimental conditions: sodium azide $1.85 \times 10^{-2}M$, potassium iodide $5.00 \times 10^{-2}M$, solution flow-rate 3.3 ml/min, pH 7.0, gas flow-rate 200 ml/min, hydrogen sulphide 500 ng.

Table 2. Effect of concentration of sodium azide on the iodine-azide reaction*

	Concentration of sodium azide, M			
	3.68×10^{-2}	1.82×10^{-2}	9.55×10^{-3}	3.51×10^{-4}
Potential, mV	27.0 (10.2)	18.8 (6.4)	11.2 (5.0)	1.7 (4.8)

*Each value is the average of 7 runs and figures in parentheses represent the relative standard deviations. Iodine $3.10 \times 10^{-5}M$, other conditions as for Table 1.

Table 3. Effect of concentration of potassium iodide on the iodine-azide reaction*

	Concentration of potassium iodide, M					
	0.150	0.100	0.050	0.010	0.005	0.001
Potential, mV	19.2	19.4	19.4	19.3	19.3	19.4

*Concentration of sodium azide $2.01 \times 10^{-2}M$ and other experimental conditions as for Table 2.

Table 4. Effect of gas flow rate on the iodine-azide reaction*

	Gas flow rate, ml/min										
	800	600	480	330	250	200	180	130	90	80	75
Potential mV	20.1 (21.1)	19.9 (10.4)	19.5 (5.4)	19.5 (3.8)	19.5 (3.7)	18.9 (6.9)	18.4 (7.3)	17.9 (11.2)	15.2 (18.5)	14.6 (20.5)	14.1 (20.6)

* Each values is the average of 7 runs and figures in the parentheses represent the relative standard deviation. Experimental conditions are similar to those in Fig. 7.

of the other components being kept constant at 10^{-3} M iodine, 0.011 M sodium azide, and pH 5.2. Such an increase in sensitivity was not observed under the experimental conditions of our study.

The use of lower concentrations of iodine and higher concentrations of azide increases the sensitivity of the reaction, but the base-line drifts when lower iodine concentrations are used, because of the volatility of iodine; reproducible results are also not obtained in the presence of large amounts of sodium azide. Thus, the concentrations of iodine, sodium azide, and potassium iodide were fixed at 3×10^{-5}, 0.02, and 0.02M respectively.

Gas flow-rate

The effect of flow-rate of the carrier gas was examined over the range 75–800 ml/min. Typical E–t curves at different gas flow-rates are shown in Fig. 7, and the results are listed in Table 4. In Fig. 7, the shapes of the curves vary with gas flow-rate, with broad jagged peaks at low flow-rates and single sharp peaks at high. The reproducibilities are better at moderate flow-rates. The potentials are approximately constant in the gas flow-rate range 250–480 ml/min, so a flow-rate of 350 ml/min was chosen.

Working electrode and glass tube

Contact between the platinum electrode and the ball was made in three ways: (*i*) *via* the bottom of the ball as shown in Fig. 2, (*ii*) *via* a platinum wire ring 5 mm in diameter at the bottom of the ball, and (*iii*) *via* a platinum wire 100 mm long wound round

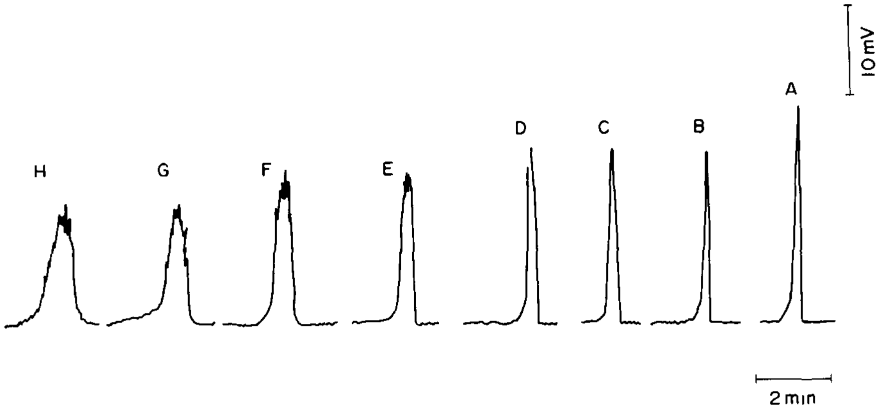

Fig. 7. Potential–time curves at various gas flow-rates. Flow rates, *ml/min*: A, 800; B, 480; C, 330; D, 250; E, 180; F, 130; G, 90; H, 75. Iodine 3.10 × $10^{-5}M$, sodium azide 2.12 × $10^{-2}M$, potassium iodide 2.00 × $10^{-2}M$, solution flow-rate 3.3 ml/min, pH 7.0, hydrogen sulphide 505 ng.

the ball. Method (*i*) gave the most sensitive and reproducible results, the other two giving poor base-lines and variable sensitivities 10–50 times poorer than those obtained by method (*i*).

A change in the linear velocity of the carrier gas in the neighbourhood of the ball made the sensitivity and reproducibility poorer. For example, when a glass tube (20 mm bore) without a bulge was used, the sensitivity was only a third of that for curve C in Fig. 7 and the relative standard deviation was 34% for seven runs, whereas with the glass tube shown in Fig. 2 the deviation was 5.6% under the same conditions. The distance between the gas inlet and the ball also affected the results. A relative standard deviation of 10% or less was obtained with a distance of 20 cm or more.

Interferences

Gaseous reducing substances such as sulphur dioxide and formaldehyde interfered, but the sensitivity towards sulphur dioxide was only about 2%, and that towards formaldehyde only about 0.1% of that towards hydrogen sulphide. The shapes of the E–t curves were symmetric and this could be used to distinguish between other reducing gas (symmetric peaks) and hydrogen sulphide (asymmetric).

Gaseous oxidizing substance such as ozone gave a potential in the opposite direction, with a magnitude similar to that for sulphur dioxide.

Gaseous substances, such as carbon disulphide and methyl mercaptan, having a catalytic effect on the iodine–azide reaction, reacted more slowly, so that a 100-fold amount relative to hydrogen sulphide merely broadened the width of the peak, but left the height unaffected. When there was 200, 300, 400, 500 and 600 times as much carbon disulphide or methyl mercaptan as hydrogen sulphide the error was 2.5, 3.2, 4.3, 7.9 and 12.0% respectively.

Gaseous organic substances which decrease the response of the flame photometric detector[28] did not interfere at any concentration.

Calibration curve

The sensitivity of the sensor to hydrogen sulphide varied somewhat with changes in conditions for electrode treatment such as cleaning time, and concentrations of sodium acetate solution and nitric acid. However, over a period up to 200 hr the following relationship held: $E = 9.61 \log C - 6.0$, where E is the potential in mV and C is the amount of hydrogen sulphide in ng. The slope of the curve varied with electrode treatment by ±0.2. The relative standard deviations (10 runs) were 9.8% for 8 ng of hydrogen sulphide, 9.4% for 10 ng, 7.7% for 50 ng, 5.0% for 100 ng, 3.5% for 500 ng and 2.7% for 1000 ng. When the amount of hydrogen sulphide was greater than 1 μg there was a negative deviation from linearity, amounting to 10% for 10 μg of hydrogen sulphide and 16% for 15 μg. The sensitivity worsened rapidly after 200 hr use of the electrodes.

The lowest detectable potential for the recorder and potentiometer used in this study was 0.7 mV. Therefore, the detection limit was 5 ng.

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A SENSOR FOR HYDROGEN SULPHIDE

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Summary—A sensor for hydrogen sulphide is described. It is based on the catalytic effect of the gas on the iodine–azide reaction. An iodine–azide solution is exuded from a sintered-glass ball (10 mm diameter) at a flow-rate of 3.30 ml/min whilst its potential is monitored by two platinum electrodes, one inside and the other outside the ball. Sample is carried in a gas at a flow-rate of 350 ml/min. Carbon disulphide, methyl mercaptan or sulphur dioxide in amounts up to a hundred times that of the hydrogen sulphide do not interfere. The detection limit is 5 ng and the determination limit is 8 ng, with a relative standard deviation of 10%.

The flame photometric detector has been widely used to monitor sulphur compounds in the atmosphere.[1–4] This detector is selective and sensitive for sulphur, but it does not differentiate one compound of sulphur from another.

The object of this work was to construct a sensor for the sensitive and selective determination of hydrogen sulphide. To achieve this we took advantage of the catalytic effect of hydrogen sulphide. It is well known that the iodine–azide reaction is catalysed by sulphides, thiosulphates, thiocyanates, mercaptans, and thioketones,[5] and this has been used as a basis for the determination of these compounds. For example, metallic sulphides, thiosulphates and thiocyanates have been determined arsenimetrically,[6–11] manometrically,[12–15] amperometrically,[16–20] and photometrically.[21,22] Carbon disulphide has been determined by the chronometric method[23] and arsenimetry.[24] Hydrogen sulphide in the atmosphere was determined manometrically as metallic sulphide,[25] but the direct determination of hydrogen sulphide based on the catalytic reaction has not been reported previously.

Although many sulphur compounds exert a catalytic effect on the reaction, the only gaseous substances able to do so at room temperature are hydrogen sulphide, carbon disulphide, and lower alkyl mercaptans. Further, the mercaptans dissolve in water and react much more slowly than hydrogen sulphide. In our procedure, iodine–azide solution is exuded from a sintered-glass ball at constant flow-rate and the difference in potential between two platinum wire electrodes, one of which is placed in the solution inside the sintered-glass ball and the other outside the ball, is measured. Hydrogen sulphide, which is transported by a carrier gas at constant flow-rate, reacts only with the solution outside the ball. The catalysed reaction results in a variation in composition of the solutions inside and outside the ball and consequently a measurable potential difference across the electrodes.

A device having a sintered-glass ball was devised first by Araki *et al.*,[26] who determined sulphur dioxide at the 0.5–20 ppm level by using an iodine concentration cell.

EXPERIMENTAL

Apparatus

The essential features of the device are shown in Fig. 1. The sintered-glass ball was a glass filter ball 10 mm in diameter. The iodine–azide solution was pumped peristaltically. Potentials were measured with a TOA potentiometer HM-5A connected to a TOA recorder EPR-10A. The platinum wire electrodes were 0.5 mm in diameter and

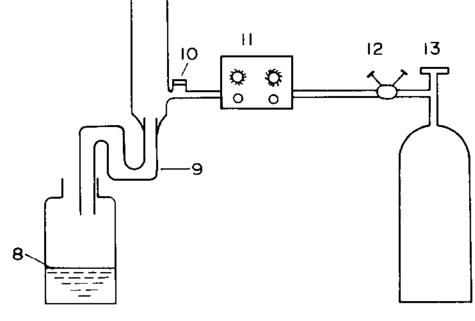

Fig. 1. Schematic diagram of apparatus. 1, Iodine–azide solution; 2, peristaltic pump; 3, potentiometer; 4, recorder; 5, gas flowmeter; 6, sintered-glass ball; 7, glass tube; 8, drain; 9, rubber tube; 10, injection port; 11, pressure controller; 12, pressure gauge; 13, nitrogen cylinder.

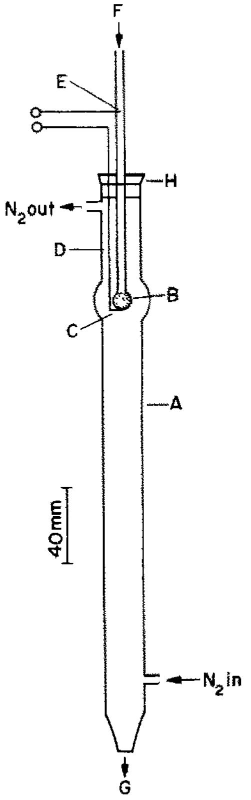

Fig. 2 Sensor. A, Glass tube; B, sintered-glass ball; C, counter-electrode; D, electric lead; E, working electrode; F, iodine–azide solution; G, solution drain; H, rubber stopper.

5 mm long. The electrode outside the ball was placed in contact with the ball as shown in Fig. 2, and the platinum wire (0.5 mm diameter and 100 mm long) was insulated with poly(vinyl chloride). The electrodes were cleaned by electrolysis in 0.2 *M* sodium acetate for 30 min at 0.0 V *vs.* S.C.E. and stored in 7.0 *M* nitric acid. This treatment allowed the electrodes to function continuously for about 200 hr

Reagents

A $10^{-3}M$ stock solution of iodine in 0.1*M* potassium iodide was prepared and standardized by titration with thiosulphate. The sodium azide was checked iodometrically by the method of Feigl *et al.*[27] Solutions were buffered with mixtures of potassium dihydrogen phosphate and sodium hydroxide.

All reagents were analytical-reagent grade and used without further purification.

Procedure

Nitrogen was used as carrier gas, at a constant flow-rate of 350 ml/min. The iodine–azide solution ($3 \times 10^{-5}M$ iodine, 0.02 *M* sodium azide, 0.02 *M* potassium iodide, buffered at pH 7.0) was exuded from the sintered-glass ball at a constant flow-rate of 3.3 ml/min by means of the peristaltic pump. When a recorder gave a steady trace, 100 μl of sample were injected with a gas-syringe. A suitable sensitivity was chosen by trial. The recorder was run at a speed of 10 mm/min. All experiments were carried out at room temperature, 25°.

Calibration was made by injecting 5 ml of hydrogen sulphide into a 2250-ml flask, equipped with a rubber stopper coated with silicone grease, and extracting sample from the flask through the rubber stopper with a 500-μl gas-syringe. The amount of hydrogen sulphide injected was determined iodometrically. When the total volume of sample extracted amounted to 2 ml, a fresh sample was prepared.

RESULTS AND DISCUSSION

The pH and flow-rate of the iodine–azide solution

The iodine–azide solution was buffered at pH 5.0, 6.0, 7.0, and 8.0 and the solutions were exuded from the ball at different flow-rates. Typical potential *vs* time (*E–t*) curves and the results, together with relative standard deviation, are shown in Figs. 3 and 4, respectively. In Fig. 3, the curves rise rapidly and then tail off. The tailing is considerable at the lower flow-rates but, the shapes of the curves do not vary with pH. At the lower flow-rates the base-lines of the curves are very unstable and the curves show several sharp peaks (A, B, E and F in Fig. 3). At higher flow-rates, the base-lines are stable, the curves show a single peak, and the values of the relative standard deviations are more reproducible than those for lower flow-rates. Figure 4 shows that the potential difference is highly dependent on both the pH and the flow-rate of the solution. A slight change of the flow-rate in the range 1.65–4.40 ml/min has a remarkable

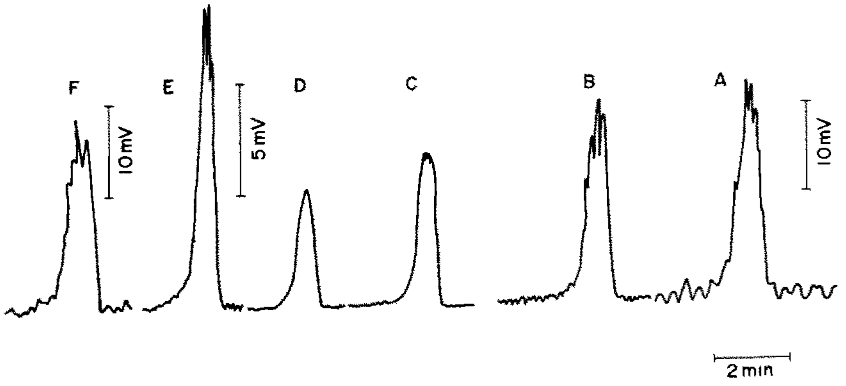

Fig. 3. Potential–time curves. pH and flow-rate of solution, ml/min: A, 7.0, 0.62; B, 7.0, 1.65; C, 7.0, 2.25; D, 7.0, 3.30; E, 8.0, 1.65; F, 6.0, 1.65. Iodine $6.30 \times 10^{-5}M$, sodium azide $1.85 \times 10^{-2}M$, potassium iodide $8.45 \times 10^{-2}M$, gas flow-rate 110 ml/min, hydrogen sulphide 190 ng.

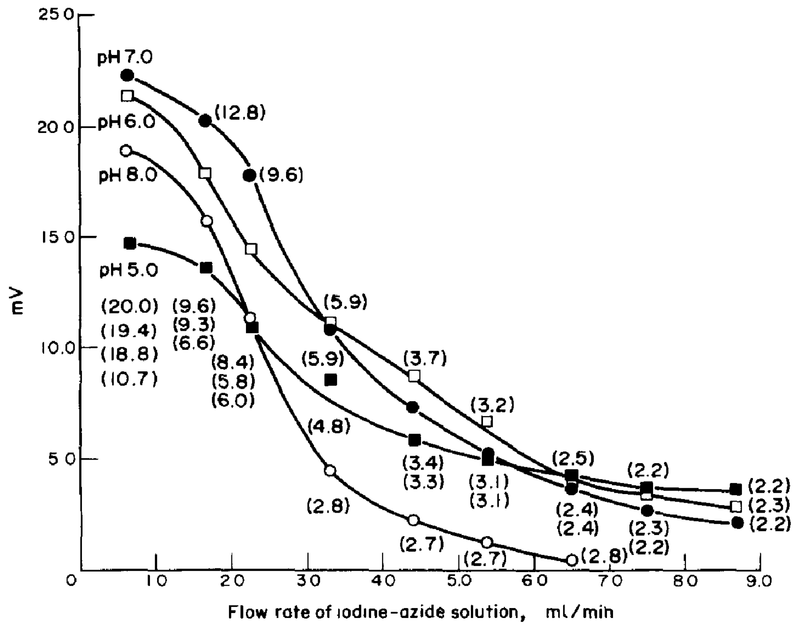

Fig. 4. Relationship between flow-rate of iodine–azide solution and potentials in solutions of different pH. Figures in parentheses represent the relative standard deviations. Each value is the average of 7 runs. Experimental conditions as for Fig. 3.

effect on the potential difference, especially at pH 8.0. When the exudation of the solution from the ball was stopped and four separate samples were successively injected at intervals (Fig. 5), a sloping base-line was obtained because of the evaporation of iodine. The curves show that the catalyst is not fully active until a while after the reaction begins. The maximum potentials were obtained at the third injection for all solutions (Fig. 6). The results (Figs. 4 and 6) show that the best compromise between sensitivity and reproducibility is given by using a pH of 7.0 and a flow-rate of about 3.3 ml/min were chosen.

Concentration of the iodine–azide solution

Measurements made on solutions with varied concentrations of iodine, of sodium azide and potassium iodide are shown in Tables 1–3. Plots of potential *vs.* log iodine or azide concentration were linear, whereas the potential was independent of iodide concentration. The results show that the sensitivity of the reaction towards hydrogen sulphide is determined mainly by the azide:iodine ratio. Babko *et al.*,[21] using a photometric method, reported that the sensitivity of the reaction increased with concentration of potassium iodide over the range 0.1–2.8 *M*, concentrations

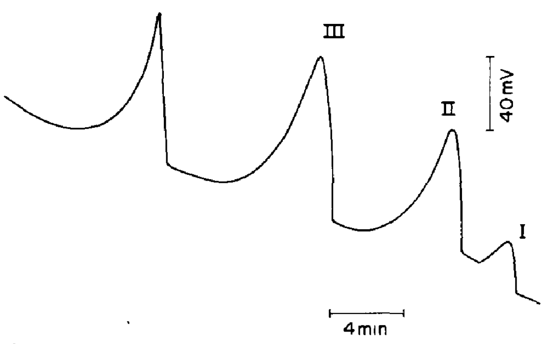

Fig. 5. Potential–time curves when the exudation of solution is stopped. I, First injection; II, second injection; III, third injection, IV, fourth injection; pH 7.0, other experimental conditions as for Fig. 3.

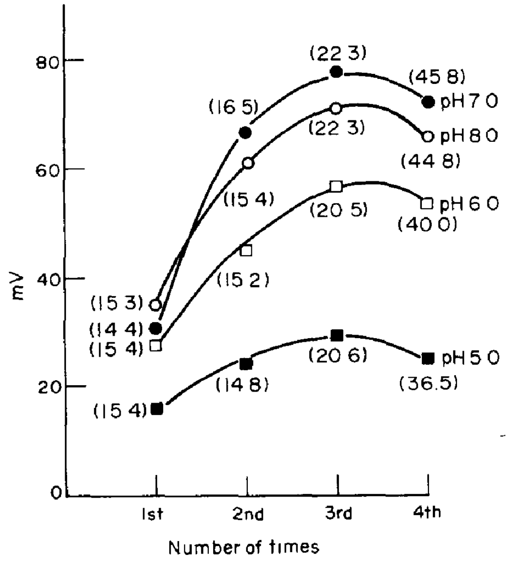

Fig. 6. Relationship between number of injections of sample and potential in solutions of different pH. Figures in parentheses represent the relative standard deviations. Each value is the average of 7 runs. Other experimental conditions as for Fig. 3.

Table 1. Effect of concentration of iodine on the iodine-azide reaction*

	Concentration of iodine, 10^{-5} M						
	9.47	6.77	5.60	4.17	2.71	1.36	0.677
Potential, mV	4.0	8.2	10.8	13.7	18.3	26.0	33.5
	(4.3)	(4.4)	(4.4)	(4.8)	(6.3)	(8.6)	(14.7)

*Each value is the average of 7 runs and figures in parentheses represent the relative standard deviations. Experimental conditions: sodium azide 1.85×10^{-2} M, potassium iodide 5.00×10^{-2} M, solution flow-rate 3.3 ml/min, pH 7.0, gas flow-rate 200 ml/min, hydrogen sulphide 500 ng.

Table 2. Effect of concentration of sodium azide on the iodine-azide reaction*

	Concentration of sodium azide, M			
	3.68×10^{-2}	1.82×10^{-2}	9.55×10^{-3}	3.51×10^{-4}
Potential, mV	27.0	18.8	11.2	1.7
	(10.2)	(6.4)	(5.0)	(4.8)

*Each value is the average of 7 runs and figures in parentheses represent the relative standard deviations. Iodine 3.10×10^{-5} M, other conditions as for Table 1.

Table 3. Effect of concentration of potassium iodide on the iodine-azide reaction*

	Concentration of potassium iodide, M					
	0.150	0.100	0.050	0.010	0.005	0.001
Potential, mV	19.2	19.4	19.4	19.3	19.3	19.4

*Concentration of sodium azide 2.01×10^{-2} M and other experimental conditions as for Table 2.

Table 4. Effect of gas flow rate on the iodine-azide reaction*

	Gas flow rate, ml/min										
	800	600	480	330	250	200	180	130	90	80	75
Potential mV	20.1	19.9	19.5	19.5	19.5	18.9	18.4	17.9	15.2	14.6	14.1
	(21.1)	(10.4)	(5.4)	(3.8)	(3.7)	(6.9)	(7.3)	(11.2)	(18.5)	(20.5)	(20.6)

* Each values is the average of 7 runs and figures in the parentheses represent the relative standard deviation. Experimental conditions are similar to those in Fig. 7.

of the other components being kept constant at 10^{-3} M iodine, 0.011 M sodium azide, and pH 5.2. Such an increase in sensitivity was not observed under the experimental conditions of our study.

The use of lower concentrations of iodine and higher concentrations of azide increases the sensitivity of the reaction, but the base-line drifts when lower iodine concentrations are used, because of the volatility of iodine; reproducible results are also not obtained in the presence of large amounts of sodium azide. Thus, the concentrations of iodine, sodium azide, and potassium iodide were fixed at 3×10^{-5}, 0.02, and 0.02M respectively.

Gas flow-rate

The effect of flow-rate of the carrier gas was examined over the range 75–800 ml/min. Typical *E–t* curves at different gas flow-rates are shown in Fig. 7, and the results are listed in Table 4. In Fig. 7, the shapes of the curves vary with gas flow-rate, with broad jagged peaks at low flow-rates and single sharp peaks at high. The reproducibilities are better at moderate flow-rates. The potentials are approximately constant in the gas flow-rate range 250–480 ml/min, so a flow-rate of 350 ml/min was chosen.

Working electrode and glass tube

Contact between the platinum electrode and the ball was made in three ways: (*i*) *via* the bottom of the ball as shown in Fig. 2, (*ii*) *via* a platinum wire ring 5 mm in diameter at the bottom of the ball, and (*iii*) *via* a platinum wire 100 mm long wound round

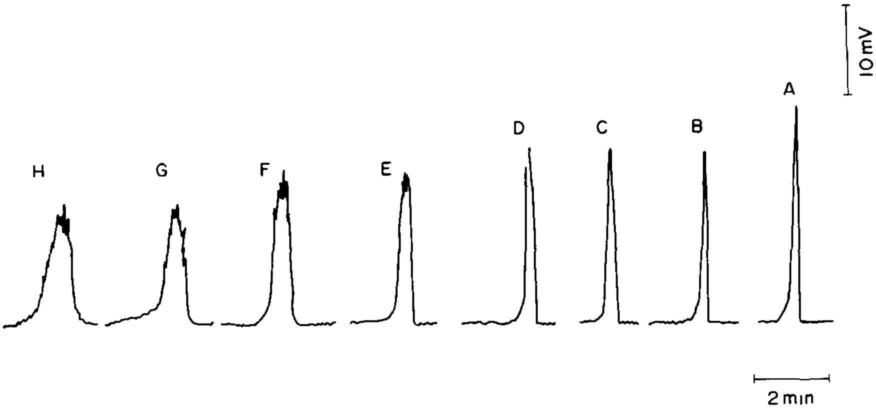

Fig. 7. Potential–time curves at various gas flow-rates. Flow rates, *ml/min*: A, 800; B, 480; C, 330; D, 250; E, 180; F, 130; G, 90; H, 75. Iodine $3.10 \times 10^{-5}M$, sodium azide $2.12 \times 10^{-2}M$, potassium iodide $2.00 \times 10^{-2}M$, solution flow-rate 3.3 ml/min, pH 7.0, hydrogen sulphide 505 ng.

the ball. Method (*i*) gave the most sensitive and reproducible results, the other two giving poor base-lines and variable sensitivities 10–50 times poorer than those obtained by method (*i*).

A change in the linear velocity of the carrier gas in the neighbourhood of the ball made the sensitivity and reproducibility poorer. For example, when a glass tube (20 mm bore) without a bulge was used, the sensitivity was only a third of that for curve C in Fig. 7 and the relative standard deviation was 34% for seven runs, whereas with the glass tube shown in Fig. 2 the deviation was 5.6% under the same conditions. The distance between the gas inlet and the ball also affected the results. A relative standard deviation of 10% or less was obtained with a distance of 20 cm or more.

Interferences

Gaseous reducing substances such as sulphur dioxide and formaldehyde interfered, but the sensitivity towards sulphur dioxide was only about 2%, and that towards formaldehyde only about 0.1% of that towards hydrogen sulphide. The shapes of the E–t curves were symmetric and this could be used to distinguish between other reducing gas (symmetric peaks) and hydrogen sulphide (asymmetric).

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THE STABILITY OF THE CERTIFIED REFERENCE ORES MP-1 KC-1 AND SU-1 TOWARDS AIR OXIDATION

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Summary—The stability of three certified reference sulphide ores, MP-1, KC-1 and SU-1, towards air oxidation has been measured at 50° and 40, 62 and 82% relative humidity, and at 62% relative humidity and 34° and 67°. Both the relative humidity and temperature affect the rate of oxidation but their relative importance depends on the mineralogical composition of the ore. Changes in the water-extractable metals and elemental sulphur content on oxidation have been determined. It is concluded that these ores may be stored safely in sealed bottles under normal laboratory conditions.

The susceptibility of sulphide ores and concentrates to air oxidation is widely known. Indeed, it is this phenomenon that can render the storage and transportation of these materials extremely hazardous.[1,2] It is also an awareness of this tendency to oxidize that has caused several enquiries to be made of the Canadian Certified Reference Materials Program concerning the long-term stability of certified reference sulphide ores during storage in the bottle. Accordingly, an investigation was undertaken to ascertain the extent and, if possible, the nature of chemical change in three sulphide reference ores under various conditions of temperature and relative humidity, chosen so as to give accelerated rates of alteration, in order for long-term effects to be predicted early.

It should be noted that these reference ores are very complex materials, both mineralogically and chemically. Further, they have undergone severe treatment during their preparation (drying, grinding *etc.*). The oxidation of the ores studied herein is a composite of the different rates and mechanisms of oxidation of the individual minerals. Accordingly, explanations proposed for trends in the oxidation behaviour of MP-1, KC-1 and SU-1 often cannot be substantiated by experiment and thus are of a speculative nature based on chemical intuition.

EXPERIMENTAL

The preparation, characterization and certification of the reference ores, MP-1,[3] KC-1[4] and SU-1,[5] has already been described. The predominant sulphide minerals present in these ores are summarized in Table 1

The procedure used to study the chemical alteration of these ores was as follows. Approximately 0.5 g of each ore was weighed in duplicate into tared 50-ml beakers. The beakers were placed in a glass tray and inserted into a Controlled Relative Humidity Chamber (Blue M, Electric Co., Blue Island, Illinois, U.S.A.) in which a preselected temperature and relative humidity, RH, was maintained. Air flowed through the system continuously. At the end of one week, the samples (plus beakers) were removed from the chamber, dried over Drierite for 16–24 hr,* weighed, remixed and inserted into the chamber again. This procedure was followed for 7 weeks at 50° and 40, 62 and 82% RH, and at 62% RH and 34° and 67°. One series of samples run at 50° and 62% RH was stopped after 3 weeks.

At the end of 7 weeks, one sample of each ore was transferred to a 200-ml polyethylene bottle, mixed with 30.00-ml of distilled water and shaken for 2 hr. The resultant suspension was centrifuged at 1800 rpm for 30 min and filtered (dry Whatman No. 42 paper) to ensure the removal of solids. A 20.00-ml portion of the filtrate was mixed with 5.00 ml of 10% nitric acid and the Fe, Pb, Cu, Ni and Zn concentrations were measured with a Techtron AA5 atomic-absorption spectro-photometer. The corresponding water-soluble content of these metals in the untreated ores was also measured as above. Originally, the metals in one sample of each ore that had been oxidized at 50° and 62% RH, and of each of the corresponding unoxidized ores, were extracted with 30.00 ml of 5% sodium acetate solution. The sodium acetate solution extracted appreciably

Table 1. Predominant sulphide minerals

	MP-1	KC-1	SU-1
Sphalerite, ZnS, %	25.1	32.7	—
Chalcopyrite, $CuFeS_2$, %	3.8	—	3.7
Galena, PbS, %	2.2	8.1	—
Pyrite, FeS_2, %	1.3	29.9	—
Arsenopyrite, FeAsS, %	1.7	—	—
Pyrrhotite, $Fe_{12}S_{13}$, %	—	—	29.1
Pentlandite $(Fe,Ni)_9S_8$, pyrite, marcasite*, %	—	—	6.1

* These minerals were indistinguishable in SU-1 by image analysis.

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* This 16–24 hr drying period corresponds to overnight drying. Several simple tests indicated that there was no further change in weight of the sample after 8 hr drying. It must be noted that this drying period was not included in the one-week treatment period.

Table 2. Gain in weight after 7 weeks

		Gain in weight, *mg/g*		
Temp., °C	RH, %	MP-1	KC-1	SU-1
34	62	9.9	12.6	1.5
50	40	3.2	2.2	0.0
50	62	15.7	18.6	4.0
50	82	32.2	58.2	8.4
67	62	21.6	24.7	35.9

Table 3. Rate of gain in weight

		Rate of gain in weight, $mg.g^{-1}.weeks^{-1}$					
	RH,	MP-1		KC-1		SU-1	
T, °C	%	1–3*	3–7*	1–3*	3–7*	1–3*	3–7*
34	62	1.26	0.84	1.59	1.03	0.16	0.14
50	40	0.86	0.32	1.02	0.41	0.0	0.0
50	62	2.17	1.21	3.02	1.67	0.68	0.58
50	82	6.31	2.23	11.7	4.76	1.34	1.05
67	62	3.85	1.96	4.52	2.33	8.65	3.49

* Weeks.

more metal from the treated and untreated ores than did water. However, the difference between the amounts extracted before and after treatment was essentially the same as when water was used. It was decided, therefore, to perform all further extractions with water because the metal concentrations obtained were more amenable to measurement by atomic absorption.

The elemental sulphur content of untreated and treated samples of the reference ores was determined by a method developed in this laboratory.[6]

RESULTS AND DISCUSSION

The values of the gain in weight, Δw, of these reference ores after the 7 weeks treatment are summarized in Table 2. Figure 1, which illustrates the results obtained at 50° and 82% RH is a typical example of Δw as a function of t, the treatment time. The slope of the observed linear functions, $\Delta w/t$, is, of course, the rate of gain in weight. The decrease in $\Delta w/t$ at 3 ± 0.2 weeks was observed in all trials, with the exception of SU-1 at 50° and 40% RH, for which no Δw was detected. The values of $\Delta w/t$ for the time periods of 1–3 and 3–7 weeks are given in Table 3. The cause of the break in $\Delta w/t$ will be discussed below.

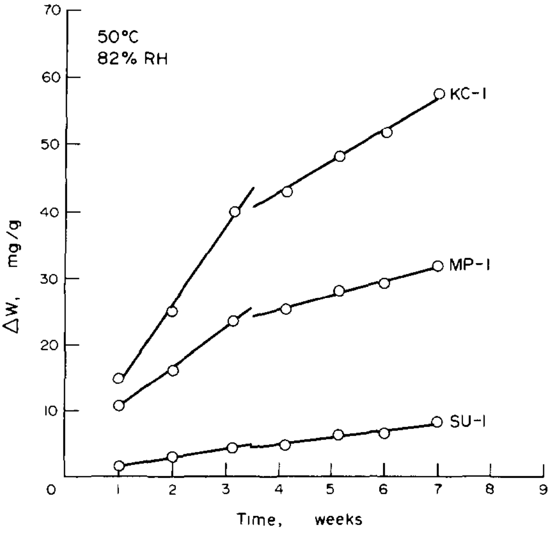

Fig. 1. The gain in weight (as a function of time) due to the treatment of MP-1, KC-1 and SU-1 at 50°C and 82% RH.

The data in Tables 2 and 3 show that RH and temperature are both important parameters in oxidation of the ores. For MP-1 and KC-1, a change in RH from 40 to 82% at 50° results in a larger Δw than does a change in temperature from 34 to 67° at 62% RH, whereas the reverse is observed for SU-1. This difference in behaviour must be a consequence of the mineralogical composition of the ores.

It must be noted that these reference ores, as available in the bottle, cannot really be termed "untreated". They have been subjected to drying, grinding, *etc.*, in their preparation, so oxidation must have occurred to an extent which is unknown but not of interest to the analyst with regard to long-term stability of these ores as reference materials. Because this study was concerned with the stability of the ores as available in the bottle, these ores were labelled as "untreated" and all values of Δw reported refer to them. On this basis, the value of Δw at the beginning of treatment for any RH and temperature should be zero. An examination of Fig. 1, however, illustrates that the linearly extrapolated rate of weight gain does not pass through the origin for MP-1 and KC-1. This behaviour was also observed for all other values of RH and temperature. It must be noted that the rate of a solid–gas reaction where a surface layer of product is formed is often initially quite fast but decreases to become essentially a linear function of time (*i.e.*, diffusion-controlled).[7] In this case, an extrapolation of the linear rate to zero time would not pass through the origin*. This observation for MP-1 and KC-1 suggests that the surface of these ores has not been oxidized completely. That the extrapolation of the linear rate for SU-1 passes through the origin does not necessarily imply that oxidation does not occur quite fast initially, but could simply be a manifestation of a low oxidation rate and the error in the experimental data.

The amounts of water-extractable metals, M_{EXT}, in the untreated reference ores are given in Table 4. MP-1 yields higher values of M_{EXT} although KC-1 has a higher iron, lead and zinc content. Herein such factors as mineralogical composition, particle size distribution and history of the ore play important roles.

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* The author has considerable data to illustrate that the rate of oxidation of sulphides such as pyrite, pyrrhotite, chalcopyrite, galena and sphalerite does indeed behave as described here.

Table 4. Water-extractable metals in untreated ores

	M_{EXT}, *mg/g*			
Ore	Fe	Pb	Zn	Ni
MP-1	0.42 (0.04)*	0.37 (0.09)	8.6 (0.5)	—
KC-1	0.11 (0.06)	0.29 (0.04)	2.4 (0.2)	—
SU-1	0.0	0.0	0.0	0.0

* Numbers in brackets are the standard deviations of 8 determinations.

Because the tendency to oxidize varies with both the nature and particle size of the minerals in an ore, the resultant water-extractability of a metal is not necessarily related to the total metal content of an ore but instead is related to the mineralogical composition and particle size. Table 5 contains the results of a screening test of MP-1, KC-1 and SU-1 and clearly illustrates the vast difference in the particle size distribution in these ores.

The history of the ores, *i.e.*, the conditions of humidity, moisture content and temperature to which they have been subjected during collection, drying, storage and preparation may differ significantly, so the extent of oxidation also differs.

In general, metal sulphides, both natural and synthetic, are sparingly soluble in water; *e.g.*, the solubility of sphalerite and pyrite is 0.07 and 0.49 mg/100 ml at 20°, respectively.[7] The observation of a water-extractability of certain metals greater than that expected according to the solubility of the sulphide mineral(s) must be attributed to the presence of soluble "thio-salts" such as thiosulphate, sulphite and sulphate.[8–11] It is reasonable to assume therefore, that oxidation of a sulphide mineral which results in "thio-salt" formation should increase the water-extractability of certain metals.[12] Lead sulphite (insoluble) and sulphate (4.3 mg/100 ml) are exceptions, with a lower solubility than galena (12.9 mg/100 ml). Galena is, however, less soluble than lead thiosulphate (30 mg/100 ml).[7] The change in the water-extractability of lead on oxidation of galena therefore depends on the products formed.[9,10]

The values of the difference between M_{EXT} for the untreated and treated ores, ΔM_{EXT}, are given in Table 6. The difference was not considered to be significant if it was less than the standard deviation of M_{EXT} in Table 4. The aqueous extracts were also analysed for copper but none was found.

Table 5. Particle size distribution of MP-1, KC-1 and SU-1 (screening test)

	%		
Mesh range (Tyler)	MP-1	KC-1	SU-1
<200	0.4	1.7	34.3
200–325	10.7	62.4	65.7
325–400	8.1	11.8	
>400	80.8	24.1	

Table 6. Difference between extractable metal values of untreated and treated ores

		ΔM_{EXT} *mg/g*			
Ore	*T*, °*C* RH, %	Fe	Pb	Zn	Ni
MP-1 (7 weeks)	34, 62	−0.25	0.0	3.59	—
	50, 40	−0.19	0.0	1.89	—
	50, 62	−0.33	0.0	4.92	—
	50, 82	−0.42	−0.18	18.5	—
	67, 62	−0.39	−0.14	16.3	—
MP-1 (3 weeks)	50, 62	−0.23	0.0	2.54	—
KC-1 (7 weeks)	34, 62	0.0	−0.12	1.76	—
	50, 40	0.0	0.0	1.70	—
	50, 62	0.0	0.06	4.00	—
	50, 82	−0.08	0.13	13.3	—
	67, 62	0.0	0.12	8.86	—
KC-1 (3 weeks)	50, 62	0.0	0.08	1.80	—
SU-1*	67, 62	0.0	0.0	0.0	1.39

* No extractable metals were found for SU-1 at any other RH or *T*.

There is a reasonably good correlation between ΔZn_{EXT} and the corresponding value of Δw for MP-1 and KC-1; this reflects oxidation of sphalerite to "thio-salts". The values of ΔZn_{EXT} illustrate the susceptibility of sphalerite to oxidation and its absence is a probable explanation of the relative stability of SU-1. The apparently greater reactivity of the sphalerite in MP-1 compared to that in KC-1 is due to smaller particle size and consequentially larger surface area. The sphalerite gave the following size distribution, measured with an image analyser:[13]

μm	MP-1, %	KC-1, %
2–6	43	0
6–15	32	41
15–32	25	33
32–60	0	26

Although the size distribution was not measured, the particle size of the other sulphide minerals in MP-1 appeared to be similar. The decrease in ΔFe_{EXT} with an increase in the extent of oxidation of MP-1 and KC-1 suggests that iron hydroxide, oxide or basic iron "thio-salts" are formed rather than the soluble "thio-salts" as is observed for zinc. Indeed, it is known that weathering of pyrite and pyrrhotite results in the formation of limonite and/or haematite.[8,11]

The change in the opposite direction for ΔPb_{EXT} suggests the oxidation of galena to $PbSO_4$ for MP-1 but to PbS_2O_3 for KC-1. Although no conclusive explanation can be given here, the difference in the composition of the ores may be important. Sulphide minerals, when mixed as in ores, can often retard or accelerate the oxidation of one another.[14]

The relationships between log $(\Delta w/t)$ and RH at 50° and between log $(\Delta w/t)$ and temperature at 62% RH are linear with slopes *a* and *b* respectively. This dual linearity of log $(\Delta w/t)$ with temperature (T) and RH permits the formulation of a combined relationship

$$\log (\Delta w/t) = a(\mathrm{RH}) + bT + d$$

where RH is in %, *T* in K and *t* in weeks. A plot of log ($\Delta w/t$) against $a(\text{RH}) + bT$ should have unit slope and intercept d. The values of a, b and d, calculated slope and correlation coefficient of this plot for MP-1, KC-1 and SU-1 are summarized in Table 7. Again, it has been necessary to separate the data into those pertaining to 1–3 weeks and to 3–7 weeks.

The parameters a and b are, in effect, a measure of the sensitivity of the rate of gain in weight and, therefore, the rate of oxidation to changes in RH and temperature, respectively. It is tempting to conclude that the order of the values of a and b for the reference ores signifies that the effect of RH on their oxidation decreases in the order KC-1 > MP-1 > SU-1 whereas the effect of temperature decreases in the order SU-1 > KC-1 $\simeq$ MP-1. This, however, would be incorrect. The rate of oxidation depends not only on RH and temperature but also on the surface area, which is, of course, related to particle size. It is a widely accepted phenomenon that the smaller the particle size, the faster a reaction proceeds. Let us suppose that the rate of oxidation of an ore for a particular set of conditions of RH and T was found to be R_i. If, however, this same ore were comminuted to a different particle size distribution, the observed rate of oxidation would differ from R_t by a factor x, i.e., the rate of oxidation for the latter sample of the ore would be xR_i. It has been assumed that a change in particle size distribution has the same proportional effect on the rate of oxidation irrespective of the values of RH and temperature, in which case a and b will also be changed by the factor x. The dependence of a and b on the particle size distribution is evident and a comparison of a and b for different ores is, therefore, meaningless without a thorough understanding of the effect of particle size distribution on the reactivity of an ore.

The values of a/b should, however, be constant for an ore regardless of the state of comminution, provided that all mineral species present are fully liberated. Thus, differences in the values of a/b for a series of ores may be related to differences in their mineralogical composition because it is improbable that the oxidation of all the minerals that comprise an ore would be affected equally by both RH and temperature. The values of a/b for the 1–3 week period for MP-1, KC-1 and SU-1 are 1.38, 1.84 and 0.28, respectively. The difference in a/b illustrates that the influence of RH and temperature on the rate of oxidation of an ore does indeed vary with its mineralogy. For example, the oxidation of nickel-bearing pyrrhotite and pentlandite in SU-1 exhibits a much greater dependence on temperature relative to RH than does the oxidation of MP-1 and KC-1 in which sphalerite must play the dominant role (Table 5). Moreover, the difference between the a/b values for MP-1 and KC-1 indicates that minerals other than sphalerite are oxidized. The abundance of pyrite and galena in KC-1 relative to MP-1 may be the explanation. If so, the larger value of a/b for KC-1 requires that the oxidation of pyrite and/or galena shows a greater dependence on RH relative to temperature than does that of sphalerite.

It is very difficult to assign significance to the intercept d. It is, of course, a concomitant of the linear relationship between log ($\Delta w/t$) and $[a(\text{RH}) + bT]$ and, as such, will vary with the values of both a and b. The main function of d is to permit the calculation of log ($\Delta w/t$) for any value of RH and T.

Some speculations on mechanisms

A satisfactory explanation for the break in $\Delta w/t$ after about 3 weeks' treatment is difficult because of the complexity of the ores. It is improbable that the decrease in $\Delta w/t$ is due to either the complete oxidation of certain minerals in the ore or the formation of an oxidized surface layer sufficiently thick to cause $\Delta w/t$ to become diffusion-controlled. Each of these hypothetical processes would occur at essentially the same extent of oxidation of the ore regardless of T and RH. The change in $\Delta w/t$, however, always occurred at 3 ± 0.2 weeks even though the extent of oxidation as measured by Δw (Table 2) varied appreciably from trial to trial.

Table 7. Relationship of equation parameters

Ore	Time interval *weeks*	$a(10^{-2})$	$b(10^{-2})$	d
MP-1	1–3	2.04* ± 0.05† slope = 1.00	1.47 ± 0.11	−5.56 r = 0.997
	3–7	2.00 ± 0.10 slope = 1.01	1.14 ± 0.03	−4.80 r = 0.972
KC-1	1–3	2.52 ± 0.14 slope = 0.99	1.37 ± 0.10	−5.45 r = 0.984
	3–7	2.54 ± 0.10 slope = 1.00	1.21 ± 0.03	−5.24 r = 1.000
SU-1	1–3	1.48 ± 0.07 slope = 0.99	5.24 ± 0.09	−17.93 r = 0.986
	3–7	1.38 ± 0.16 slope = 0.99	4.21 ± 0.23	−14.52 r = 0.998

* Average of two samples.
† Corresponding deviation.

A comparison of the water-extractable metals (Table 6) for MP-1 and KC-1 for 3 and 7 weeks at 50° and 62% RH clearly illustrates that sphalerite undergoes oxidation throughout the 7 week period but, unfortunately, the results for Fe and Pb are either inconsistent or (because of the zero values) meaningless. The different mineralogical composition of MP-1, KC-1 and SU-1, however, would preclude the change in $\Delta w/t$ being due to the complete oxidation of certain minerals. The magnitude of this change would require that these minerals be present in appreciable quantities.

Although a change in RH or temperature affects the rate of oxidation of an ore, the overall mechanism remains the same, such that the oxidation reaction gives rise to a constant ratio of the amounts of the products. The absolute amount of the products, however, is dependent on the rate of oxidation and, therefore, on RH and temperature. Once formed by oxidation of the ores, the products are themselves subject to further reaction.

A comparison of the a and b values shows that $\Delta w/t$ for the 3–7 week period is affected to a lesser extent by temperature than is $\Delta w/t$ for the 1–3 week period. This does not necessarily mean that the oxidation becomes less sensitive to temperature after 3 weeks, but could indicate the start of some reaction resulting in a loss in weight so that the observed overall $\Delta w/t$ is lower than expected. The ratios of the $\Delta w/t$ values for the first and last periods of exposure (weeks 1–3 and 4–7) at 34, 50 and 67° and 62% RH show that the decrease in $\Delta w/t$ at 3 weeks increases with increasing temperature for all three ores, *i.e.*, the rate of weight loss increases with temperature.

The formation of elemental sulphur during the mild oxidation or weathering of sulphide minerals is well known.[8] This is also illustrated by the sulphur values for the unoxidized and oxidized ores, in Table 8. The results for 50° clearly show that the formation of sulphur increases with RH. The apparent anomaly of a decrease in the formation of sulphur with an increase in temperature is the result of the interplay of two factors. First, an increase in temperature enhances the rate of oxidation of an ore and, therefore, increases the formation of sulphur. Secondly, however, increase in temperature enhances the oxidation and/or volatilization of the sulphur thus formed.

It is reasonable to assume that the quantity of sulphur formed should vary with the extent of oxidation, *i.e.*, with the gain in weight. The quantity of sulphur formed should, therefore, increase with temperature, which is the opposite of what is found experimentally. The quantity of sulphur lost because of oxidation and/or volatilization must therefore also increase with temperature but to a greater extent, which, of course, parallels the magnitude of the decrease in $\Delta w/t$ at 3 weeks. It must be noted that the decomposition of metal thiosulphates or sulphates to the oxide[11,15] will also cause a loss in weight.

Table 8. Elemental sulphur in ores

	S, *mg/g*		
T, °C, RH, %	MP-1	KC-1	SU-1
Untreated	0.09	1.24	0.02
34, 62	0.37	2.94	0.03
50, 40	0.03	0.09	0.02
50, 62	0.22	1.10	0.02
50, 82	0.55	4.29	0.05
67, 62	0.09	0.06	0.63

The decrease in $\Delta w/t$ at 3 weeks can be explained as follows. By their very nature, sulphur and metal thio-salts are less susceptible to air-oxidation than are sulphides. Because sulphur and metal thio-salts are themselves products of oxidation, it is necessary for the oxidation to have proceeded to an extent at which their quantity is sufficiently large to compensate for their lower oxidation/decomposition rate and result in an observable decrease in $\Delta w/t$. In a system where the oxidation yields sulphur and metal thio-salts regardless of the RH and temperature, the decrease in the rate of gain in weight should be detected at approximately the same time, which is ~3 wk for MP-1, KC-1 and SU-1. The cause of the break in $\Delta w/t$ at 3 weeks can only be determined from a study of the mechanism of oxidation. Such a study, which is now under way, requires use of the pure minerals and the identification and determination of the oxidation products.

Stability of MP-1, KC-1 and SU-1 as reference ores

The stability of MP-1, KC-1 and SU-1 towards oxidation under laboratory conditions is readily calculated by extrapolation* of the data in Table 7. For example, when exposed to the atmosphere at 20° and 40% RH, MP-1 and KC-1 would undergo a 1% change in weight in about 45 weeks. SU-1 is stable. It can, therefore, be concluded that these certified reference ores should undergo no significant alteration at normal laboratory temperature and RH when stored in tightly sealed bottles.

Acknowledgement—The author wishes to thank Mr. R. G. Pinard, Mineral Sciences Laboratories, for his assistance in the mineralogical assessment of these ores.

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* Extrapolation is, in general, a dangerous practice and as such can be expected at best to yield an approximate result. The experimental alternative would, of course, be inordinately lengthy.

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THE STABILITY OF THE CERTIFIED REFERENCE ORES MP-1 KC-1 AND SU-1 TOWARDS AIR OXIDATION

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Summary—The stability of three certified reference sulphide ores, MP-1, KC-1 and SU-1, towards air oxidation has been measured at 50° and 40, 62 and 82% relative humidity, and at 62% relative humidity and 34° and 67°. Both the relative humidity and temperature affect the rate of oxidation but their relative importance depends on the mineralogical composition of the ore. Changes in the water-extractable metals and elemental sulphur content on oxidation have been determined. It is concluded that these ores may be stored safely in sealed bottles under normal laboratory conditions.

The susceptibility of sulphide ores and concentrates to air oxidation is widely known. Indeed, it is this phenomenon that can render the storage and transportation of these materials extremely hazardous.[1,2] It is also an awareness of this tendency to oxidize that has caused several enquiries to be made of the Canadian Certified Reference Materials Program concerning the long-term stability of certified reference sulphide ores during storage in the bottle. Accordingly, an investigation was undertaken to ascertain the extent and, if possible, the nature of chemical change in three sulphide reference ores under various conditions of temperature and relative humidity, chosen so as to give accelerated rates of alteration, in order for long-term effects to be predicted early.

It should be noted that these reference ores are very complex materials, both mineralogically and chemically. Further, they have undergone severe treatment during their preparation (drying, grinding *etc.*). The oxidation of the ores studied herein is a composite of the different rates and mechanisms of oxidation of the individual minerals. Accordingly, explanations proposed for trends in the oxidation behaviour of MP-1, KC-1 and SU-1 often cannot be substantiated by experiment and thus are of a speculative nature based on chemical intuition.

EXPERIMENTAL

The preparation, characterization and certification of the reference ores, MP-1,[3] KC-1[4] and SU-1,[5] has already been described. The predominant sulphide minerals present in these ores are summarized in Table 1

The procedure used to study the chemical alteration of these ores was as follows. Approximately 0.5 g of each ore was weighed in duplicate into tared 50-ml beakers. The beakers were placed in a glass tray and inserted into a Controlled Relative Humidity Chamber (Blue M, Electric Co., Blue Island, Illinois, U.S.A.) in which a preselected temperature and relative humidity, RH, was maintained. Air flowed through the system continuously. At the end of one week, the samples (plus beakers) were removed from the chamber, dried over Drierite for 16–24 hr,* weighed, remixed and inserted into the chamber again. This procedure was followed for 7 weeks at 50° and 40, 62 and 82% RH, and at 62% RH and 34° and 67°. One series of samples run at 50° and 62% RH was stopped after 3 weeks.

At the end of 7 weeks, one sample of each ore was transferred to a 200-ml polyethylene bottle, mixed with 30.00-ml of distilled water and shaken for 2 hr. The resultant suspension was centrifuged at 1800 rpm for 30 min and filtered (dry Whatman No. 42 paper) to ensure the removal of solids. A 20.00-ml portion of the filtrate was mixed with 5.00 ml of 10% nitric acid and the Fe, Pb, Cu, Ni and Zn concentrations were measured with a Techtron AA5 atomic-absorption spectro-photometer. The corresponding water-soluble content of these metals in the untreated ores was also measured as above. Originally, the metals in one sample of each ore that had been oxidized at 50° and 62% RH, and of each of the corresponding unoxidized ores, were extracted with 30.00 ml of 5% sodium acetate solution. The sodium acetate solution extracted appreciably

Table 1. Predominant sulphide minerals

	MP-1	KC-1	SU-1
Sphalerite, ZnS, %	25.1	32.7	—
Chalcopyrite, $CuFeS_2$, %	3.8	—	3.7
Galena, PbS, %	2.2	8.1	—
Pyrite, FeS_2, %	1.3	29.9	—
Arsenopyrite, FeAsS, %	1.7	—	—
Pyrrhotite, $Fe_{12}S_{13}$, %	—	—	29.1
Pentlandite $(Fe,Ni)_9S_8$, pyrite, marcasite*, %	—	—	6.1

* These minerals were indistinguishable in SU-1 by image analysis.

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* This 16–24 hr drying period corresponds to overnight drying. Several simple tests indicated that there was no further change in weight of the sample after 8 hr drying. It must be noted that this drying period was not included in the one-week treatment period.

Table 2. Gain in weight after 7 weeks

		Gain in weight, *mg/g*		
Temp., °C	RH, %	MP-1	KC-1	SU-1
34	62	9.9	12.6	1.5
50	40	3.2	2.2	0.0
50	62	15.7	18.6	4.0
50	82	32.2	58.2	8.4
67	62	21.6	24.7	35.9

more metal from the treated and untreated ores than did water. However, the difference between the amounts extracted before and after treatment was essentially the same as when water was used. It was decided, therefore, to perform all further extractions with water because the metal concentrations obtained were more amenable to measurement by atomic absorption.

The elemental sulphur content of untreated and treated samples of the reference ores was determined by a method developed in this laboratory.[6]

RESULTS AND DISCUSSION

The values of the gain in weight, Δw, of these reference ores after the 7 weeks treatment are summarized in Table 2. Figure 1, which illustrates the results obtained at 50° and 82% RH is a typical example of Δw as a function of t, the treatment time. The slope of the observed linear functions, $\Delta w/t$, is, of course, the rate of gain in weight. The decrease in $\Delta w/t$ at 3 ± 0.2 weeks was observed in all trials, with the exception of SU-1 at 50° and 40% RH, for which no Δw was detected. The values of $\Delta w/t$ for the time periods of 1–3 and 3–7 weeks are given in Table 3. The cause of the break in $\Delta w/t$ will be discussed below.

Table 3. Rate of gain in weight

		Rate of gain in weight, $mg . g^{-1} . weeks^{-1}$					
	RH,	MP-1		KC-1		SU-1	
T, °C	%	1–3*	3–7*	1–3*	3–7*	1–3*	3–7*
34	62	1.26	0.84	1.59	1.03	0.16	0.14
50	40	0.86	0.32	1.02	0.41	0.0	0.0
50	62	2.17	1.21	3.02	1.67	0.68	0.58
50	82	6.31	2.23	11.7	4.76	1.34	1.05
67	62	3.85	1.96	4.52	2.33	8.65	3.49

* Weeks.

The data in Tables 2 and 3 show that RH and temperature are both important parameters in oxidation of the ores. For MP-1 and KC-1, a change in RH from 40 to 82% at 50° results in a larger Δw than does a change in temperature from 34 to 67° at 62% RH, whereas the reverse is observed for SU-1. This difference in behaviour must be a consequence of the mineralogical composition of the ores.

It must be noted that these reference ores, as available in the bottle, cannot really be termed "untreated". They have been subjected to drying, grinding, *etc.*, in their preparation, so oxidation must have occurred to an extent which is unknown but not of interest to the analyst with regard to long-term stability of these ores as reference materials. Because this study was concerned with the stability of the ores as available in the bottle, these ores were labelled as "untreated" and all values of Δw reported refer to them. On this basis, the value of Δw at the beginning of treatment for any RH and temperature should be zero. An examination of Fig. 1, however, illustrates that the linearly extrapolated rate of weight gain does not pass through the origin for MP-1 and KC-1. This behaviour was also observed for all other values of RH and temperature. It must be noted that the rate of a solid–gas reaction where a surface layer of product is formed is often initially quite fast but decreases to become essentially a linear function of time (*i.e.*, diffusion-controlled).[7] In this case, an extrapolation of the linear rate to zero time would not pass through the origin*. This observation for MP-1 and KC-1 suggests that the surface of these ores has not been oxidized completely. That the extrapolation of the linear rate for SU-1 passes through the origin does not necessarily imply that oxidation does not occur quite fast initially, but could simply be a manifestation of a low oxidation rate and the error in the experimental data.

The amounts of water-extractable metals, M_{EXT}, in the untreated reference ores are given in Table 4. MP-1 yields higher values of M_{EXT} although KC-1 has a higher iron, lead and zinc content. Herein such factors as mineralogical composition, particle size distribution and history of the ore play important roles.

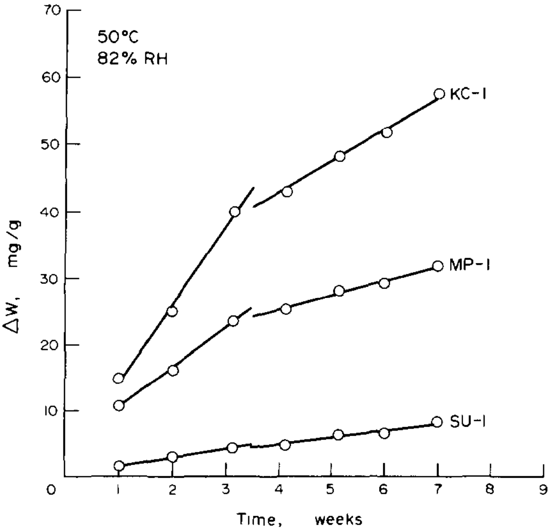

Fig. 1. The gain in weight (as a function of time) due to the treatment of MP-1, KC-1 and SU-1 at 50°C and 82% RH.

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* The author has considerable data to illustrate that the rate of oxidation of sulphides such as pyrite, pyrrhotite, chalcopyrite, galena and sphalerite does indeed behave as described here.

Table 4. Water-extractable metals in untreated ores

	M_{EXT}, *mg/g*			
Ore	Fe	Pb	Zn	Ni
MP-1	0.42 (0.04)*	0.37 (0.09)	8.6 (0.5)	—
KC-1	0.11 (0.06)	0.29 (0.04)	2.4 (0.2)	—
SU-1	0.0	0.0	0.0	0.0

* Numbers in brackets are the standard deviations of 8 determinations.

Because the tendency to oxidize varies with both the nature and particle size of the minerals in an ore, the resultant water-extractability of a metal is not necessarily related to the total metal content of an ore but instead is related to the mineralogical composition and particle size. Table 5 contains the results of a screening test of MP-1, KC-1 and SU-1 and clearly illustrates the vast difference in the particle size distribution in these ores.

The history of the ores, *i.e.*, the conditions of humidity, moisture content and temperature to which they have been subjected during collection, drying, storage and preparation may differ significantly, so the extent of oxidation also differs.

In general, metal sulphides, both natural and synthetic, are sparingly soluble in water; *e.g.*, the solubility of sphalerite and pyrite is 0.07 and 0.49 mg/100 ml at 20°, respectively.[7] The observation of a water-extractability of certain metals greater than that expected according to the solubility of the sulphide mineral(s) must be attributed to the presence of soluble "thio-salts" such as thiosulphate, sulphite and sulphate.[8–11] It is reasonable to assume therefore, that oxidation of a sulphide mineral which results in "thio-salt" formation should increase the water-extractability of certain metals.[12] Lead sulphite (insoluble) and sulphate (4.3 mg/100 ml) are exceptions, with a lower solubility than galena (12.9 mg/100 ml). Galena is, however, less soluble than lead thiosulphate (30 mg/100 ml).[7] The change in the water-extractability of lead on oxidation of galena therefore depends on the products formed.[9,10]

The values of the difference between M_{EXT} for the untreated and treated ores, ΔM_{EXT}, are given in Table 6. The difference was not considered to be significant if it was less than the standard deviation of M_{EXT} in Table 4. The aqueous extracts were also analysed for copper but none was found.

Table 5. Particle size distribution of MP-1, KC-1 and SU-1 (screening test)

	%		
Mesh range (Tyler)	MP-1	KC-1	SU-1
<200	0.4	1.7	34.3
200–325	10.7	62.4	65.7
325–400	8.1	11.8	
>400	80.8	24.1	

Table 6. Difference between extractable metal values of untreated and treated ores

Ore	*T*, °*C* RH, %	ΔM_{EXT} *mg/g* Fe	Pb	Zn	Ni
MP-1 (7 weeks)	34, 62	−0.25	0.0	3.59	—
	50, 40	−0.19	0.0	1.89	—
	50, 62	−0.33	0.0	4.92	—
	50, 82	−0.42	−0.18	18.5	—
	67, 62	−0.39	−0.14	16.3	—
MP-1 (3 weeks)	50, 62	−0.23	0.0	2.54	—
KC-1 (7 weeks)	34, 62	0.0	−0.12	1.76	—
	50, 40	0.0	0.0	1.70	—
	50, 62	0.0	0.06	4.00	—
	50, 82	−0.08	0.13	13.3	—
	67, 62	0.0	0.12	8.86	—
KC-1 (3 weeks)	50, 62	0.0	0.08	1.80	—
SU-1*	67, 62	0.0	0.0	0.0	1.39

* No extractable metals were found for SU-1 at any other RH or *T*.

There is a reasonably good correlation between ΔZn_{EXT} and the corresponding value of Δw for MP-1 and KC-1; this reflects oxidation of sphalerite to "thio-salts". The values of ΔZn_{EXT} illustrate the susceptibility of sphalerite to oxidation and its absence is a probable explanation of the relative stability of SU-1. The apparently greater reactivity of the sphalerite in MP-1 compared to that in KC-1 is due to smaller particle size and consequentially larger surface area. The sphalerite gave the following size distribution, measured with an image analyser:[13]

μm	MP-1, %	KC-1, %
2–6	43	0
6–15	32	41
15–32	25	33
32–60	0	26

Although the size distribution was not measured, the particle size of the other sulphide minerals in MP-1 appeared to be similar. The decrease in ΔFe_{EXT} with an increase in the extent of oxidation of MP-1 and KC-1 suggests that iron hydroxide, oxide or basic iron "thio-salts" are formed rather than the soluble "thio-salts" as is observed for zinc. Indeed, it is known that weathering of pyrite and pyrrhotite results in the formation of limonite and/or haematite.[8,11]

The change in the opposite direction for ΔPb_{EXT} suggests the oxidation of galena to $PbSO_4$ for MP-1 but to PbS_2O_3 for KC-1. Although no conclusive explanation can be given here, the difference in the composition of the ores may be important. Sulphide minerals, when mixed as in ores, can often retard or accelerate the oxidation of one another.[14]

The relationships between log $(\Delta w/t)$ and RH at 50° and between log $(\Delta w/t)$ and temperature at 62% RH are linear with slopes *a* and *b* respectively. This dual linearity of log $(\Delta w/t)$ with temperature (*T*) and RH permits the formulation of a combined relationship

$$\log(\Delta w/t) = a(\text{RH}) + bT + d$$

where RH is in %, *T* in K and *t* in weeks. A plot of log $(\Delta w/t)$ against $a(\mathrm{RH}) + bT$ should have unit slope and intercept d. The values of a, b and d, calculated slope and correlation coefficient of this plot for MP-1, KC-1 and SU-1 are summarized in Table 7. Again, it has been necessary to separate the data into those pertaining to 1–3 weeks and to 3–7 weeks.

The parameters a and b are, in effect, a measure of the sensitivity of the rate of gain in weight and, therefore, the rate of oxidation to changes in RH and temperature, respectively. It is tempting to conclude that the order of the values of a and b for the reference ores signifies that the effect of RH on their oxidation decreases in the order KC-1 > MP-1 > SU-1 whereas the effect of temperature decreases in the order SU-1 > KC-1 $\simeq$ MP-1. This, however, would be incorrect. The rate of oxidation depends not only on RH and temperature but also on the surface area, which is, of course, related to particle size. It is a widely accepted phenomenon that the smaller the particle size, the faster a reaction proceeds. Let us suppose that the rate of oxidation of an ore for a particular set of conditions of RH and T was found to be R_i. If, however, this same ore were comminuted to a different particle size distribution, the observed rate of oxidation would differ from R_t by a factor x, i.e., the rate of oxidation for the latter sample of the ore would be xR_i. It has been assumed that a change in particle size distribution has the same proportional effect on the rate of oxidation irrespective of the values of RH and temperature, in which case a and b will also be changed by the factor x. The dependence of a and b on the particle size distribution is evident and a comparison of a and b for different ores is, therefore, meaningless without a thorough understanding of the effect of particle size distribution on the reactivity of an ore.

The values of a/b should, however, be constant for an ore regardless of the state of comminution, provided that all mineral species present are fully liberated. Thus, differences in the values of a/b for a series of ores may be related to differences in their mineralogical composition because it is improbable that the oxidation of all the minerals that comprise an ore would be affected equally by both RH and temperature. The values of a/b for the 1–3 week period for MP-1, KC-1 and SU-1 are 1.38, 1.84 and 0.28, respectively. The difference in a/b illustrates that the influence of RH and temperature on the rate of oxidation of an ore does indeed vary with its mineralogy. For example, the oxidation of nickel-bearing pyrrhotite and pentlandite in SU-1 exhibits a much greater dependence on temperature relative to RH than does the oxidation of MP-1 and KC-1 in which sphalerite must play the dominant role (Table 5). Moreover, the difference between the a/b values for MP-1 and KC-1 indicates that minerals other than sphalerite are oxidized. The abundance of pyrite and galena in KC-1 relative to MP-1 may be the explanation. If so, the larger value of a/b for KC-1 requires that the oxidation of pyrite and/or galena shows a greater dependence on RH relative to temperature than does that of sphalerite.

It is very difficult to assign significance to the intercept d. It is, of course, a concomitant of the linear relationship between log $(\Delta w/t)$ and $[a(\mathrm{RH}) + bT]$ and, as such, will vary with the values of both a and b. The main function of d is to permit the calculation of log $(\Delta w/t)$ for any value of RH and T.

Some speculations on mechanisms

A satisfactory explanation for the break in $\Delta w/t$ after about 3 weeks' treatment is difficult because of the complexity of the ores. It is improbable that the decrease in $\Delta w/t$ is due to either the complete oxidation of certain minerals in the ore or the formation of an oxidized surface layer sufficiently thick to cause $\Delta w/t$ to become diffusion-controlled. Each of these hypothetical processes would occur at essentially the same extent of oxidation of the ore regardless of T and RH. The change in $\Delta w/t$, however, always occurred at 3 ± 0.2 weeks even though the extent of oxidation as measured by Δw (Table 2) varied appreciably from trial to trial.

Table 7. Relationship of equation parameters

Ore	Time interval *weeks*	$a(10^{-2})$	$b(10^{-2})$	d
MP-1	1–3	2.04* ± 0.05† slope = 1.00	1.47 ± 0.11	−5.56 r = 0.997
	3–7	2.00 ± 0.10 slope = 1.01	1.14 ± 0.03	−4.80 r = 0.972
KC-1	1–3	2.52 ± 0.14 slope = 0.99	1.37 ± 0.10	−5.45 r = 0.984
	3–7	2.54 ± 0.10 slope = 1.00	1.21 ± 0.03	−5.24 r = 1.000
SU-1	1–3	1.48 ± 0.07 slope = 0.99	5.24 ± 0.09	−17.93 r = 0.986
	3–7	1.38 ± 0.16 slope = 0.99	4.21 ± 0.23	−14.52 r = 0.998

* Average of two samples.
† Corresponding deviation.

A comparison of the water-extractable metals (Table 6) for MP-1 and KC-1 for 3 and 7 weeks at 50° and 62% RH clearly illustrates that sphalerite undergoes oxidation throughout the 7 week period but, unfortunately, the results for Fe and Pb are either inconsistent or (because of the zero values) meaningless. The different mineralogical composition of MP-1, KC-1 and SU-1, however, would preclude the change in $\Delta w/t$ being due to the complete oxidation of certain minerals. The magnitude of this change would require that these minerals be present in appreciable quantities.

Although a change in RH or temperature affects the rate of oxidation of an ore, the overall mechanism remains the same, such that the oxidation reaction gives rise to a constant ratio of the amounts of the products. The absolute amount of the products, however, is dependent on the rate of oxidation and, therefore, on RH and temperature. Once formed by oxidation of the ores, the products are themselves subject to further reaction.

A comparison of the a and b values shows that $\Delta w/t$ for the 3–7 week period is affected to a lesser extent by temperature than is $\Delta w/t$ for the 1–3 week period. This does not necessarily mean that the oxidation becomes less sensitive to temperature after 3 weeks, but could indicate the start of some reaction resulting in a loss in weight so that the observed overall $\Delta w/t$ is lower than expected. The ratios of the $\Delta w/t$ values for the first and last periods of exposure (weeks 1–3 and 4–7) at 34, 50 and 67° and 62% RH show that the decrease in $\Delta w/t$ at 3 weeks increases with increasing temperature for all three ores, *i.e.*, the rate of weight loss increases with temperature.

The formation of elemental sulphur during the mild oxidation or weathering of sulphide minerals is well known.[8] This is also illustrated by the sulphur values for the unoxidized and oxidized ores, in Table 8. The results for 50° clearly show that the formation of sulphur increases with RH. The apparent anomaly of a decrease in the formation of sulphur with an increase in temperature is the result of the interplay of two factors. First, an increase in temperature enhances the rate of oxidation of an ore and, therefore, increases the formation of sulphur. Secondly, however, increase in temperature enhances the oxidation and/or volatilization of the sulphur thus formed.

It is reasonable to assume that the quantity of sulphur formed should vary with the extent of oxidation, *i.e.*, with the gain in weight. The quantity of sulphur formed should, therefore, increase with temperature, which is the opposite of what is found experimentally. The quantity of sulphur lost because of oxidation and/or volatilization must therefore also increase with temperature but to a greater extent, which, of course, parallels the magnitude of the decrease in $\Delta w/t$ at 3 weeks. It must be noted that the decomposition of metal thiosulphates or sulphates to the oxide[11,15] will also cause a loss in weight.

Table 8. Elemental sulphur in ores

	S, *mg/g*		
T, °C, RH, %	MP-1	KC-1	SU-1
Untreated	0.09	1.24	0.02
34, 62	0.37	2.94	0.03
50, 40	0.03	0.09	0.02
50, 62	0.22	1.10	0.02
50, 82	0.55	4.29	0.05
67, 62	0.09	0.06	0.63

The decrease in $\Delta w/t$ at 3 weeks can be explained as follows. By their very nature, sulphur and metal thio-salts are less susceptible to air-oxidation than are sulphides. Because sulphur and metal thio-salts are themselves products of oxidation, it is necessary for the oxidation to have proceeded to an extent at which their quantity is sufficiently large to compensate for their lower oxidation/decomposition rate and result in an observable decrease in $\Delta w/t$. In a system where the oxidation yields sulphur and metal thio-salts regardless of the RH and temperature, the decrease in the rate of gain in weight should be detected at approximately the same time, which is ~3 wk for MP-1, KC-1 and SU-1. The cause of the break in $\Delta w/t$ at 3 weeks can only be determined from a study of the mechanism of oxidation. Such a study, which is now under way, requires use of the pure minerals and the identification and determination of the oxidation products.

Stability of MP-1, KC-1 and SU-1 as reference ores

The stability of MP-1, KC-1 and SU-1 towards oxidation under laboratory conditions is readily calculated by extrapolation* of the data in Table 7. For example, when exposed to the atmosphere at 20° and 40% RH, MP-1 and KC-1 would undergo a 1% change in weight in about 45 weeks. SU-1 is stable. It can, therefore, be concluded that these certified reference ores should undergo no significant alteration at normal laboratory temperature and RH when stored in tightly sealed bottles.

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* Extrapolation is, in general, a dangerous practice and as such can be expected at best to yield an approximate result. The experimental alternative would, of course, be inordinately lengthy.

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QUANTITATIVE NMR-SPEKTROSKOPISCHE SIMULTANANALYSE VON MEHRKOMPONENTENGEMISCHEN UNTER EINSATZ EINES RECHNERS IM ON-LINE-BETRIEB

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Zusammenfassung—Die Voraussetzungen und der Algorithmus des on-line-Verfahrens zur quantitativen NMR-Analyse von Mehrkomponentensystemen, deren NMR-Spektren sich vollständig überlagern, werden vorgestellt. Am Beispiel der ^{1}H-NMR-Analyse einer 3-Komponentenmischung von isomeren Heptylsulfochloriden werden die Vor- und Nachteile dieser Methode diskutiert.

Mit der hochauflösenden NMR-Spektroskopie steht dem Chemiker eine zerstörungsfreie Analysenmethode für flüssige und gelöste Stoffe zur Verfügung, die in bestimmten Anwendungsfällen, ähnlich wie z.B. die UV-[1,2] oder IR-[3,4] Spektroskopie zur Konzentrationsbestimmung von Komponenten in Gemischen, deren Spektren sich vollständig überlagern*, eingesetzt werden kann.

Als nachteilig erweist sich bei der hochauflösenden NMR-Spektroskopie die gegenüber anderen Verfahren vergleichsweise geringe Nachweisempfindlichkeit, deren starke Abhängigkeit vom dem zur Analyse ausgewählten Resonanzkern (z.B. ^{1}H, ^{13}C, ^{19}F, ^{31}P) und der damit verbundene relativ hohe Substanzeinsatz†.

Die wesentlichen methodenspezifischen Voraussetzungen‡ zur Durchführung einer zuverlässigen quantitativen Analyse, die heute ein breites Anwendungsgebiet der hochauflösenden NMR-Spektroskopie bildet,[6–11] sind in zahlreichen Veröffentlichungen dargestellt worden. Zusätzlich zu diesen Voraussetzungen müssen für das hier vorgestellte Verfahren der Mehrkomponentenanalyse folgende Bedingungen erfüllt sein.

(1) Die Spektren der k reinen Komponenten müssen bekannt sein.

(2) Es existieren genau k Komponenten in der Mischung, deren Signale sich nur additiv in Abhängigkeit von ihren relativen Konzentrationen überlagern, d.h. nichtadditive Mischungseffekte dürfen nicht auftreten.

(3) Es müssen mindestens k signifikante Unterschiede bezüglich Linienlage bzw. Linienprofil zwischen den Spektren der reinen Komponenten existieren (lineare Unabhängigkeit der Spektren voneinander).

(4) Es müssen mindestens $n = k + 1$ geeignete Samplingpunkte unter reproduzierbaren Bedingungen bezüglich der Stabilität der Geräteparameter (wie Auflösung, Phase, Probentemperatur, Hochfrequenzmagnetfeldstärke, Abtastgeschwindigkeit, Lock usw.) ausgewählt werden können.

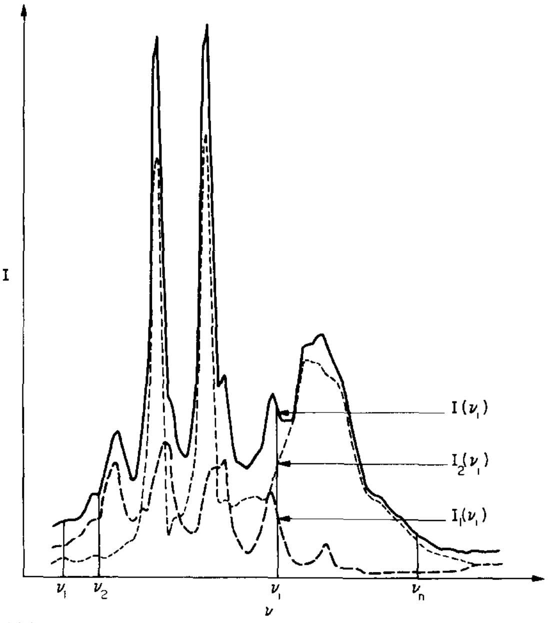

Abb. 1. Prinzip der Datenerfassung im NMR-Spektrum eines 2-Komponentengemisches. —— NMR-Spektrum der Mischung; – – – NMR-Spektrum der Komponente 1; - - NMR-Spektrum der Komponente 2.

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* Damit ist die vom Analytiker angestrebte Selektivität bzw. Spezifität des Analysenverfahrens[5] aufgehoben, die sonst eine möglichst hohe Analysengenauigkeit bei relativ geringem Aufwand erlaubt.

† So beträgt z.B. die Nachweisgrenze für die ^{1}H-NMR (CW-Betrieb bei 100 MHz) *ca.* 10^{18}–10^{17} Protonen. Das entspricht einem Substanzeinsatz von einigen hundert Mikrogramm für eine Substanz mit dem Molekulargewicht 100 und 10 Wasserstoffatomen im Molekül, wobei das Signal eines isolierten Protons im Spektrum nicht aufspalten darf.

‡ Z.B. müssen die Hochfrequenzmagnetfeldstärke und die Spektrenabtastgeschwindigkeit optimiert werden, um den Einfluß von Sättigungs- und Relaxationseffekten, die die Signalintensität verfälschen, möglichst zu vermeiden, bzw. über Eichkurven korrigieren zu können.

Unter diesen Bedingungen folgt für den Intensitätswert $I(v_i)$ im Samplingpunkt v_i des k-Komponentengemisches

$$I(v_i) = \sum_{j=1}^{k} X_j I_j(v_i) \qquad (1)$$

mit

X_j = Regressionskonstante, die der Konzentration der Komponente j direkt proportional ist.
$I_j(v_i)$ = Intensität der j-ten Komponente im Samplingpunkt v_i.
v_i = Chemische Verschiebung in ppm oder Hz bezüglich eines Referenzsignals.

Zur Bestimmung der Konzentrationswerte x_j wird das Verfahren der mehrfachen linearen Regression[12–14] herangezogen. Die Regressionskonstanten X_j ergeben sich aus der Forderung

$$\sum_{i=1}^{n} \sum_{j=1}^{k} [X_j I_j(v_i) - I(v_i)]^2 = [\mathrm{vv}] \rightarrow \mathrm{Min} \qquad (2)$$

bzw. für alle $j = 1, 2, \ldots, k$

$$\frac{\partial[\mathrm{vv}]}{\partial X_j} = 0 \qquad (3)$$

worin [vv] die Summe der Fehlerquadrate bedeutet. Daraus folgt in bekannter Weise ein lineares Gleichungssystem zur Bestimmung der X_j, dessen Lösung sich nach den Methoden der linearen Algebra in Matrizenschreibweise zu

$$\bar{\mathrm{X}} = \bar{\mathrm{B}} \cdot \bar{\mathrm{Y}} \qquad (4)$$

ergibt.

Die Elemente des Lösungsvektors $\bar{\mathrm{X}}$ sind die gesuchten Regressionskonstanten X_j. $\bar{\mathrm{B}}$ ist die inverse Matrix zur sogenannten Kovarianzmatrix, deren Elemente nur aus den Summen von Produkten der Intensitätswerte $I_j(v_i)$ der reinen Komponenten gebildet werden. Deshalb kann man sie als "Eichmatrix" für das zu untersuchende Mischungssystem bezeichnen. $\bar{\mathrm{Y}}$ ist ebenfalls ein Spaltenvektor, wie der Lösungsvektor, dessen Elemente aus Summen von Produkten der Intensitätswerte der Mischung $I(v_i)$ und denen der reinen Komponenten zusammengesetzt sind.

Der Zusammenhang zwischen den gesuchten Molenbruchkonzentrationen x_j der k Mischungskomponenten und den entsprechenden k Regressionskonstanten X_j wird noch durch Einführen von k Korrekturfaktoren F_j modifiziert.

Dann gilt:

$$x_j = \frac{F_j X_j x_k}{X_k} \qquad (5)$$

und wegen

$$\sum_{j=1}^{k} x_j = 1 \qquad (6)$$

wird $F_k = 1$ gesetzt.

Auf diese Weise können mögliche systematische Fehler bei der Konzentrationsbestimmung in Mehrkomponentengemischen eingeschränkt werden. So lassen sich z.B. unterschiedliche Verstärkungs- oder Akkumulationsgrade bei der Aufnahme der reinen Komponenten korrigieren.

Die Nützlichkeit dieser Faktoren sollte sich auch bei der Eichung der durch Relaxationsprozesse und den Kern-Overhauser-Effekt (NOE)[15,16] beeinflußten Signalintensitäten in der ^{13}C-Fourier-Transform-NMR-Spektroskopie mit Protonenrauschentkopplung erweisen.

Unter Einhaltung einer hohen Reproduzierbarkeit der apparativen Einstellungen könnten mit der ^{13}C-NMR ebenfalls derartige quantitative Analysen durchgeführt werden, wie sie sich z.B. für bestimmte Fragestellungen der Polymeren- oder Kohlenwasserstoffanalytik ergeben.

In Abb. 2 ist der Programmablaufplan skizziert. Die mit "Eichen" bezeichnete Programmverzweigung erlaubt die Bestimmung der Korrekturfaktoren F_j mittels vorgegebenen Testgemischen. Größen, wie die Standardabweichungen $m(I)$ der Einzelmessung und $m(X_k)$ der Regressionskonstanten, die Summe der Fehlerquadrate [vv] und das Bestimmtheitsmaß *BM*, dessen Betrag bei fehlerfreier Regression den Wert 1 annimmt und der F(Test)-Wert* nach Fisher dienen zur Beurteilung der Güte der Regression.

Die Mehrkomponentenanalyse nach dem vorgestellten Verfahren wurde für 2- bzw. 3-Komponenten-

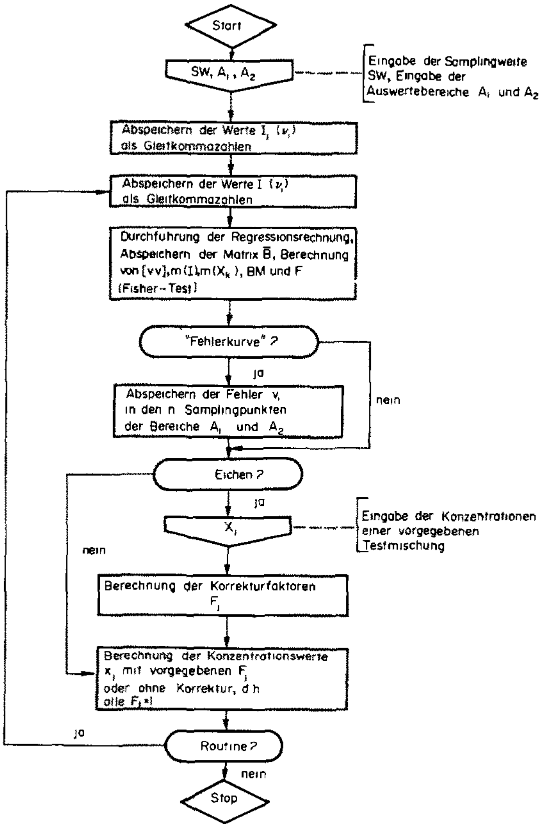

Abb. 2. Programmablaufplan (Skizze).

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* S. 251 ff. im Citat 13.

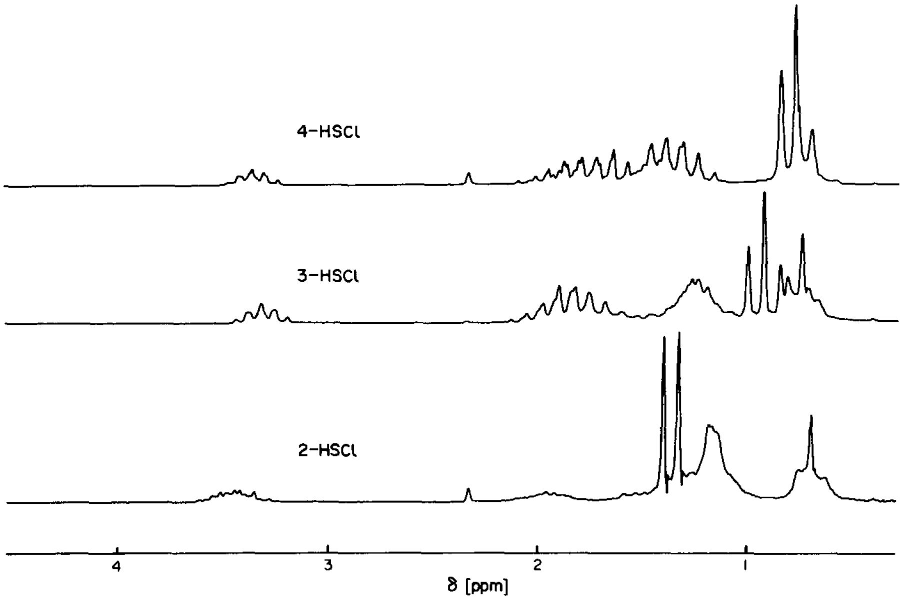

Abb. 3. ^{1}H-NMR-Spektren der reinen Komponenten A, B und C. 2-HSCl: n-Heptylsulfochlorid (2); 3-HSCl: n-Heptylsulfochlorid (3); 4-HSCl: n-Heptylsulfochlorid (4).

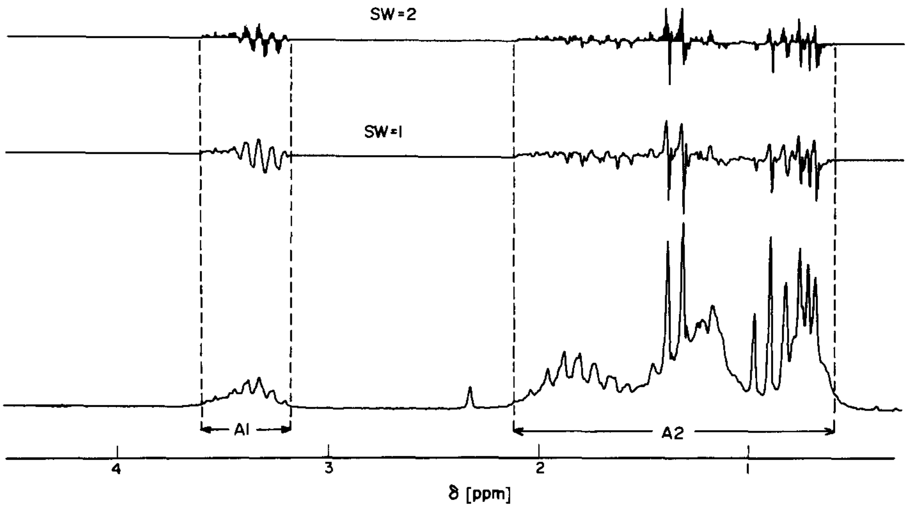

Abb. 4. ^{1}H-NMR-Spektrum der 3-Komponentenmischung I mit den in zwei aktuellen Auswertebereichen (*A*1, *A*2) erhaltenen Fehlerkurven für eine Samplingweite $SW = 1$ ($n = 462$ Samplingpunkte) bzw. $SW = 2$ ($n = 231$).

gemische mit einem hochauflösenden NMR-Spektrometer Typ JNM-PS-100/PFT-100 der Fa. JEOL, Tokio (Japan) mit dem "dedicated" Computersystem NICOLET-1085* der Fa. Nicolet, Madison (USA) erprobt. Der in Abb. 2 skizzierte Programmablauf wurde in der NIC-Assembler-Sprache programmiert, wobei für die 3-Komponentenanalyse *ca.* 2K (1K = 1024) Speicherplätze belegt wurden. Abbildung 3 zeigt die ^{1}H-NMR-Spektren der drei reinen Komponenten.

Die Spektren wurden in jeweils 1K Datenspeicherplätze über den AD-Wandler des Rechners mit 2 Scans (CW-Akkumulation) im Bereich von $\delta = 0{,}292$–$4{,}542$ ppm (entsprechend einem Frequenzbereich von 425 Hz bei einer Protonenresonanzfrequenz von 100 MHz) abgespeichert. Somit betrug die minimal mögliche Samplingweite ($SW = 1$) bei 1024 Datenpunkten 0,415 Hz. Die gewählte Abtastgeschwindigkeit von 540 Hz/250 s bei 10 Hz Filterbreite ergab eine Abtastzeit von *ca.* 3,3 min/Scan.

Aus praktischen Gründen wurden sowohl die reinen Komponenten als auch die zu untersuchenden Gemische derselben in etwa 60% (Vol.) CCl_4, in dem etwas Hexamethyldisiloxan für den internen Probenlock enthalten war, gelöst.

---

* Das NICOLET-1085 Datenerfassungs- und Verarbeitungssystem (Zykluszeit: 2 µs, 20 Bit Wortlänge) ist mit einer für die moderne NMR-Spektroskopie zweckmäßigen Peripherie, wie z. B. AD- und DA-Wandler, Filter, Teletype und Datensichtgerät (Display) ausgestattet.

Tabelle 1. Gegenüberstellung der durch Einwaage vorgegebenen (v) und der mittels des on-line-Verfahrens erhaltenen (e) Analysenergebnisse für drei 3-Komponentensysteme unterschiedlicher Zusammensetzung

Mischung		Zusammensetzung (Molenbrüche) $x(A)$	$x(B)$	$x(C)$
I	v	0,328	0,461	0,211
	e	0,300	0,461	0,237
II	v	0,155	0,614	0,231
	e	0,154	0,602	0,242
III	v	0,074	0,313	0,612
	e	0,101	0,326	0,572

In Tabelle 1 sind die Analysenergebnisse für drei Testgemische isomerer n-Heptylsulfochloride angegeben.

Mit einer Absolutabweichung von maximal ± 0,04 (Molenbruch) sind die Konzentrationsbestimmungen der Mischungskomponenten zufriedenstellend.

Mit Hilfe des auf dem Oszillograph angezeigten Signalpegels im Lock-Kanal des Spektrometers wurde die Auflösung (*ca.* $5 \cdot 10^{-9}$) eingestellt und deren Stabilität während des Meßvorganges überwacht. Der abgetastete Frequenzbereich wurde mit dem im Spektrometer eingebauten Frequenzzähler (auf ± 0,1 Hz genau) ständig kontrolliert. Es wurden sowohl der Signalbereich der Methyl- und Methylengruppen ($A2$) als auch der Bereich der den Substituenten $-SO_2Cl$ tragenen CH-Gruppe ($A1$) zur Auswertung herangezogen, wie aus Abb. 4 hervorgeht. Für eine Samplingweite von $SW = 1$ umfaßt der Bereich $A1$ 101 Kanäle und der Bereich $A2$ 361 Kanäle.

Gleiche Erfahrungen bezüglich der erzielbaren Analysengenauigkeit wurden bei der ^{1}H-NMR-spektroskopischen Untersuchung von Testgemischen (2 bzw. 3 Komponenten) aus Alkanen gemacht. Allerdings konnte wegen Verstoßes gegen die Bedingung 3) des Verfahrens ein Gemisch aus n-Hexan, n-Oktan und n-Undekan nicht analysiert werden.

Die Abbildungen 5 und 6 zeigen die NMR-Spektren der Mischungen II und III und die Teletype-Protokolle der Analyse nebst den in den zwei Auswertebereichen dargestellten Fehlerkurven der für SW = 1 in insgesamt N = 462 Samplingpunkten durchgeführten Regressionsrechnung.*

Bei der Analyse dieser drei Testgemische wurde so verfahren, daß nach Analyse der Mischung I die Programmverzweigung "Routine" bejaht wurde (s. Abb. 2), damit ist für die getroffene Auswahl der Samplingbereiche und der Samplingpunkte die "systemcharakteristische" Matrix $\bar{B}$ fixiert und in allen weiteren Analysenfällen sind nur noch die Spektren der zu analysierenden Gemische dieser Komponenten aufzunehmen. Somit ist im Routinebetrieb eine quantitative Analyse in etwa 5–10 min—vom Einbringen der Probe bis zum Ergebnisausdruck—zu erhalten.

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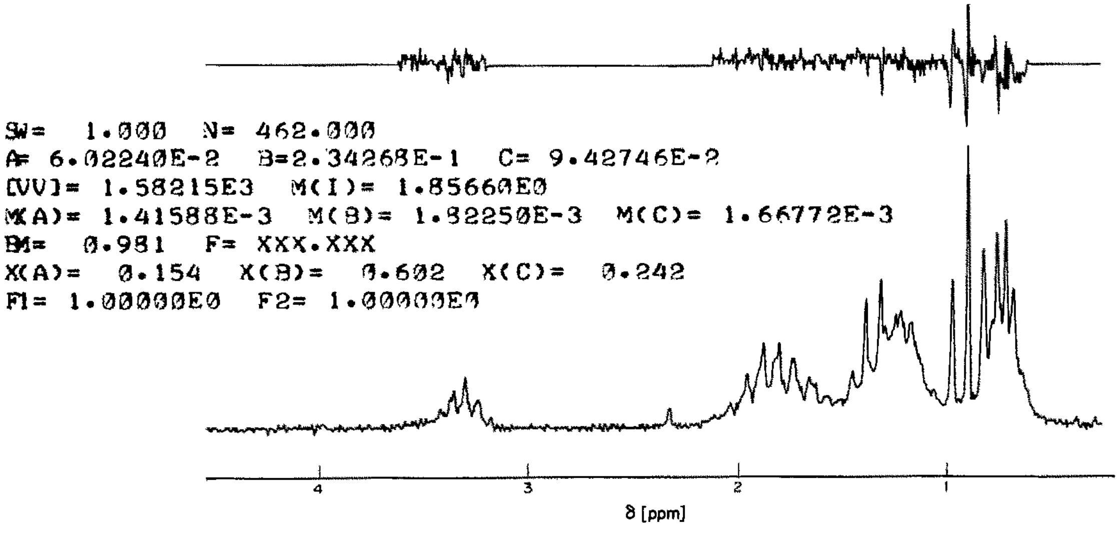
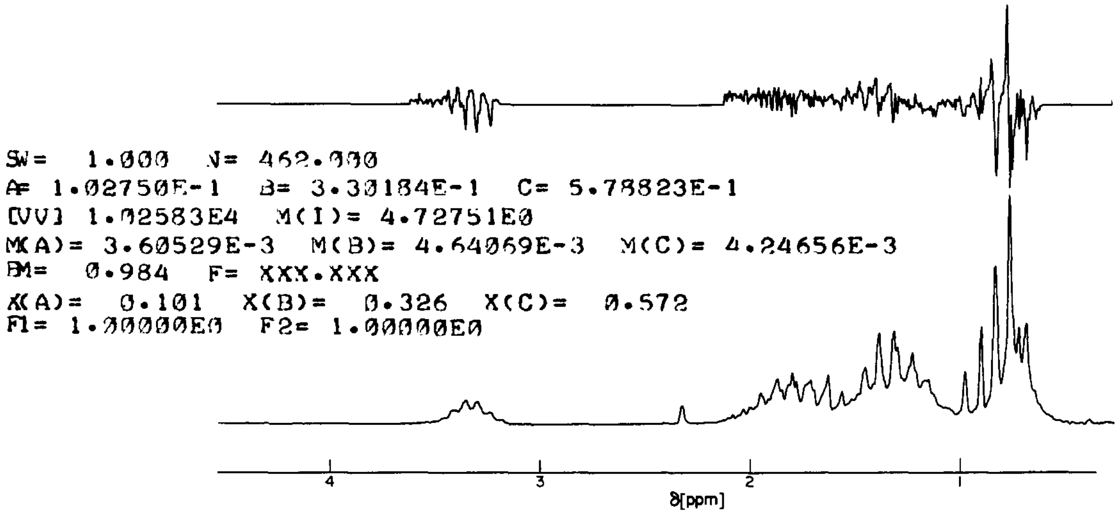
* F = XXX.XXX bedeutet, daß der F(Test)-Wert nach Fisher größer bzw. gleich 1000 ist.



```
SW=  1.000  N= 462.000
A= 6.02240E-2  B=2.34268E-1  C= 9.42746E-2
[VV]= 1.58215E3  M(I)= 1.85660E0
M(A)= 1.41588E-3  M(B)= 1.32250E-3  M(C)= 1.66772E-3
BM=  0.981  F= XXX.XXX
X(A)=  0.154  X(B)=  0.602  X(C)=  0.242
F1= 1.00000E0  F2= 1.00000E0
```

Abb. 5. ^{1}H-NMR-Spektrum der 3-Komponentenmischung II mit der für zwei Auswertebereiche erhaltenen Fehlerkurve (Verstärkungsfaktor: 2) und dem dafür vom Rechner ausgegebenen Analysenprotokoll.



```
SW=   1.000  N= 462.030
A= 1.02750E-1  B= 3.30184E-1  C= 5.78823E-1
[VV] 1.02583E4  M(I)= 4.72751E0
M(A)= 3.60529E-3  M(B)= 4.64069E-3  M(C)= 4.24656E-3
BM=  0.984  F= XXX.XXX
X(A)=  0.101  X(B)=  0.326  X(C)=  0.572
F1= 1.00000E0  F2= 1.00000E0
```

Abb. 6. ^{1}H-NMR-Spektrum der 3-Komponentenmischung III nebst Fehlerkurve (Verstärkungsfaktor: 4) und Analysenprotokoll.

Die wesentlichen Vorteile des on-line-Verfahrens kann man in folgenden Punkten erkennen:

—die zeitaufwendige und fehleranfällige manuelle Datenerfassung entfällt;

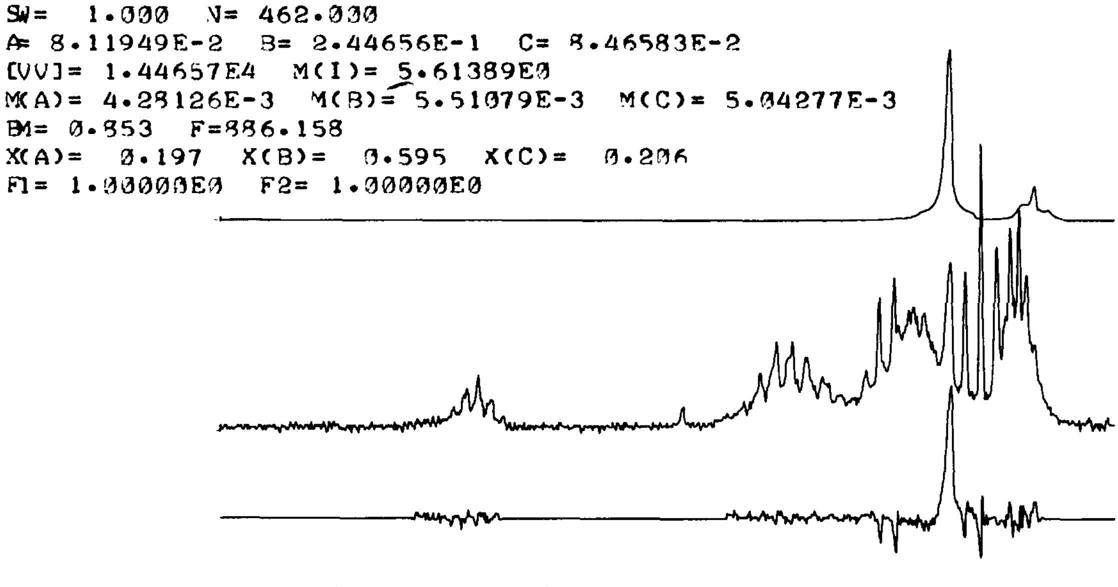
—durch die Möglichkeit der Spektrenakkumulation ist eine Erhöhung der Nachweisempfindlichkeit bzw. eine Herabsetzung des statistischen Fehlers bei der Analyse zu erreichen;

—Nachteile der off-line-Verarbeitung, wie z.B. Datenträgertransporte oder Wartezeiten, entfallen;

—es können die Samplingweiten und die Auswertebereiche beliebig variiert werden und damit das Analysenverfahren optimiert werden. Durch Zugabe einer Referenzsubstanz zu allen reinen Komponenten und deren Gemischen, deren Signal ebenfalls erfaßt wird, lassen sich Drift- oder Lösungsmitteleinflüsse korrigieren.

—der Datenspeicherinhalt des Computers kann jederzeit auf dem Display visuell kontrolliert werden, so daß z.B. systematische Fehler oder das Vorliegen von Verunreinigungen in der Fehlerkurve der Analyse des *k*-Komponentengemisches erkannt werden können.

In Abb. 7 (Oben) ist das ^{1}H-NMR-Spektrum des n-Undekans dargestellt, dessen Signale ebenfalls im



```
SW=   1.000  N= 462.030
A= 8.11949E-2  B= 2.44656E-1  C= 8.46583E-2
[VV]= 1.44657E4  M(I)= 5.61389E0
M(A)= 4.28126E-3  M(B)= 5.51079E-3  M(C)= 5.04277E-3
BM= 0.853  F=886.158
X(A)=  0.197  X(B)=  0.595  X(C)=  0.206
F1= 1.00000E0  F2= 1.00000E0
```

Abb 7. Oben: ^{1}H-NMR-Spektrum des n-Undekans. Mitte: ^{1}H-NMR-Spektrum der mit n-Undekan verunreinigten Mischung II; Unten: Fehlerkurve dieser in zwei Auswertebereichen analysierten Mischung mit den durch die Störkomponente verursachten systematischen Abweichungen; Oben links: Analysenprotokoll der mit n-Undekan verunreinigten Mischung II.

aktuellen Auswertebereich $A2$ der isomeren Heptylsulfochloride liegen. Durch Spektrenaddition mittels des Rechners wurde die Mischung II mit n-Undekan als Störkomponente "verunreinigt", wie aus Abb. 7 (Mitte) hervorgeht. Die Fehlerkurve dieses analysierten Systems zeigt deutlich die durch die Störkomponente im Bereich der Methylengruppen des n-Undekans hervorgerufene systematische Abweichung [Abb. 7 (Unten)]. Aus diesem Beispiel geht hervor, daß aus der Fehlerkurve nur bei einer sehr hohen Störkomponentenkonzentration ein identifizierbares Spektrum der verursachenden Substanz zu erhalten sein wird.

Verunreinigungen verschlechtern sofort das Analysenergebnis, da diese aufgrund der Voraussetzungen nicht erkannt und auf die k Komponenten "aufgeteilt" werden, wie z.B. das Analysenprotokoll in Abb. 7 für die "verunreinigte" Mischung II zeigt.

Äußerst empfindlich reagiert das Verfahren auf systematische Fehler, wo die Voraussetzung der strengen additiven Überlagerung der Spektren verletzt wird. Derartige Fehler liegen bei Abweichungen von der Phase des reinen Absorptionssignals vor oder bei geringfügigen Änderungen der chemischen Verschiebung (Größenordnung von einigen 10^{-3} ppm) infolge von Drift- oder Lösungsmitteleffekten.

Der erforderliche Speicherplatzbedarf steigt mit der Zahl der zu analysierenden Komponenten schnell an. So werden in der Regel pro reine Komponente und das Gemisch derselben 1K Speicherplätze reserviert und für $n \geqslant k + 1$ Samplingpunkte werden $2n(k + 1)$ weitere Speicherplätze belegt, da die Werte $I_j(v_i)$ und $I(v_i)$ als Gleitkommazahlen abgespeichert werden und somit jeweils zwei Speicherplätze beanspruchen. Für die Darstellung der Fehlerkurve werden ebenfalls 1K Speicherplätze reserviert. Zusammen mit dem eigentlichen Programm werden somit für $n = 500$ Samplingpunkte im Fall einer 3-Komponentenanalyse etwa 11K Speicherplätze benötigt. Nach der Festlegung der Matrix $\bar{\text{B}}$ (Routinebetrieb) werden noch 8K Speicherplätze benötigt.

Dagegen fallen Rechenzeiten kaum ins Gewicht, da z.B. nach der Datenerfassung für das vorgestellte Beispiel der 3-Komponentenanalyse mit 462 Samplingpunkten für die Regressionsrechnung nur *ca.* 15 s erforderlich waren und die restliche Zeit des Ergebnisausdruckes durch die Druckgeschwindigkeit des benutzten Teletype bedingt war.

Eine Verbesserung des Verfahrens sollte noch unter Einbeziehung von Gewichtsfaktoren möglich sein,[17,18] während Bemühungen zur Optimierung der Zahl der Samplingpunkte[19] aufgrund der hohen Rechengeschwindigkeit nicht so wesentlich erscheinen.

Eine weitere Anwendungsmöglichkeit ist dadurch gegeben, daß es z.B. möglich ist, die Konzentration einer Komponente in einem k-Komponentengemisch relativ gegenüber allen anderen zu bestimmen, d.h. durch Zusammenfassen der restlichen $(k - 1)$ zu einer "Komponente". Damit ist dieser Spezialfall auf die Analyse einer 2-Komponentenmischung zurückgeführt.

Die Grenzen der hier beschriebenen Methode dürften im Rahmen einer vertretbaren Analysengenauigkeit (Molenbruch ± 0,07) und Eindeutigkeit für die Analyse eines Systems mit 5–8 Komponenten erreicht sein. Die Nützlichkeit des relativ aufwendigen Verfahrens kommt erst bei einer hohen Wiederholrate der Analysen (Routinebetrieb)—wie sie z.B. bei der Produktkontrolle in der chemischen oder pharmazeutischen Industrie erforderlich sein kann—voll zur Geltung.

Die Substanzen wurden von Herrn Dr. Ch. Duschek von der Sektion Verfahrenschemie der TH Leuna-Merseburg zur Verfügung gestellt, wofür auch an dieser Stelle nochmals gedankt werden soll.

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QUANTITATIVE NMR-SPEKTROSKOPISCHE SIMULTANANALYSE VON MEHRKOMPONENTENGEMISCHEN UNTER EINSATZ EINES RECHNERS IM ON-LINE-BETRIEB

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(*Eingegangen am* 9. *Juni* 1975. *Angenommen am* 15. *Dezember* 1975)

Zusammenfassung—Die Voraussetzungen und der Algorithmus des on-line-Verfahrens zur quantitativen NMR-Analyse von Mehrkomponentensystemen, deren NMR-Spektren sich vollständig überlagern, werden vorgestellt. Am Beispiel der ^{1}H-NMR-Analyse einer 3-Komponentenmischung von isomeren Heptylsulfochloriden werden die Vor- und Nachteile dieser Methode diskutiert.

Mit der hochauflösenden NMR-Spektroskopie steht dem Chemiker eine zerstörungsfreie Analysenmethode für flüssige und gelöste Stoffe zur Verfügung, die in bestimmten Anwendungsfällen, ähnlich wie z.B. die UV-[1,2] oder IR-[3,4] Spektroskopie zur Konzentrationsbestimmung von Komponenten in Gemischen, deren Spektren sich vollständig überlagern*, eingesetzt werden kann.

Als nachteilig erweist sich bei der hochauflösenden NMR-Spektroskopie die gegenüber anderen Verfahren vergleichsweise geringe Nachweisempfindlichkeit, deren starke Abhängigkeit vom dem zur Analyse ausgewählten Resonanzkern (z.B. ^{1}H, ^{13}C, ^{19}F, ^{31}P) und der damit verbundene relativ hohe Substanzeinsatz†.

Die wesentlichen methodenspezifischen Voraussetzungen‡ zur Durchführung einer zuverlässigen quantitativen Analyse, die heute ein breites Anwendungsgebiet der hochauflösenden NMR-Spektroskopie bildet,[6-11] sind in zahlreichen Veröffentlichungen dargestellt worden. Zusätzlich zu diesen Voraussetzungen müssen für das hier vorgestellte Verfahren der Mehrkomponentenanalyse folgende Bedingungen erfüllt sein.

(1) Die Spektren der k reinen Komponenten müssen bekannt sein.

(2) Es existieren genau k Komponenten in der Mischung, deren Signale sich nur additiv in Abhängigkeit von ihren relativen Konzentrationen überlagern, d.h. nichtadditive Mischungseffekte dürfen nicht auftreten.

(3) Es müssen mindestens k signifikante Unterschiede bezüglich Linienlage bzw. Linienprofil zwischen den Spektren der reinen Komponenten existieren (lineare Unabhängigkeit der Spektren voneinander).

(4) Es müssen mindestens $n = k + 1$ geeignete Samplingpunkte unter reproduzierbaren Bedingungen bezüglich der Stabilität der Geräteparameter (wie Auflösung, Phase, Probentemperatur, Hochfrequenzmagnetfeldstärke, Abtastgeschwindigkeit, Lock usw.) ausgewählt werden können.

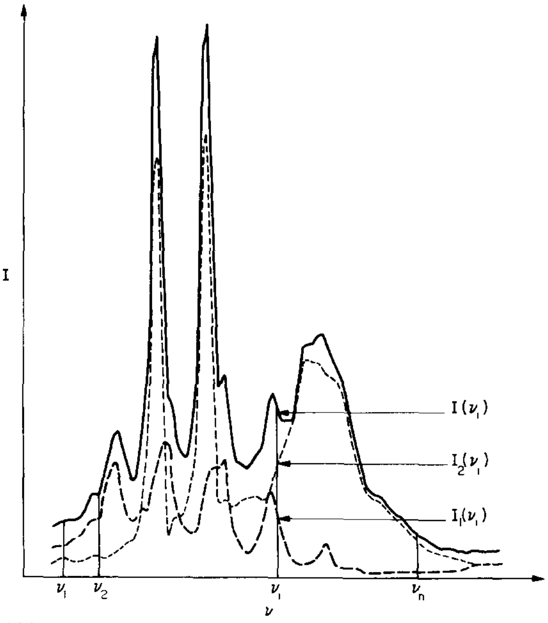

Abb. 1. Prinzip der Datenerfassung im NMR-Spektrum eines 2-Komponentengemisches. —— NMR-Spektrum der Mischung; – – – NMR-Spektrum der Komponente 1; -- NMR-Spektrum der Komponente 2.

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* Damit ist die vom Analytiker angestrebte Selektivität bzw. Spezifität des Analysenverfahrens[5] aufgehoben, die sonst eine möglichst hohe Analysengenauigkeit bei relativ geringem Aufwand erlaubt.

† So beträgt z.B. die Nachweisgrenze für die ^{1}H-NMR (CW-Betrieb bei 100 MHz) *ca.* 10^{18}–10^{17} Protonen. Das entspricht einem Substanzeinsatz von einigen hundert Mikrogramm für eine Substanz mit dem Molekulargewicht 100 und 10 Wasserstoffatomen im Molekül, wobei das Signal eines isolierten Protons im Spektrum nicht aufspalten darf.

‡ Z.B. müssen die Hochfrequenzmagnetfeldstärke und die Spektrenabtastgeschwindigkeit optimiert werden, um den Einfluß von Sättigungs- und Relaxationseffekten, die die Signalintensität verfälschen, möglichst zu vermeiden, bzw. über Eichkurven korrigieren zu können.

Unter diesen Bedingungen folgt für den Intensitätswert $I(v_i)$ im Samplingpunkt v_i des k-Komponentengemisches

$$I(v_i) = \sum_{j=1}^{k} X_j I_j(v_i) \tag{1}$$

mit

X_j = Regressionskonstante, die der Konzentration der Komponente j direkt proportional ist.

$I_j(v_i)$ = Intensität der j-ten Komponente im Samplingpunkt v_i.

v_i = Chemische Verschiebung in ppm oder Hz bezüglich eines Referenzsignals.

Zur Bestimmung der Konzentrationswerte x_j wird das Verfahren der mehrfachen linearen Regression[12–14] herangezogen. Die Regressionskonstanten X_j ergeben sich aus der Forderung

$$\sum_{i=1}^{n} \sum_{j=1}^{k} [X_j I_j(v_i) - I(v_i)]^2 = [\mathrm{vv}] \rightarrow \mathrm{Min} \tag{2}$$

bzw. für alle $j = 1, 2, \ldots, k$

$$\frac{\partial[\mathrm{vv}]}{\partial X_j} = 0 \tag{3}$$

worin [vv] die Summe der Fehlerquadrate bedeutet. Daraus folgt in bekannter Weise ein lineares Gleichungssystem zur Bestimmung der X_j, dessen Lösung sich nach den Methoden der linearen Algebra in Matrizenschreibweise zu

$$\bar{\mathrm{X}} = \bar{\mathrm{B}} \cdot \bar{\mathrm{Y}} \tag{4}$$

ergibt.

Die Elemente des Lösungsvektors $\bar{\mathrm{X}}$ sind die gesuchten Regressionskonstanten X_j. $\bar{\mathrm{B}}$ ist die inverse Matrix zur sogenannten Kovarianzmatrix, deren Elemente nur aus den Summen von Produkten der Intensitätswerte $I_j(v_i)$ der reinen Komponenten gebildet werden. Deshalb kann man sie als "Eichmatrix" für das zu untersuchende Mischungssystem bezeichnen.

$\bar{\mathrm{Y}}$ ist ebenfalls ein Spaltenvektor, wie der Lösungsvektor, dessen Elemente aus Summen von Produkten der Intensitätswerte der Mischung $I(v_i)$ und denen der reinen Komponenten zusammengesetzt sind.

Der Zusammenhang zwischen den gesuchten Molenbruchkonzentrationen x_j der k Mischungskomponenten und den entsprechenden k Regressionskonstanten X_j wird noch durch Einführen von k Korrekturfaktoren F_j modifiziert.

Dann gilt:

$$x_j = \frac{F_j X_j x_k}{X_k} \tag{5}$$

und wegen

$$\sum_{j=1}^{k} x_j = 1 \tag{6}$$

wird $F_k = 1$ gesetzt.

Auf diese Weise können mögliche systematische Fehler bei der Konzentrationsbestimmung in Mehrkomponentengemischen eingeschränkt werden. So lassen sich z.B. unterschiedliche Verstärkungs- oder Akkumulationsgrade bei der Aufnahme der reinen Komponenten korrigieren.

Die Nützlichkeit dieser Faktoren sollte sich auch bei der Eichung der durch Relaxationsprozesse und den Kern-Overhauser-Effekt (NOE)[15,16] beeinflußten Signalintensitäten in der ^{13}C-Fourier-Transform-NMR-Spektroskopie mit Protonenrauschentkopplung erweisen.

Unter Einhaltung einer hohen Reproduzierbarkeit der apparativen Einstellungen könnten mit der ^{13}C-NMR ebenfalls derartige quantitative Analysen durchgeführt werden, wie sie sich z.B. für bestimmte Fragestellungen der Polymeren- oder Kohlenwasserstoffanalytik ergeben.

In Abb. 2 ist der Programmablaufplan skizziert. Die mit "Eichen" bezeichnete Programmverzweigung erlaubt die Bestimmung der Korrekturfaktoren F_j mittels vorgegebenen Testgemischen. Größen, wie die Standardabweichungen $m(I)$ der Einzelmessung und $m(X_k)$ der Regressionskonstanten, die Summe der Fehlerquadrate [vv] und das Bestimmtheitsmaß BM, dessen Betrag bei fehlerfreier Regression den Wert 1 annimmt und der F(Test)-Wert* nach Fisher dienen zur Beurteilung der Güte der Regression.

Die Mehrkomponentenanalyse nach dem vorgestellten Verfahren wurde für 2- bzw. 3-Komponenten-

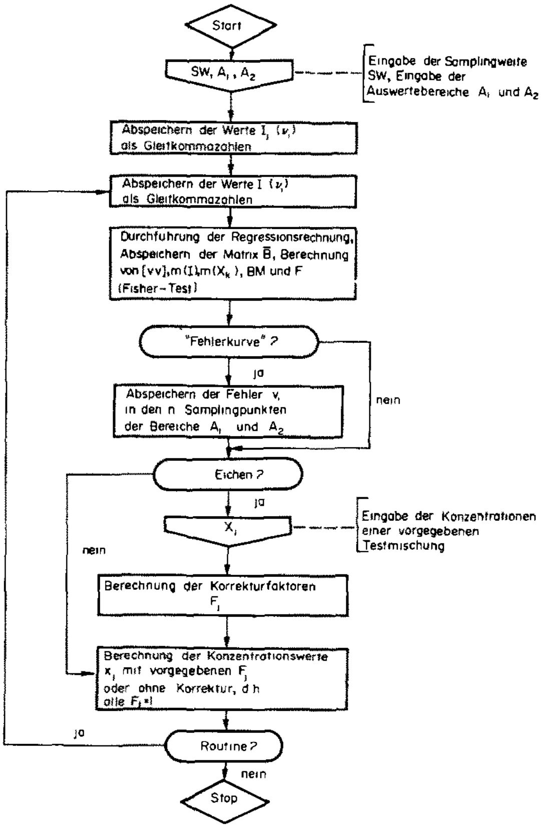

Abb. 2. Programmablaufplan (Skizze).

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* S: 251 ff. im Citat 13.

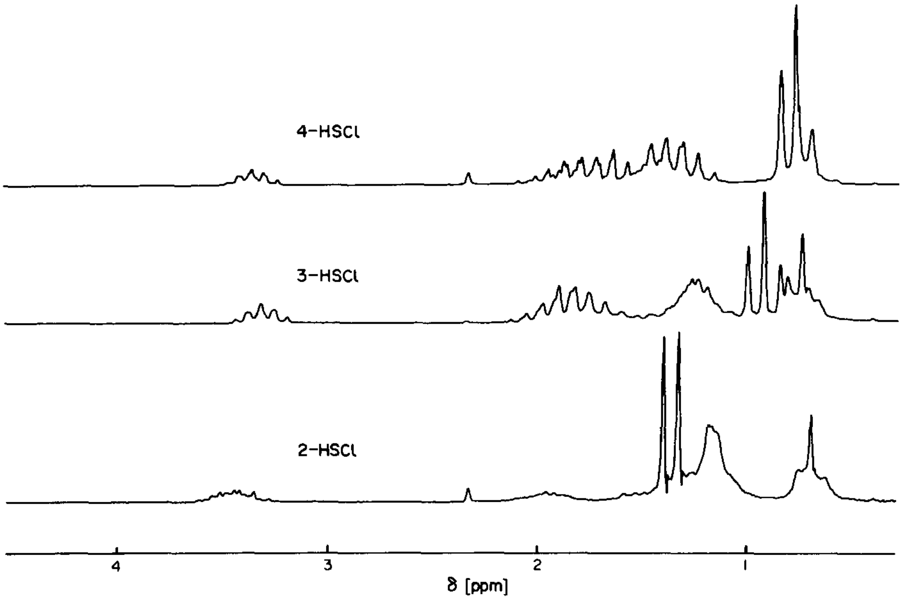

Abb. 3. ¹H-NMR-Spektren der reinen Komponenten A, B und C. 2-HSCl: n-Heptylsulfochlorid (2); 3-HSCl: n-Heptylsulfochlorid (3); 4-HSCl: n-Heptylsulfochlorid (4).

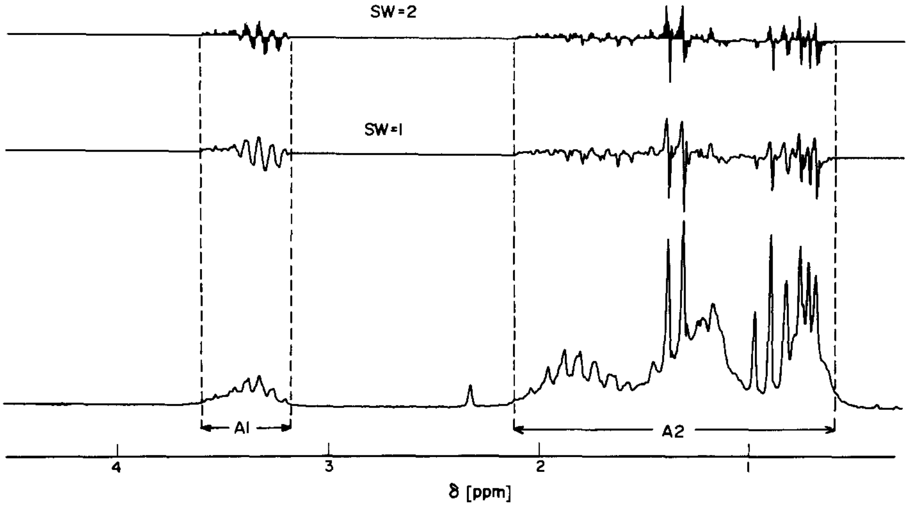

Abb. 4. ¹H-NMR-Spektrum der 3-Komponentenmischung I mit den in zwei aktuellen Auswertebereichen (*A*1, *A*2) erhaltenen Fehlerkurven für eine Samplingweite *SW* = 1 (*n* = 462 Samplingpunkte) bzw. *SW* = 2 (*n* = 231).

gemische mit einem hochauflösenden NMR-Spektrometer Typ JNM-PS-100/PFT-100 der Fa. JEOL, Tokio (Japan) mit dem "dedicated" Computersystem NICOLET-1085* der Fa. Nicolet, Madison (USA) erprobt. Der in Abb. 2 skizzierte Programmablauf wurde in der NIC-Assembler-Sprache programmiert, wobei für die 3-Komponentenanalyse *ca.* 2K (1K = 1024) Speicherplätze belegt wurden. Abbildung 3 zeigt die ¹H-NMR-Spektren der drei reinen Komponenten.

Die Spektren wurden in jeweils 1K Datenspeicherplätze über den AD-Wandler des Rechners mit 2 Scans (CW-Akkumulation) im Bereich von δ = 0,292–4,542 ppm (entsprechend einem Frequenzbereich von 425 Hz bei einer Protonenresonanzfrequenz von 100 MHz) abgespeichert. Somit betrug die minimal mögliche Samplingweite (*SW* = 1) bei 1024 Datenpunkten 0,415 Hz. Die gewählte Abtastgeschwindigkeit von 540 Hz/250 s bei 10 Hz Filterbreite ergab eine Abtastzeit von *ca.* 3,3 min/Scan.

Aus praktischen Gründen wurden sowohl die reinen Komponenten als auch die zu untersuchenden Gemische derselben in etwa 60% (Vol.) CCl_4, in dem etwas Hexamethyldisiloxan für den internen Probenlock enthalten war, gelöst.

---

* Das NICOLET-1085 Datenerfassungs- und Verarbeitungssystem (Zykluszeit: 2 μs, 20 Bit Wortlänge) ist mit einer für die moderne NMR-Spektroskopie zweckmäßigen Peripherie, wie z. B. AD- und DA-Wandler, Filter, Teletype und Datensichtgerät (Display) ausgestattet.

Tabelle 1. Gegenüberstellung der durch Einwaage vorgegebenen (v) und der mittels des on-line-Verfahrens erhaltenen (e) Analysenergebnisse für drei 3-Komponentensysteme unterschiedlicher Zusammensetzung

Mischung		Zusammensetzung (Molenbrüche) x(A)	x(B)	x(C)
I	v	0,328	0,461	0,211
	e	0,300	0,461	0,237
II	v	0,155	0,614	0,231
	e	0,154	0,602	0,242
III	v	0,074	0,313	0,612
	e	0,101	0,326	0,572

In Tabelle 1 sind die Analysenergebnisse für drei Testgemische isomerer n-Heptylsulfochloride angegeben.

Mit einer Absolutabweichung von maximal ± 0,04 (Molenbruch) sind die Konzentrationsbestimmungen der Mischungskomponenten zufriedenstellend.

Mit Hilfe des auf dem Oszillograph angezeigten Signalpegels im Lock-Kanal des Spektrometers wurde die Auflösung (*ca.* $5 \cdot 10^{-9}$) eingestellt und deren Stabilität während des Meßvorganges überwacht. Der abgetastete Frequenzbereich wurde mit dem im Spektrometer eingebauten Frequenzzähler (auf ± 0,1 Hz genau) ständig kontrolliert. Es wurden sowohl der Signalbereich der Methyl- und Methylengruppen ($A2$) als auch der Bereich der den Substituenten $-SO_2Cl$ tragenen CH-Gruppe ($A1$) zur Auswertung herangezogen, wie aus Abb. 4 hervorgeht. Für eine Samplingweite von $SW = 1$ umfaßt der Bereich $A1$ 101 Kanäle und der Bereich $A2$ 361 Kanäle.

Gleiche Erfahrungen bezüglich der erzielbaren Analysengenauigkeit wurden bei der ^{1}H-NMR-spektroskopischen Untersuchung von Testgemischen (2 bzw. 3 Komponenten) aus Alkanen gemacht. Allerdings konnte wegen Verstoßes gegen die Bedingung 3) des Verfahrens ein Gemisch aus n-Hexan, n-Oktan und n-Undekan nicht analysiert werden.

Die Abbildungen 5 und 6 zeigen die NMR-Spektren der Mischungen II und III und die Teletype-Protokolle der Analyse nebst den in den zwei Auswertebereichen dargestellten Fehlerkurven der für SW = 1 in insgesamt N = 462 Samplingpunkten durchgeführten Regressionsrechnung.*

Bei der Analyse dieser drei Testgemische wurde so verfahren, daß nach Analyse der Mischung I die Programmverzweigung "Routine" bejaht wurde (s. Abb. 2), damit ist für die getroffene Auswahl der Samplingbereiche und der Samplingpunkte die "systemcharakteristische" Matrix $\bar{B}$ fixiert und in allen weiteren Analysenfällen sind nur noch die Spektren der zu analysierenden Gemische dieser Komponenten aufzunehmen. Somit ist im Routinebetrieb eine quantitative Analyse in etwa 5–10 min—vom Einbringen der Probe bis zum Ergebnisausdruck—zu erhalten.

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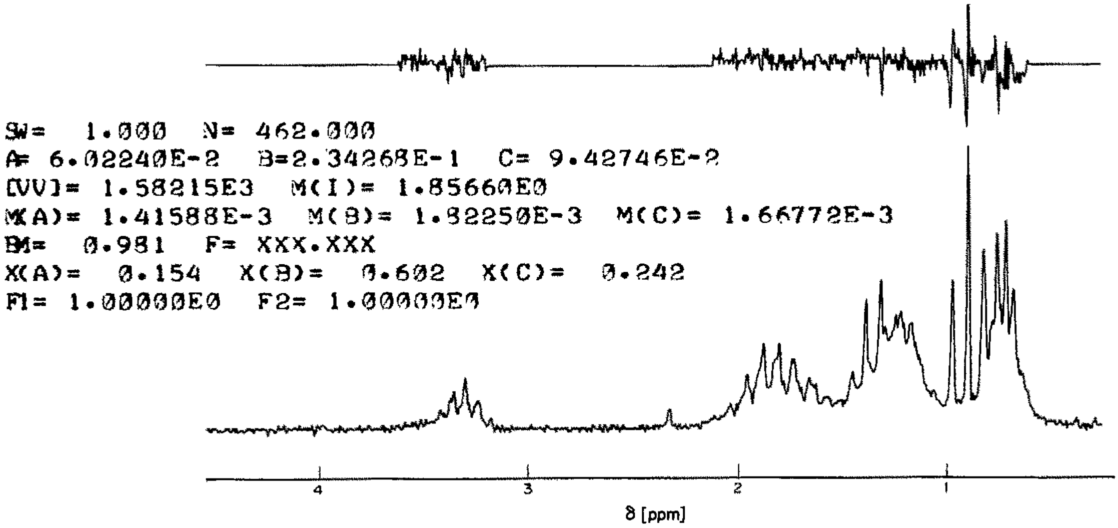
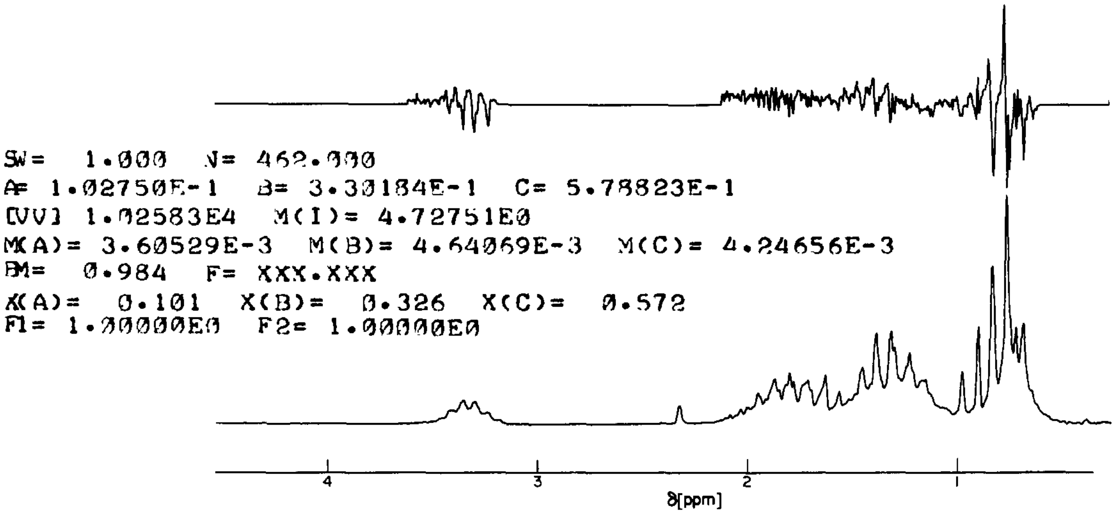
* F = XXX.XXX bedeutet, daß der F(Test)-Wert nach Fisher größer bzw. gleich 1000 ist.



```
SW=  1.000  N= 462.000
A= 6.02240E-2  B=2.34268E-1  C= 9.42746E-2
[VV]= 1.58215E3  M(I)= 1.85660E0
M(A)= 1.41588E-3  M(B)= 1.82250E-3  M(C)= 1.66772E-3
BM=  0.981  F= XXX.XXX
X(A)=  0.154  X(B)=  0.602  X(C)=  0.242
F1= 1.00000E0  F2= 1.00000E0
```

Abb. 5. ^{1}H-NMR-Spektrum der 3-Komponentenmischung II mit der für zwei Auswertebereiche erhaltenen Fehlerkurve (Verstärkungsfaktor: 2) und dem dafür vom Rechner ausgegebenen Analysenprotokoll.



```
SW=   1.000  N= 462.000
A= 1.02750E-1  B= 3.30184E-1  C= 5.78823E-1
[VV] 1.02583E4  M(I)= 4.72751E0
M(A)= 3.60529E-3  M(B)= 4.64069E-3  M(C)= 4.24656E-3
BM=  0.984  F= XXX.XXX
X(A)=  0.101  X(B)=  0.326  X(C)=  0.572
F1= 1.00000E0  F2= 1.00000E0
```

Abb. 6. ^{1}H-NMR-Spektrum der 3-Komponentenmischung III nebst Fehlerkurve (Verstärkungsfaktor: 4) und Analysenprotokoll.

Die wesentlichen Vorteile des on-line-Verfahrens kann man in folgenden Punkten erkennen:

—die zeitaufwendige und fehleranfällige manuelle Datenerfassung entfällt;

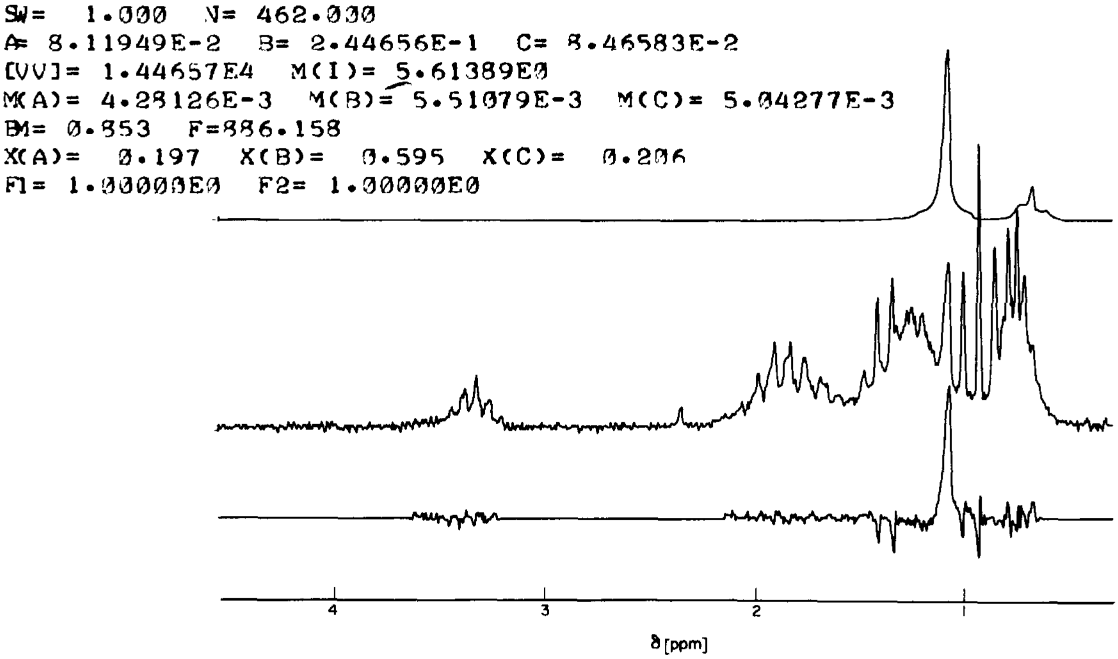
—durch die Möglichkeit der Spektrenakkumulation ist eine Erhöhung der Nachweisempfindlichkeit bzw. eine Herabsetzung des statistischen Fehlers bei der Analyse zu erreichen;

—Nachteile der off-line-Verarbeitung, wie z.B. Datenträgertransporte oder Wartezeiten, entfallen;

—es können die Samplingweiten und die Auswertebereiche beliebig variiert werden und damit das Analysenverfahren optimiert werden. Durch Zugabe einer Referenzsubstanz zu allen reinen Komponenten und deren Gemischen, deren Signal ebenfalls erfaßt wird, lassen sich Drift- oder Lösungsmitteleinflüsse korrigieren.

—der Datenspeicherinhalt des Computers kann jederzeit auf dem Display visuell kontrolliert werden, so daß z.B. systematische Fehler oder das Vorliegen von Verunreinigungen in der Fehlerkurve der Analyse des *k*-Komponentengemisches erkannt werden können.

In Abb. 7 (Oben) ist das ^{1}H-NMR-Spektrum des n-Undekans dargestellt, dessen Signale ebenfalls im



```
SW=   1.000  N= 462.000
A= 8.11949E-2  B= 2.44656E-1  C= 8.46583E-2
[VV]= 1.44657E4  M(I)= 5.61389E0
M(A)= 4.28126E-3  M(B)= 5.51079E-3  M(C)= 5.04277E-3
BM= 0.853  F=886.158
X(A)=  0.197  X(B)=  0.595  X(C)=  0.206
F1= 1.00000E0  F2= 1.00000E0
```

Abb 7. Oben: ^{1}H-NMR-Spektrum des n-Undekans. Mitte: ^{1}H-NMR-Spektrum der mit n-Undekan verunreinigten Mischung II; Unten: Fehlerkurve dieser in zwei Auswertebereichen analysierten Mischung mit den durch die Störkomponente verursachten systematischen Abweichungen; Oben links: Analysenprotokoll der mit n-Undekan verunreinigten Mischung II.

aktuellen Auswertebereich $A2$ der isomeren Heptylsulfochloride liegen. Durch Spektrenaddition mittels des Rechners wurde die Mischung II mit n-Undekan als Störkomponente "verunreinigt", wie aus Abb. 7 (Mitte) hervorgeht. Die Fehlerkurve dieses analysierten Systems zeigt deutlich die durch die Störkomponente im Bereich der Methylengruppen des n-Undekans hervorgerufene systematische Abweichung [Abb. 7 (Unten)]. Aus diesem Beispiel geht hervor, daß aus der Fehlerkurve nur bei einer sehr hohen Störkomponentenkonzentration ein identifizierbares Spektrum der verursachenden Substanz zu erhalten sein wird.

Verunreinigungen verschlechtern sofort das Analysenergebnis, da diese aufgrund der Voraussetzungen nicht erkannt und auf die k Komponenten "aufgeteilt" werden, wie z.B. das Analysenprotokoll in Abb. 7 für die "verunreinigte" Mischung II zeigt.

Äußerst empfindlich reagiert das Verfahren auf systematische Fehler, wo die Voraussetzung der strengen additiven Überlagerung der Spektren verletzt wird. Derartige Fehler liegen bei Abweichungen von der Phase des reinen Absorptionssignals vor oder bei geringfügigen Änderungen der chemischen Verschiebung (Größenordnung von einigen 10^{-3} ppm) infolge von Drift- oder Lösungsmitteleffekten.

Der erforderliche Speicherplatzbedarf steigt mit der Zahl der zu analysierenden Komponenten schnell an. So werden in der Regel pro reine Komponente und das Gemisch derselben 1K Speicherplätze reserviert und für $n \geqslant k + 1$ Samplingpunkte werden $2n(k + 1)$ weitere Speicherplätze belegt, da die Werte $I_j(v_i)$ und $I(v_i)$ als Gleitkommazahlen abgespeichert werden und somit jeweils zwei Speicherplätze beanspruchen. Für die Darstellung der Fehlerkurve werden ebenfalls 1K Speicherplätze reserviert. Zusammen mit dem eigentlichen Programm werden somit für $n = 500$ Samplingpunkte im Fall einer 3-Komponentenanalyse etwa 11K Speicherplätze benötigt. Nach der Festlegung der Matrix $\bar{B}$ (Routinebetrieb) werden noch 8K Speicherplätze benötigt.

Dagegen fallen Rechenzeiten kaum ins Gewicht, da z.B. nach der Datenerfassung für das vorgestellte Beispiel der 3-Komponentenanalyse mit 462 Samplingpunkten für die Regressionsrechnung nur *ca.* 15 s erforderlich waren und die restliche Zeit des Ergebnisausdruckes durch die Druckgeschwindigkeit des benutzten Teletype bedingt war.

Eine Verbesserung des Verfahrens sollte noch unter Einbeziehung von Gewichtsfaktoren möglich sein,[17,18] während Bemühungen zur Optimierung der Zahl der Samplingpunkte[19] aufgrund der hohen Rechengeschwindigkeit nicht so wesentlich erscheinen.

Eine weitere Anwendungsmöglichkeit ist dadurch gegeben, daß es z.B. möglich ist, die Konzentration einer Komponente in einem k-Komponentengemisch relativ gegenüber allen anderen zu bestimmen, d.h. durch Zusammenfassen der restlichen $(k - 1)$ zu einer "Komponente". Damit ist dieser Spezialfall auf die Analyse einer 2-Komponentenmischung zurückgeführt.

Die Grenzen der hier beschriebenen Methode dürften im Rahmen einer vertretbaren Analysengenauigkeit (Molenbruch ± 0,07) und Eindeutigkeit für die Analyse eines Systems mit 5–8 Komponenten erreicht sein. Die Nützlichkeit des relativ aufwendigen Verfahrens kommt erst bei einer hohen Wiederholrate der Analysen (Routinebetrieb)—wie sie z.B. bei der Produktkontrolle in der chemischen oder pharmazeutischen Industrie erforderlich sein kann—voll zur Geltung.

Die Substanzen wurden von Herrn Dr. Ch. Duschek von der Sektion Verfahrenschemie der TH Leuna-Merseburg zur Verfügung gestellt, wofür auch an dieser Stelle nochmals gedankt werden soll.

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STÖRENDE EINFLÜSSE VON BORSÄURE UND KOHLENDIOXID BEI DER MASSANALYTISCHEN AMMONIAKBESTIMMUNG

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Zusammenfassung—Die erreichbare Genauigkeit der maßanalytischen Ammoniakbestimmung mit potentiometrischer oder visueller Indikation bei Anwesenheit von Fremdstoffen (Borsäure und Kohlendioxid) wurde auf Grund des Verlaufes der Ammoniaktitrationskurven festgelegt und die Fehler dieses Verfahrens ausgewertet.

Die Mehrzahl der Verfahren für die Ammoniakbestimmung beruhen in seiner vorherigen Überführung durch Destillation, Diffusion oder Belüftung in eine starke Mineralsäure, in der es indirekt alkalimetrisch bestimmt wird, oder in eine Lösung der Borsäure mit anschließender azidimetrischer Bestimmung.[1,2] Im Verlaufe des Prozesses, bei dem Ammoniak in gasförmiger Zustand aus der analysierten Lösung ausgetrieben wird, können die in der Probe enthaltenden Fremdstoffe unter den gegebenen Bedingungen in die Absorptionslösung überführt werden und die nachfolgende Ammoniakbestimmung stören.

Handelt es sich um Basen (z.B. Pyridin), die mit Ammoniak aus alkalischen Lösungen freigemacht werden, läßt sich ihr Einfluß auf die Titrationsbedingungen aus den in der Literatur angeführten Diagrammen bestimmen.[3] In der vorliegenden Arbeit ist vor allem die Aufmerksammkeit den sauren Komponenten—der Borsäure und Kohlensäure—gewidmet. Der Einfluß der Borsäure wird deshalb untersucht, weil ihre Lösung oft zur Absorption des Ammoniaks nach seiner Abtrennung verwendet wird. Kohlensäure (bzw. Karbonate) ist ein üblicher Bestandteil der analysierten Lösungen und es kann während der Destillation eine Beträchtliche Menge von CO_2 in die Vorlage überführt werden.

Ableitung der Titrationskurven

Der Verlauf der Ammoniaktitrationskurve läßt sich aus den Gleichgewichtsbedingungen der beteiligten Ionen und aus den Elektroneutralitätsbedingungen in der Lösung berechnen. Bei der vereinfachten Voraussetzung der Volumenunveränderlichkeit der titrierten Lösung wird er durch die Gleichung (1) ausgedrückt:

$$c_t = [H^+] + \frac{c_a \cdot K_a \cdot [H^+]}{K_a \cdot [H^+] + K_w} - \frac{K_w}{[H^+]} \qquad (1)$$

worin K_a und K_w die Dissoziationskonstanten der Ammoniumionen und des Wassers, c_a und c_t die analytischen Konzentrationen des Ammoniaks und der Normallösung (starken Säure), die in Äquivalenten pro Liter in der titrierten Lösung ausgedrückt werden, bedeuten. Anstatt von der jetzt üblichen Bezeichnung der Wasserstoffionen H_3O^+ wird im Text der Einfachheit wegen die ältere Bezeichnung H^+ verwendet.

Die Gleichung (1) kann man auch zur Ermittlung der Titrationskurve verwenden, die die Rücktitration einer starken Säure bei Anwesenheit des Ammoniumsalzes mit einer starken Base darstellt. In diesem Falle entspricht c_t der Differenz zwischen der Äquivalenzkonzentration der starken Säure und Base.

Enthält die titrierte Lösung einige weitere sauer oder basisch reagierende Bestandteile, geht die Gleichung (1) in die folgende Form über:

$$c_t + \Sigma[A] - \Sigma[B] = [H^+] + \frac{c_a \cdot K_a [H^+]}{K_a \cdot [H^+] + K_w} - \frac{K_w}{[H^+]} \qquad (2)$$

Hier entspricht $\Sigma[A]$ der Summe von sauer- und $\Sigma[B]$ von alkalisch reagierenden Komponenten. Handelt es sich um eine Säure H_nA, die in n Stufen dissoziiert, gilt:

$$[A] = c_A \cdot \frac{K_{A1}[H^+]^{n-1} + 2K_{A1}K_{A2}[H^+]^{n-2} + \ldots + nK_{A1}K_{A2}\ldots K_{An}}{[H^+]^n + K_{A1}[H^+]^{n-1} + K_{A1}K_{A2}[H^+]^{n-2} + \ldots + K_{A1}K_{A2}\ldots K_{An}} \qquad (3)$$

Analogisch, wenn eine in m Stufen dissoziierte Base vorliegt, gilt:

$$[B] = c_B \cdot \frac{K_{B1}K_w^{m-1}[H^+] + 2K_{B1}K_{B2}K_w^{m-2}[H^+]^2 + \ldots + mK_{B1}K_{B2}\ldots K_{Bm}[H^+]^m}{K_w^m + K_{B1}K_w^{m-1}[H^+] + K_{B1}K_{B2}K_w^{m-2}[H^+]^2 + \ldots + K_{B1}K_{B2}\ldots K_{Bm}[H^+]^m} \qquad (4)$$

Darin bedeuten K_{A1}, K_{A2} ... K_{An} bzw. K_{B1}, K_{B2} ... K_{Bm} die Dissoziationskonstanten der Säure bzw. Base, c_A und c_B ihre analytischen Konzentrationen, die in Äquivalenten pro Liter ausgedrückt werden. Sind die angeführten Bestandteile Borsäure und Kohlensäure, gilt:

$$\Sigma[\mathrm{B}] = 0$$

$$\Sigma[\mathrm{A}] = \frac{c_b K_b}{K_b + [\mathrm{H}^+]} + c_k \frac{K_{k1}[\mathrm{H}^+] + 2K_{k1}K_{k2}}{[\mathrm{H}^+]^2 + K_{k1}[\mathrm{H}^+] + K_{k1}K_{k2}} \qquad (5)$$

In diesen Ausdrücken bedeuten K_b, K_{k1}, K_{k2} die Dissoziationskonstanten der Borsäure und Kohlensäure (beide Stufen), c_b und c_k ihre molare Konzentration.

Der pH-Wert des Äquivalenzpunktes der Ammoniaktitrationskurve bzw. bei Anwesenheit von Borsäure und Kohlensäure wird aus den Gleichungen (2) und (5) nach der Einsetzung $c_t = c_a$ ermittelt. Nach Fortlassung einiger vernachlässigbaren kleinen Gliedern bekommt man:

$$\mathrm{pH} = -\tfrac{1}{2}\log\left(\frac{c_a \cdot K_w}{K_a} + c_b \cdot K_b + c_k \cdot K_{k1}\right) \qquad (6)$$

Für die Beurteilung der Genauigkeit der Titrationsmethode ist es wichtig die Steigerung der Titrationskurve im Äquivalenzpunkt, die durch den Richtungskoeffizient der Tangente in diesem Punkt ermittelt wird, zu kennen. Er wird aus der zugehörigen Funktionsabhängigkeit zwischen pH und c_t durch Differenzieren berechnet. Diese Abhängigkeit wird für Ammoniak und Borsäure durch die Gleichung (2), in der für die $[\mathrm{H}^+]$-Werte ein äquivalenter Ausdruck $10^{-\mathrm{pH}}$ eingesetzt wird, dargestellt. Der Differenzialquotient wird aus dem implizierten Ausdruck der Funktion $F(c_t, \mathrm{pH})$ ermittelt:

$$-\frac{\mathrm{d}c_t}{\mathrm{dpH}} = \frac{\partial F(c_t, \mathrm{pH})/\partial \mathrm{pH}}{\partial F(c_t, \mathrm{pH})/\partial c_t} \qquad (7)$$

Aus den Gleichungen (7) und (2) bzw. (5) bekommt man für den Äquivalenzpunkt ($c_t = c_a$) nach der Vereinfachung durch Fortlassung der vernachlässigbaren kleinen Gliedern (siehe Appendix):

$$-\frac{\mathrm{d}c_t}{\mathrm{dpH}} = \frac{2\ln 10(2K_a \cdot 10^{-2\mathrm{pH}} - c_a K_w - c_b K_a K_b)}{K_a 10^{-\mathrm{pH}}} \qquad (8)$$

Ermittlung der Titrationskurven

Nach den oben angeführten Beziehungen wird die Berechnung der Ammoniaktitrationskurven auch bei Anwesenheit von Borsäure und Kohlensäure durchgeführt. Wie erwähnt, wird dabei eine Volumenveränderung während der Titration nicht errechnet.

Die für sehr verdünnte Lösungen gültigen Tabellenwerte der Dissoziationskonstanten wurden mit Rücksicht auf die Ionenstärke der Lösung (im Äquivalenzpunkt) umgerechnet—Tabelle 1.

$$-\log f_i = i^2 \frac{0{,}511\sqrt{J}}{(1 + 1{,}5\sqrt{J})} - 0{,}2\,J \qquad (9)$$

$$K'_1 = f_1^2 \cdot K_1 \qquad (10)$$

$$K'_2 = f_2 \cdot K_2 \qquad (10a)$$

In diesen Gleichungen bedeuten K' die Tabellenwerte der Dissoziationskonstanten der unendlich verdünnten Lösungen, K die Dissoziationskonstanten der Lösungen mit der Ionenstärke J, f_i sind die Aktivitätskoeffizienten der i-Wertigen Ionen. Für die Berechnung der Ionenstärke wird die Ammoniumchlorid konzentration (im Äquivalenzpunkt) in Betracht genommen, während Borsäure und Kohlensäure wegen ihrer vernachlässigbarer Dissoziation unbeachtet bleiben.

Bei der hier verwendeten Konzentration der Borsäure (0,1*M*) ist nur die Ionenstärke der Lösung bei Berechnung der Dissoziationskonstante K_b in Betracht zu ziehen. Wenn die Borsäurekonzentration höher als 0,1*M* vorliegt, werden stärkere Polyborsäuren gebildet. Der K_b-Wert verändert sich dann mehr als der erhöhten Ionenstärke entspricht, und er muß aus der empirisch bestimmten Abhängigkeit pH von der Borsäurekonzentration abgeleitet werden.[4]

Der untersuchte Ammoniakkonzentrationsbereich war 10^{-4} bis $10^{-2}M$. Der Konzentrationsbegrenzung der Borsäure wurde die Anforderung für die quantitative Absorption des Ammoniaks im Verlaufe seiner Abtrennung aus der analysierten Lösung in Betracht gezogen. Die erforderliche Menge der Borsäure und ihre Konzentration in der Vorlage hängt von der Menge des Destillierten Ammoniaks ab. Zur Absorption von 20 mg Ammoniak sind 25 ml 2%iger Borsäure hinreichend. Nach Abdestillieren des erforderlichen Volumens wird die Lösung in der Vorlage verdünnt und die resultierende Borsäurekonzentration ist dann ungefähr 0,1*M*.

Tabelle 1. Die für die Berechnung verwendeten Dissoziationskonstanten (für 18°C)

		Ionenstärke der Lösung			
Komponente		0	10^{-4}	10^{-3}	10^{-2}
Wasser	K_w	$0{,}74 \cdot 10^{-14}$	$0{,}75 \cdot 10^{-14}$	$0{,}79 \cdot 10^{-14}$	$0{,}90 \cdot 10^{-14}$
Ammoniak	K_a	$1{,}75 \cdot 10^{-5}$	$1{,}76 \cdot 10^{-5}$	$1{,}88\ 10^{-5}$	$2{,}13 \cdot 10^{-5}$
Borsäure	K_b	$7{,}3 \cdot 10^{-10}$	$7{,}4 \cdot 10^{-10}$	$7{,}8 \cdot 10^{-10}$	$8{,}9\ 10^{-10}$
Kohlensäure	K_{k1}	$4{,}01 \cdot 10^{-7}$	$4{,}07 \cdot 10^{-7}$	$4{,}30 \cdot 10^{-7}$	$4{,}87 \cdot 10^{-7}$
Kohlensäure	K_{k2}	$5{,}2 \cdot 10^{-11}$	$5{,}4 \cdot 10^{-11}$	$6{,}0 \cdot 10^{-11}$	$7{,}8 \cdot 10^{-11}$

Tabelle 2. Die Richtungskoeffizienten der Tangente im Wendepunkt der Titrationskurve

$[NH_3]$, *M*	$[H_3BO_3]$, *M*	$-dc_t/d$ pH *Äquiv/l.*
10^{-4}	0	$1{,}1 \cdot 10^{-6}$
10^{-3}	0	$3{,}1 \cdot 10^{-6}$
10^{-2}	0	$9{,}3 \cdot 10^{-6}$
10^{-4}	10^{-2}	$1{,}3 \cdot 10^{-5}$
10^{-3}	10^{-2}	$1{,}3 \cdot 10^{-5}$
10^{-2}	10^{-2}	$1{,}9 \cdot 10^{-5}$
10^{-4}	10^{-1}	$3{,}9 \cdot 10^{-5}$
10^{-3}	10^{-1}	$4{,}3 \cdot 10^{-5}$

Bei den Titrationskurven des Ammoniaks, auch in Anwesenheit von Borsäure, werden die Richtungskoeffizienten der Tangenten im Wendepunkt nach der Gleichung (8) berechnet und die Ergebnisse in Tabelle 2 zusammengefaßt.

Karbonate liegen in verschiedenen Materialen häufig vor. Zum Beispiel in Naturwässern sind sie in einer Konzentration bis $10^{-2}M$ und ausnahmsweise noch höher enthalten. Bei der Destillation aus gepufferten Lösungen von pH 7,4, der bei der Wasseranalyse vorgeschrieben wird,[5] geht ein beträchtlicher Anteil von CO_2 in die Vorlage über. Kohlendioxid, als Bestandteil der Luft, kann in die Maßlösung oder in das zur Analyse verwendete redestillierte Wasser eindringen. Deshalb wird sein Einfluß schon von sehr niedrigen Mengen, die ihren Ursprung in der atmosphärischen Verunreinigungen haben können, untersucht.

Die charakteristischen Angaben der Titrationskurven-pH im Äquivalenzpunkt [berechnet aus der Gleichung (6)], pH im Wendepunkt (graphisch aus der berechneten Titrationskurve ermittelt) und die Differenz des Normallösungsverbrauches zwischen dem Äquivalentspunkt und dem Wendepunkt [aus den Gleichungen (2) und (5) berechnet], sind in Tabelle 3 verzeichnet. Einige ausgewählte Titrationskürven sind in Abb. 1 und 2 wiedergegeben.

Der berechnete Verlauf von Titrationskurven wurde experimentell mit Hilfe des pH-meters Radelkis OP-206 überprüft, wobei eine gute Übereinstimmung erreicht wurde (siehe Abbildungen 1 und 2).

Die Lösungen wurden aus redestilliertem, von CO_2 durch Auskochen befreitem Wasser, vorbereitet. Nach Herstellung der einzelnen Lösungen durch Vermischung der Grundlösungen ($0{,}01M$ NH_3, $0{,}01M$ HCl, $0{,}4M$ H_3BO_3 und $2{,}1 \times 10^{-3}M$ CO_2) wurde der

Tabelle 3. Charakteristische Angaben der Ammoniaktitrationskurven bei Anwesenheit von Borsäure und Kohlensäure

		$[CO_2]$, *M*				
$[NH_3]$, *M*	$[H_3BO_3]$, *M*	0	$5 \cdot 10^{-5}$	10^{-4}	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
(*a*) pH im Äquivalenzpunkt						
10^{-4}	0	6,65	5,34	5,19	5,04	4,84
10^{-4}	10^{-2}	5,56	5,28	5,16	5,02	4,84
10^{-4}	10^{-1}	5,07	4,99	4,96	4,89	4,77
10^{-3}	0	6,18	5,33	5,18	5,01	4,83
10^{-3}	10^{-2}	5,54	5,26	5,14	5,01	4,82
10^{-3}	10^{-1}	5,05	5,00	4,96	4,89	4,76
10^{-2}	0	5,69	5,27	5,14	5,00	4,80
10^{-2}	10^{-2}	5,44	5,21	5,10	4,98	4,79
10^{-2}	10^{-1}	5,02	4,96	4,92	4,86	4,73
(*b*) pH im Wendepunkt						
10^{-4}	0	6,65	$6{,}81^+$	$6{,}93^+$	$7{,}30^+$	—
10^{-4}	10^{-2}	5,56	5,46	5,34	5,14	4,86
10^{-4}	10^{-1}	5,07	5,05	5,02	4,96	4,82
10^{-3}	0	6,18	$6{,}16^+$	$6{,}14^+$	$6{,}00^+$	4,88
10^{-3}	10^{-2}	5,54	5,45	5,37	5,20	4,87
10^{-3}	10^{-1}	5,05	5,03	4,99	4,93	4,81
10^{-2}	0	5,69	5,51	5,46	5,22	4,86
10^{-2}	10^{-2}	5,44	5,39	5,34	5,16	4,83
10^{-2}	10^{-1}	5,02	4,99	4,95	4,90	4,74
(*c*) Die Differenz der Konzentrationen der Normallösung in der titrierten Lösung beim Erreichen des Äquivalenz- und Wendepunktes ($c_e - c_i$). In 10^{-6} Äquivalent pro Liter.						
10^{-4}	0	0	36*	77*	179*	—
10^{-4}	10^{-2}	0	4	6	4	6
10^{-4}	10^{-1}	0	1	2	2	2
10^{-3}	0	0	18*	39*	58*	3
10^{-3}	10^{-2}	0	4	6	7	5
10^{-3}	10^{-1}	0	1	2	2	3
10^{-2}	0	0	5	10	10	2
10^{-2}	10^{-2}	0	2	3	5	0
10^{-2}	10^{-1}	0	0	1	1	2

* Aus dem fiktiven Wendepunkt der Titrationskurve, bei der die zwei der Kohlensäure entsprechende Stufen nicht unterschieden werden, berechnet.

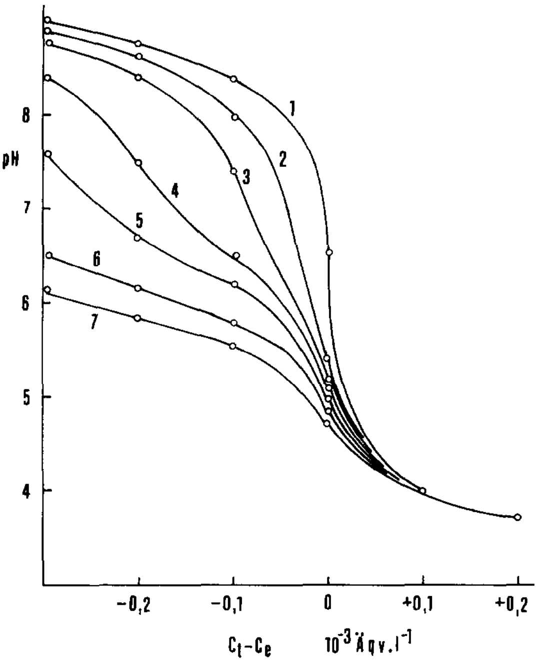

Abb. 1. Ammoniaktitrationskurven bei Anwesenheit von Kohlensäure $[NH_3] = 10^{-3}M$; ○ = gemessen, —— = berechnet.

Kurve Nr.	$[CO_2]$	Kurve Nr.	$[CO_2]$
1	0	5	$3 \cdot 10^{-4}M$
2	$5 \cdot 10^{-5}M$	6	$5 \cdot 10^{-4}M$
3	$10^{-4}M$	7	$10^{-3}M$
4	$2 \cdot 10^{-4}M$		

pH-Wert bestimmt. Die gewünschte CO_2-Konzentration wurde durch Zugabe von kohlendioxidgesättigtem redistilliertem Wasser, in dem CO_2 gleich vor Verwendung alkalimetrisch bestimmt wurde, hergestellt.

Diskussion der Ergebnisse

Die pH-Werte im Äquivalenzpunkt der Ammoniaktitrationskurven sind eine logarithmische Funktion der NH_3-Konzentration [siehe Gleichung (6)], die auch ihren Verlauf als Folge der Hydrolyse des Ammoniumsalzes beeinflußt. Äquivalenz- und Wendepunkte der Ammoniaktitrationskurven unterscheiden sich durch nicht mehr als 0,01 pH (Tabelle 3).

Aus dem Richtungskoeffizient dc_t/dpH in der Nähe des Äquivalenzpunktes (der in diesem Falle mit dem Wendepunkt identisch ist) läßt sich ableiten, daß eine Konzentrationsänderung der starken Säure in der titrierten Lösung (für $[NH_3] < 0{,}01M$) um 10^{-7} bis 10^{-8} Äquivalent pro Liter den pH-Wert nur um ein Hundertstel ändert (Tabelle 2). Bei der pH-Ablesung mit einer Genauigkeit von einem Hundertstel kann die Ammoniakkonzentration unter Verwendung der maßanalytischen, potentiometrisch indizierten Methode mit der theoretisch maximal erreichbaren Genauigkeit auf $10^{-7}M$ bestimmt werden. Bei der pH-Ablesung auf Zehntel, ist die erreichbare Genauigkeit der Ammoniakbestimmung zehnmal kleiner. Bei diesen extrem genauen Bestimmungen ist es nötig, die Volumsänderungen der Lösung während der Titration, und besonders die Anwesenheit von Kohlendioxid zu beachten. Es ist außerdem notwendig, daß die Maßlösung in die Probelösung mit entsprechender Genauigkeit zugesetzt werden kann.

Die Beeinflußung des Verlaufes von Ammoniaktitrationskurven durch schwache Säuren ist aus den Abb. 1 und 2 für Borsäure und Kohlendioxid ersichtlich. Da Säuren die Titrationskurven im alkalischen Gebiete deformieren, verschiebt sich der Äquivalenzpunkt zu niedrigen pH-Werten. Diese Wirkung ist von der Säurekonzentration und von der Größe ihrer Dissoziationskonstante abhängig. Die Identität des Aquivalenzpunktes mit dem Wendepunkt der Titrationskurve von Ammoniak bei Anwesenheit der Borsäure stimmt mit einer Genauigkeit auf Hundertstel pH-Wert (Tabelle 3).

Der Richtungskoeffizient der Tangente im Äquivalenzpunkt wird durch eine Borsäurezugabe auf Werte von 10^{-5} bis 5×10^{-5} Äquivalent pro Liter erhöht. Die Änderung der Säurekonzentration c_t um etwa 10^{-6} Äquivalent pro Liter bewirkt in der Umgebung dieses Punktes eine pH-Änderung von 0,01. Deshalb ist bei Anwesenheit der Borsäure die theoretisch erreichbare Genauigkeit der Ammoniakbestimmung $10^{-6}M$ unter Verwendung der potentiometrischen Indikation bei pH-Ablesung auf Hundertstel. Bei pH-Ablesung auf Zehntel ist die erreichbare Genauigkeit $10^{-5}M$.

Ähnlich wie Borsäure verhält sich auch Kohlensäure, deren Wirkung aber deutlicher in Übereinstimmung mit der Größe ihrer Dissoziationskonstante ist. Bei dieser Säure ist ihre zweite Dissoziationsstufe zu beachten, erkennbar durch einen zweiten Wendepunkt, besonders eindeutig bei höheren CO_2-Konzentrationen. Bei niedrigen CO_2-Konzentrationen ist nur ein Wendepunkt deutlich, der aber stark vom Äquivalenzpunkt abweicht (Tabelle 3). Bei einer Kohlensäurekonzentration höher als $3 \times 10^{-4}M$,

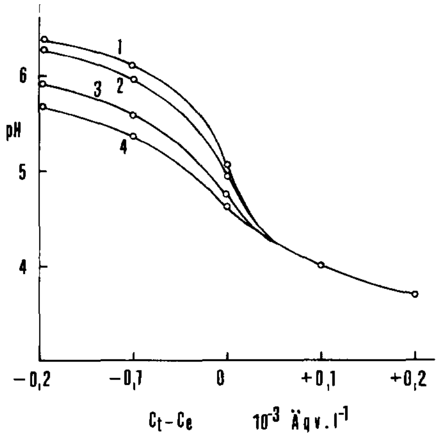

Abb. 2. Ammoniaktitrationskurven bei Anwesenheit von Borsäure und Kohlensäure $[NH_3] = 10^{-3}M$; $[H_3BO_3] = 10^{-1}M$

Kurve Nr.	$[CO_2]$	Kurve Nr.	$[CO_2]$
1	0	3	$5 \cdot 10^{-4}M$
2	$10^{-4}M$	4	$10^{-3}M$

Tabelle 4. Die maximal zulässige CO_2-Konzentrationen (M) für die massanalytische Ammoniakbestimmung der verlangten Genauigkeit

	verlangte Genauigkeit der Bestimmung (in Mol NH_3 pro Liter)			
$[NH_3]$, M	10^{-4}	10^{-5}	10^{-6}	10^{-7}
(a) potentiometrische Indikation:				
für $[H_3BO_3] = 0$				
10^{-4}	10^{-3}	$2\cdot10^{-5}$	$2\cdot10^{-6}$	$2\cdot10^{-7}$
10^{-3}	10^{-3}	$3\cdot10^{-5}$	$3\cdot10^{-6}$	$3\cdot10^{-7}$
10^{-2}	10^{-3}	10^{-3}	10^{-5}	10^{-6}
für $[H_3BO_3] = 10^{-2}$–$10^{-1}M$				
10^{-4}–10^{-2}	10^{-3}	10^{-3}	$5\cdot10^{-5}$	—
(b) visuelle Indikation (im pH-Bereiche 5,7–4,1):				
für $[H_3BO_3] = 0$–$10^{-1}M$				
10^{-4}–10^{-2}	10^{-4}	—	—	—
(c) visuelle Indikation (im pH-Bereiche 5,0–4,8):				
für $[H_3BO_3] = 0$–$10^{-1}M$				
10^{-4}–10^{-2}	10^{-3}	10^{-4}	—	—

oder in Anwesenheit von Borsäure kann man den Wendepunkt der ersten Stufe, dessen Abweichung vom Äquivalenzpunkt kleiner ist, bestimmen. Liegt die CO_2-Konzentration höher als $10^{-3}M$ vor, wird die Titrationskurve so flach, daß die Ammoniakbestimmung sich nur mit einer Genauigkeit von $10^{-3}M$ durchführen läßt.

Die Angaben über den zulässigen CO_2-Konzentrationen bei der maßanalytischen Ammoniakbestimmung mit der verlangten Genauigkeit sind in Tabelle 4 verzeichnet. Sie gehen aus dem Verlauf der Titrationskurven und aus den in Tabellen 3 und 5 angeführten Werten hervor. Diese Angaben dokumentieren die Abhängigkeit der angeführten Grenzwerte von der Ammoniak- und Borsäurekonzentration in der analysierten Probe.

Von den azidobasischen Indikatoren, die bei der maßanalytischen Ammoniakbestimmung am häufig-

Tabelle 5. Die Differenz (mÄquiv./l.) der Konzentration der Normallösung in der titrierten Lösung beim Erreichen des angeführten pH-Wertes und des Äquivalenzpunktes ($c_t - c_e$)

		$[H_3BO_3] = 0$		$[H_3BO_3] = 10^{-1}M$	
$[NH_3]$, M	$[CO_2]$, M	pH 5,7	pH 4,1	pH 5,7	pH 4,1
10^{-2}	0	0	+0,079	−0,044	+0,078
	$5\cdot10^{-5}$	−0,010	+0,079	−0,054	+0,078
	10^{-4}	−0,020	+0,079	−0,064	+0,078
	$5\cdot10^{-4}$	−0,098	+0,076	−0,142	+0,075
	10^{-3}	−0,196	+0,073	−0,240	+0,072
	$5\cdot10^{-3}$	−0,981	+0,049	−1,025	+0,048
10^{-4}	0	+0,002	+0,079	−0,037	+0,078
	$5\cdot10^{-5}$	−0,006	+0,079	−0,045	+0,078
	10^{-4}	−0,015	+0,079	−0,054	+0,078
	$5\cdot10^{-4}$	−0,082	+0,077	−0,121	+0,076
	10^{-3}	−0,167	+0,074	−0,206	+0,073
	$5\cdot10^{-3}$	−0,845	+0,054	−0,884	+0,053
		pH 5,0	pH 4,8	pH 5,0	pH 4,8
10^{-2}	0	+0,010	+0,016	+0,001	+0,010
	$5\cdot10^{-5}$	+0,008	+0,015	−0,001	+0,009
	10^{-4}	+0,005	+0,013	−0,004	+0,007
	$5\cdot10^{-4}$	−0,013	+0,001	−0,001	−0,005
	10^{-3}	−0,036	−0,014	−0,045	−0,020
	$5\cdot10^{-3}$	−0,222	−0,133	−0,231	−0,139
10^{-4}	0	+0,010	+0,016	+0,003	+0,011
	$5\cdot10^{-5}$	+0,008	+0,015	+0,001	+0,010
	10^{-4}	+0,006	+0,014	+0,001	+0,009
	$5\cdot10^{-4}$	−0,010	+0,003	−0,017	−0,002
	10^{-3}	−0,029	−0,009	−0,036	−0,019
	$5\cdot10^{-3}$	−0,186	−0,109	−0,193	−0,114

stens verwendet werden, ist Methylrot oder seine Mischung mit Methylenblau (Indikator nach Taschiro) zu nennen. Die Indikatorkonstante ($pK_i = 4{,}9$) ist durch den ersten Bestandteil bestimmt. Methylenblau macht nur den Farbumschlag für das menschliche Auge deutlicher. Die Farbänderung des Indikators wird durch den Bereich von 10 bis 90% aus der erreichbaren Intensität der roten Farbe, die in diesem Falle maßgebend ist, bestimmt. Das entspricht dem pH-Bereiche 4,1–5,7. Eine genauere Unterscheidung kann man durch Verwendung einer auf den pH-Wert 4,9 gepufferten Vergleichslösung erreichen, In diesem Falle läßt sich in der Nähe von pK_{i1} die Farbintensität mit Genauigkeit auf ± 6% gegenüber ihrer maximaler Intensität, die bei einer extremen Azidität erreicht wird, zuverlässig unterscheiden. Dieses Farbintervall entspricht dem pH-Bereich 4,8–5,0.

Die Differenzen des Verbrauches an Normallösung der Säure beim Erreichen des gewünschten pH-Wertes und Äquivalenzpunktes im Verlaufe der Ammoniaktitration sind in Tabelle 5 angegeben. Diese Differenzen sind für die Beurteilung der erreichbaren Genauigkeit entscheidend.

Im ersten Falle, d.h. für den Farbumschlag, der durch den pH-Bereich 5,7–4,1 bestimmt wird, ist bei der Ammoniaktitration, auch in Anwesenheit der Borsäure, die maximal erreichbare Genauigkeit der Ammoniakbestimmung $10^{-4}M$. Durch das Verengen des pH-Intervalls, in dem der Farbumschlag wahrnehmbar ist, auf 5,0 bis 4,8, wird die Genauigkeit auf $10^{-5}M$ erhöht.

Bei Anwesenheit von Kohlendioxid wird die Titrationskurve flacher, wodurch die Indikation erschwert wird. Die erreichbare Genauigkeit der Ammoniakbestimmung ist bei der Indikation mit Methylrot $10^{-4}M$ unter Voraussetzung, daß die CO_2-Konzentration $10^{-4}M$ nicht übersteigt. Unter den gleichen Bedingungen kann man durch die Verwendung von Indikatorvergleichslösung eine Genauigkeit von $10^{-5}M$ erzielen. Liegt die CO_2-Konzentration höher als $10^{-4}M$ vor (bis ungefähr $2 \cdot 10^{-3}M$), läßt sich bei visueller Indikation nur eine Genauigkeit von $10^{-3}M$. bzw. unter Verwendung von Vergleichslösung $10^{-4}M$ erreichen.

Bei der genauen maßanalytischen Bestimmung muß man aber berücksichtigen, daß auch der Indikator beim Übergang von einer Form in die andere einen gewissen Verbrauch an Normallösung aufweist. Methylrot in der Menge von 0,1 ml 0,1%iger Lösung verbraucht bei dieser Umwandlung 0,003 ml 0,1*N* Normallösung.[2] Diese Tatsache wurde bei den in Tabelle 5 angegebenen Werten außer Acht gelassen.

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APPENDIX

Berechnung der Gleichung (8) aus der Gleichung (2): $c_t + \dfrac{c_b K_b}{K_b + [H^+]} = [H^+] + \dfrac{c_a K_a [H^+]}{K_a[H^+] + K_w} - \dfrac{K_w}{[H^+]}$

oder $F'(c_t, [H^+]) \equiv [H^+]^4 A + [H^+]^3 B + [H^+]^3 c_t D + [H^+]^2 E + [H^+]^2 c_t L + [H^+] P + [H^+] c_t S + T = 0$

wo $A = K_a$, $B = K_a K_b + K_a c_a + K_w$; $D = -K_a$; $E = K_a K_b c_a - K_a K_b c_b + K_b K_w - K_a K_w$, $L = -K_a K_b - K_w$. $P = -K_a K_b K_w - K_b K_w c_b - K_w^2$; $S = -K_b K_w$; $T = -K_b K_w^2$

$$F'(c_t, 10^{-pH}) = F(c_t, pH)$$

$$\frac{\partial F(c_t, pH)}{\partial c_t} = 10^{-3pH} D + 10^{-2pH} L + 10^{-pH} S$$

$$\frac{\partial F(c_t, pH)}{\partial pH} = -\ln 10 \{4 \cdot 10^{-4pH} A + 3 \cdot 10^{-3pH}(B + c_t D) + 2 \cdot 10^{-2pH}(E + c_t L) + 10^{-pH}(P + c_t S)\}$$

aus der Gleichung (7):

$$-\frac{dc_t}{dpH} = \frac{\ln 10 \{4\ 10^{-3pH} A + 3 \cdot 10^{-2pH}(B + c_t D) + 2 \cdot 10^{-pH}(E + c_t L) + (P + c_t S)\}}{10^{-2pH} D + 10^{-pH} L + S}$$

für $c_t = c_a$ (Äquivalenzpunkt):

$$-\frac{dc_t}{dpH} = \frac{\ln 10 \{4\ 10^{-3pH} K_a + 3 \cdot 10^{-2pH}(K_a K_b + K_w) + 2\ 10^{-pH}(K_b K_w - K_a K_w - K_a K_b c_b - K_w c_a) - K_a K_b K_w - K_w^2 - K_b K_w c_b - K_b K_w c_a\}}{10^{-2pH} K_a + 10^{-pH} K_a K_b + 10^{-pH} K_w + K_b K_w}$$

vereinfacht durch Vernachlässigung der kleinen Gliedern:

$$-\frac{dc_t}{dpH} = \frac{\ln 10 \{4\ 10^{-3pH} K_a - 2\ 10^{-pH}(K_a K_b c_b + K_w c_a)\}}{10^{-2pH} K_a}$$

daraus läßt sich schon leicht die Gleichung (8) ableiten.

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STÖRENDE EINFLÜSSE VON BORSÄURE UND KOHLENDIOXID BEI DER MASSANALYTISCHEN AMMONIAKBESTIMMUNG

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Zusammenfassung—Die erreichbare Genauigkeit der maßanalytischen Ammoniakbestimmung mit potentiometrischer oder visueller Indikation bei Anwesenheit von Fremdstoffen (Borsäure und Kohlendioxid) wurde auf Grund des Verlaufes der Ammoniaktitrationskurven festgelegt und die Fehler dieses Verfahrens ausgewertet.

Die Mehrzahl der Verfahren für die Ammoniakbestimmung beruhen in seiner vorherigen Überführung durch Destillation, Diffusion oder Belüftung in eine starke Mineralsäure, in der es indirekt alkalimetrisch bestimmt wird, oder in eine Lösung der Borsäure mit anschließender azidimetrischer Bestimmung.[1,2] Im Verlaufe des Prozesses, bei dem Ammoniak in gasförmiger Zustand aus der analysierten Lösung ausgetrieben wird, können die in der Probe enthaltenden Fremdstoffe unter den gegebenen Bedingungen in die Absorptionslösung überführt werden und die nachfolgende Ammoniakbestimmung stören.

Handelt es sich um Basen (z.B. Pyridin), die mit Ammoniak aus alkalischen Lösungen freigemacht werden, läßt sich ihr Einfluß auf die Titrationsbedingungen aus den in der Literatur angeführten Diagrammen bestimmen.[3] In der vorliegenden Arbeit ist vor allem die Aufmerksammkeit den sauren Komponenten—der Borsäure und Kohlensäure—gewidmet. Der Einfluß der Borsäure wird deshalb untersucht, weil ihre Lösung oft zur Absorption des Ammoniaks nach seiner Abtrennung verwendet wird. Kohlensäure (bzw. Karbonate) ist ein üblicher Bestandteil der analysierten Lösungen und es kann während der Destillation eine Beträchtliche Menge von CO_2 in die Vorlage überführt werden.

Ableitung der Titrationskurven

Der Verlauf der Ammoniaktitrationskurve läßt sich aus den Gleichgewichtsbedingungen der beteiligten Ionen und aus den Elektroneutralitätsbedingungen in der Lösung berechnen. Bei der vereinfachten Voraussetzung der Volumenunveränderlichkeit der titrierten Lösung wird er durch die Gleichung (1) ausgedrückt:

$$c_t = [H^+] + \frac{c_a \cdot K_a \cdot [H^+]}{K_a \cdot [H^+] + K_w} - \frac{K_w}{[H^+]} \qquad (1)$$

worin K_a und K_w die Dissoziationskonstanten der Ammoniumionen und des Wassers, c_a und c_t die analytischen Konzentrationen des Ammoniaks und der Normallösung (starken Säure), die in Äquivalenten pro Liter in der titrierten Lösung ausgedrückt werden, bedeuten. Anstatt von der jetzt üblichen Bezeichnung der Wasserstoffionen H_3O^+ wird im Text der Einfachheit wegen die ältere Bezeichnung H^+ verwendet.

Die Gleichung (1) kann man auch zur Ermittlung der Titrationskurve verwenden, die die Rücktitration einer starken Säure bei Anwesenheit des Ammoniumsalzes mit einer starken Base darstellt. In diesem Falle entspricht c_t der Differenz zwischen der Äquivalenzkonzentration der starken Säure und Base.

Enthält die titrierte Lösung einige weitere sauer oder basisch reagierende Bestandteile, geht die Gleichung (1) in die folgende Form über:

$$c_t + \Sigma[A] - \Sigma[B] = [H^+] + \frac{c_a \cdot K_a [H^+]}{K_a \cdot [H^+] + K_w} - \frac{K_w}{[H^+]} \qquad (2)$$

Hier entspricht $\Sigma[A]$ der Summe von sauer- und $\Sigma[B]$ von alkalisch reagierenden Komponenten. Handelt es sich um eine Säure H_nA, die in n Stufen dissoziiert, gilt:

$$[A] = c_A \cdot \frac{K_{A1}[H^+]^{n-1} + 2K_{A1}K_{A2}[H^+]^{n-2} + \ldots + nK_{A1}K_{A2}\ldots K_{An}}{[H^+]^n + K_{A1}[H^+]^{n-1} + K_{A1}K_{A2}[H^+]^{n-2} + \ldots + K_{A1}K_{A2}\ldots K_{An}} \qquad (3)$$

Analogisch, wenn eine in m Stufen dissoziierte Base vorliegt, gilt:

$$[B] = c_B \cdot \frac{K_{B1}K_w^{m-1}[H^+] + 2K_{B1}K_{B2}K_w^{m-2}[H^+]^2 + \ldots + mK_{B1}K_{B2}\ldots K_{Bm}[H^+]^m}{K_w^m + K_{B1}K_w^{m-1}[H^+] + K_{B1}K_{B2}K_w^{m-2}[H^+]^2 + \ldots + K_{B1}K_{B2}\ldots K_{Bm}[H^+]^m} \qquad (4)$$

Darin bedeuten $K_{A1}, K_{A2} \ldots K_{An}$ bzw. $K_{B1}, K_{B2} \ldots K_{Bm}$ die Dissoziationskonstanten der Säure bzw. Base, c_A und c_B ihre analytischen Konzentrationen, die in Äquivalenten pro Liter ausgedrückt werden. Sind die angeführten Bestandteile Borsäure und Kohlensäure, gilt:

$$\Sigma[\mathrm{B}] = 0$$

$$\Sigma[\mathrm{A}] = \frac{c_b K_b}{K_b + [\mathrm{H}^+]} + c_k \frac{K_{k1}[\mathrm{H}^+] + 2K_{k1}K_{k2}}{[\mathrm{H}^+]^2 + K_{k1}[\mathrm{H}^+] + K_{k1}K_{k2}} \qquad (5)$$

In diesen Ausdrücken bedeuten K_b, K_{k1}, K_{k2} die Dissoziationskonstanten der Borsäure und Kohlensäure (beide Stufen), c_b und c_k ihre molare Konzentration.

Der pH-Wert des Äquivalenzpunktes der Ammoniaktitrationskurve bzw. bei Anwesenheit von Borsäure und Kohlensäure wird aus den Gleichungen (2) und (5) nach der Einsetzung $c_t = c_a$ ermittelt. Nach Fortlassung einiger vernachlässigbaren kleinen Gliedern bekommt man:

$$\mathrm{pH} = -\tfrac{1}{2}\log\left(\frac{c_a \cdot K_w}{K_a} + c_b \cdot K_b + c_k \cdot K_{k1}\right) \qquad (6)$$

Für die Beurteilung der Genauigkeit der Titrationsmethode ist es wichtig die Steigerung der Titrationskurve im Äquivalenzpunkt, die durch den Richtungskoeffizient der Tangente in diesem Punkt ermittelt wird, zu kennen. Er wird aus der zugehörigen Funktionsabhängigkeit zwischen pH und c_t durch Differenzieren berechnet. Diese Abhängigkeit wird für Ammoniak und Borsäure durch die Gleichung (2), in der für die $[\mathrm{H}^+]$-Werte ein äquivalenter Ausdruck $10^{-\mathrm{pH}}$ eingesetzt wird, dargestellt. Der Differenzialquotient wird aus dem implizierten Ausdruck der Funktion $F(c_t, \mathrm{pH})$ ermittelt:

$$-\frac{\mathrm{d}c_t}{\mathrm{dpH}} = \frac{\partial F(c_t, \mathrm{pH})/\partial \mathrm{pH}}{\partial F(c_t, \mathrm{pH})/\partial c_t} \qquad (7)$$

Aus den Gleichungen (7) und (2) bzw. (5) bekommt man für den Äquivalenzpunkt ($c_t = c_a$) nach der Vereinfachung durch Fortlassung der vernachlässigbaren kleinen Gliedern (siehe Appendix):

$$-\frac{\mathrm{d}c_t}{\mathrm{dpH}} = \frac{2\ln 10(2K_a \cdot 10^{-2\mathrm{pH}} - c_a K_w - c_b K_a K_b)}{K_a 10^{-\mathrm{pH}}} \qquad (8)$$

Ermittlung der Titrationskurven

Nach den oben angeführten Beziehungen wird die Berechnung der Ammoniaktitrationskurven auch bei Anwesenheit von Borsäure und Kohlensäure durchgeführt. Wie erwähnt, wird dabei eine Volumenveränderung während der Titration nicht errechnet.

Die für sehr verdünnte Lösungen gültigen Tabellenwerte der Dissoziationskonstanten wurden mit Rücksicht auf die Ionenstärke der Lösung (im Äquivalenzpunkt) umgerechnet—Tabelle 1.

$$-\log f_i = i^2 \frac{0{,}511\sqrt{J}}{(1 + 1{,}5\sqrt{J})} - 0{,}2\,J \qquad (9)$$

$$K'_1 = f_1^2 \cdot K_1 \qquad (10)$$

$$K'_2 = f_2 \cdot K_2 \qquad (10a)$$

In diesen Gleichungen bedeuten K' die Tabellenwerte der Dissoziationskonstanten der unendlich verdünnten Lösungen, K die Dissoziationskonstanten der Lösungen mit der Ionenstärke J, f_i sind die Aktivitätskoeffizienten der i-Wertigen Ionen. Für die Berechnung der Ionenstärke wird die Ammoniumchlorid konzentration (im Äquivalenzpunkt) in Betracht genommen, während Borsäure und Kohlensäure wegen ihrer vernachlässigbarer Dissoziation unbeachtet bleiben.

Bei der hier verwendeten Konzentration der Borsäure (0,1*M*) ist nur die Ionenstärke der Lösung bei Berechnung der Dissoziationskonstante K_b in Betracht zu ziehen. Wenn die Borsäurekonzentration höher als 0,1*M* vorliegt, werden stärkere Polyborsäuren gebildet. Der K_b-Wert verändert sich dann mehr als der erhöhten Ionenstärke entspricht, und er muß aus der empirisch bestimmten Abhängigkeit pH von der Borsäurekonzentration abgeleitet werden.[4]

Der untersuchte Ammoniakkonzentrationsbereich war 10^{-4} bis $10^{-2}M$. Der Konzentrationsbegrenzung der Borsäure wurde die Anforderung für die quantitative Absorption des Ammoniaks im Verlaufe seiner Abtrennung aus der analysierten Lösung in Betracht gezogen. Die erforderliche Menge der Borsäure und ihre Konzentration in der Vorlage hängt von der Menge des Destillierten Ammoniaks ab. Zur Absorption von 20 mg Ammoniak sind 25 ml 2%iger Borsäure hinreichend. Nach Abdestillieren des erforderlichen Volumens wird die Lösung in der Vorlage verdünnt und die resultierende Borsäurekonzentration ist dann ungefähr 0,1*M*.

Tabelle 1. Die für die Berechnung verwendeten Dissoziationskonstanten (für 18°C)

		Ionenstärke der Lösung			
Komponente		0	10^{-4}	10^{-3}	10^{-2}
Wasser	K_w	$0{,}74 \cdot 10^{-14}$	$0{,}75 \cdot 10^{-14}$	$0{,}79 \cdot 10^{-14}$	$0{,}90 \cdot 10^{-14}$
Ammoniak	K_a	$1{,}75 \cdot 10^{-5}$	$1{,}76 \cdot 10^{-5}$	$1{,}88\ 10^{-5}$	$2{,}13 \cdot 10^{-5}$
Borsäure	K_b	$7{,}3 \cdot 10^{-10}$	$7{,}4 \cdot 10^{-10}$	$7{,}8 \cdot 10^{-10}$	$8{,}9\ 10^{-10}$
Kohlensäure	K_{k1}	$4{,}01 \cdot 10^{-7}$	$4{,}07 \cdot 10^{-7}$	$4{,}30 \cdot 10^{-7}$	$4{,}87 \cdot 10^{-7}$
Kohlensäure	K_{k2}	$5{,}2 \cdot 10^{-11}$	$5{,}4 \cdot 10^{-11}$	$6{,}0 \cdot 10^{-11}$	$7{,}8 \cdot 10^{-11}$

Tabelle 2. Die Richtungskoeffizienten der Tangente im Wendepunkt der Titrationskurve

$[NH_3]$, *M*	$[H_3BO_3]$, *M*	$-dc_t/d$ pH *Äquiv/l.*
10^{-4}	0	$1{,}1 \cdot 10^{-6}$
10^{-3}	0	$3{,}1 \cdot 10^{-6}$
10^{-2}	0	$9{,}3 \cdot 10^{-6}$
10^{-4}	10^{-2}	$1{,}3 \cdot 10^{-5}$
10^{-3}	10^{-2}	$1{,}3 \cdot 10^{-5}$
10^{-2}	10^{-2}	$1{,}9 \cdot 10^{-5}$
10^{-4}	10^{-1}	$3{,}9 \cdot 10^{-5}$
10^{-3}	10^{-1}	$4{,}3 \cdot 10^{-5}$

Bei den Titrationskurven des Ammoniaks, auch in Anwesenheit von Borsäure, werden die Richtungskoeffizienten der Tangenten im Wendepunkt nach der Gleichung (8) berechnet und die Ergebnisse in Tabelle 2 zusammengefaßt.

Karbonate liegen in verschiedenen Materialen häufig vor. Zum Beispiel in Naturwässern sind sie in einer Konzentration bis $10^{-2}M$ und ausnahmsweise noch höher enthalten. Bei der Destillation aus gepufferten Lösungen von pH 7,4, der bei der Wasseranalyse vorgeschrieben wird,[5] geht ein beträchtlicher Anteil von CO_2 in die Vorlage über. Kohlendioxid, als Bestandteil der Luft, kann in die Maßlösung oder in das zur Analyse verwendete redestillierte Wasser eindringen. Deshalb wird sein Einfluß schon von sehr niedrigen Mengen, die ihren Ursprung in der atmosphärischen Verunreinigungen haben können, untersucht.

Die charakteristischen Angaben der Titrationskurven-pH im Äquivalenzpunkt [berechnet aus der Gleichung (6)], pH im Wendepunkt (graphisch aus der berechneten Titrationskurve ermittelt) und die Differenz des Normallösungsverbrauches zwischen dem Äquivalentspunkt und dem Wendepunkt [aus den Gleichungen (2) und (5) berechnet], sind in Tabelle 3 verzeichnet. Einige ausgewählte Titrationskürven sind in Abb. 1 und 2 wiedergegeben.

Der berechnete Verlauf von Titrationskurven wurde experimentell mit Hilfe des pH-meters Radelkis OP-206 überprüft, wobei eine gute Übereinstimmung erreicht wurde (siehe Abbildungen 1 und 2).

Die Lösungen wurden aus redestilliertem, von CO_2 durch Auskochen befreitem Wasser, vorbereitet. Nach Herstellung der einzelnen Lösungen durch Vermischung der Grundlösungen ($0{,}01M$ NH_3, $0{,}01M$ HCl, $0{,}4M$ H_3BO_3 und $2{,}1 \times 10^{-3}M$ CO_2) wurde der

Tabelle 3. Charakteristische Angaben der Ammoniaktitrationskurven bei Anwesenheit von Borsäure und Kohlensäure

		$[CO_2]$, *M*				
$[NH_3]$, *M*	$[H_3BO_3]$, *M*	0	$5 \cdot 10^{-5}$	10^{-4}	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
(*a*) pH im Äquivalenzpunkt						
10^{-4}	0	6,65	5,34	5,19	5,04	4,84
10^{-4}	10^{-2}	5,56	5,28	5,16	5,02	4,84
10^{-4}	10^{-1}	5,07	4,99	4,96	4,89	4,77
10^{-3}	0	6,18	5,33	5,18	5,01	4,83
10^{-3}	10^{-2}	5,54	5,26	5,14	5,01	4,82
10^{-3}	10^{-1}	5,05	5,00	4,96	4,89	4,76
10^{-2}	0	5,69	5,27	5,14	5,00	4,80
10^{-2}	10^{-2}	5,44	5,21	5,10	4,98	4,79
10^{-2}	10^{-1}	5,02	4,96	4,92	4,86	4,73
(*b*) pH im Wendepunkt						
10^{-4}	0	6,65	$6{,}81^{+}$	$6{,}93^{+}$	$7{,}30^{+}$	—
10^{-4}	10^{-2}	5,56	5,46	5,34	5,14	4,86
10^{-4}	10^{-1}	5,07	5,05	5,02	4,96	4,82
10^{-3}	0	6,18	$6{,}16^{+}$	$6{,}14^{+}$	$6{,}00^{+}$	4,88
10^{-3}	10^{-2}	5,54	5,45	5,37	5,20	4,87
10^{-3}	10^{-1}	5,05	5,03	4,99	4,93	4,81
10^{-2}	0	5,69	5,51	5,46	5,22	4,86
10^{-2}	10^{-2}	5,44	5,39	5,34	5,16	4,83
10^{-2}	10^{-1}	5,02	4,99	4,95	4,90	4,74
(*c*) Die Differenz der Konzentrationen der Normallösung in der titrierten Lösung beim Erreichen des Äquivalenz- und Wendepunktes ($c_e - c_i$). In 10^{-6} Äquivalent pro Liter.						
10^{-4}	0	0	36*	77*	179*	—
10^{-4}	10^{-2}	0	4	6	4	6
10^{-4}	10^{-1}	0	1	2	2	2
10^{-3}	0	0	18*	39*	58*	3
10^{-3}	10^{-2}	0	4	6	7	5
10^{-3}	10^{-1}	0	1	2	2	3
10^{-2}	0	0	5	10	10	2
10^{-2}	10^{-2}	0	2	3	5	0
10^{-2}	10^{-1}	0	0	1	1	2

* Aus dem fiktiven Wendepunkt der Titrationskurve, bei der die zwei der Kohlensäure entsprechende Stufen nicht unterschieden werden, berechnet.

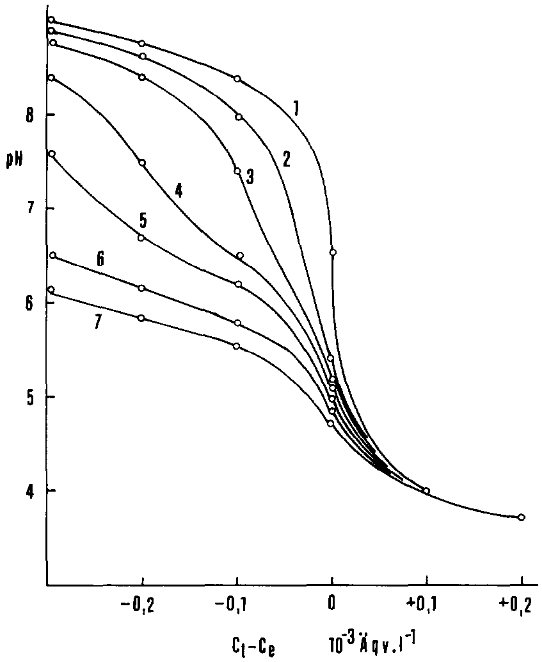

Abb. 1. Ammoniaktitrationskurven bei Anwesenheit von Kohlensäure $[NH_3] = 10^{-3}M$; ○ = gemessen, —— = berechnet.

Kurve Nr.	$[CO_2]$	Kurve Nr.	$[CO_2]$
1	0	5	$3\cdot10^{-4}M$
2	$5\cdot10^{-5}M$	6	$5\cdot10^{-4}M$
3	$10^{-4}M$	7	$10^{-3}M$
4	$2\cdot10^{-4}M$		

pH-Wert bestimmt. Die gewünschte CO_2-Konzentration wurde durch Zugabe von kohlendioxidgesättigtem redistilliertem Wasser, in dem CO_2 gleich vor Verwendung alkalimetrisch bestimmt wurde, hergestellt.

Diskussion der Ergebnisse

Die pH-Werte im Äquivalenzpunkt der Ammoniaktitrationskurven sind eine logarithmische Funktion der NH_3-Konzentration [siehe Gleichung (6)], die auch ihren Verlauf als Folge der Hydrolyse des Ammoniumsalzes beeinflußt. Äquivalenz- und Wendepunkte der Ammoniaktitrationskurven unterscheiden sich durch nicht mehr als 0,01 pH (Tabelle 3).

Aus dem Richtungskoeffizient dc_t/dpH in der Nähe des Äquivalenzpunktes (der in diesem Falle mit dem Wendepunkt identisch ist) läßt sich ableiten, daß eine Konzentrationsänderung der starken Säure in der titrierten Lösung (für $[NH_3] < 0{,}01M$) um 10^{-7} bis 10^{-8} Äquivalent pro Liter den pH-Wert nur um ein Hundertstel ändert (Tabelle 2). Bei der pH-Ablesung mit einer Genauigkeit von einem Hundertstel kann die Ammoniakkonzentration unter Verwendung der maßanalytischen, potentiometrisch indizierten Methode mit der theoretisch maximal erreichbaren Genauigkeit auf $10^{-7}M$ bestimmt werden. Bei der pH-Ablesung auf Zehntel, ist die erreichbare Genauigkeit der Ammoniakbestimmung zehnmal kleiner. Bei diesen extrem genauen Bestimmungen ist es nötig, die Volumsänderungen der Lösung während der Titration, und besonders die Anwesenheit von Kohlendioxid zu beachten. Es ist außerdem notwendig, daß die Maßlösung in die Probelösung mit entsprechender Genauigkeit zugesetzt werden kann.

Die Beeinflußung des Verlaufes von Ammoniaktitrationskurven durch schwache Säuren ist aus den Abb. 1 und 2 für Borsäure und Kohlendioxid ersichtlich. Da Säuren die Titrationskurven im alkalischen Gebiete deformieren, verschiebt sich der Äquivalenzpunkt zu niedrigen pH-Werten. Diese Wirkung ist von der Säurekonzentration und von der Größe ihrer Dissoziationskonstante abhängig. Die Identität des Aquivalenzpunktes mit dem Wendepunkt der Titrationskurve von Ammoniak bei Anwesenheit der Borsäure stimmt mit einer Genauigkeit auf Hundertstel pH-Wert (Tabelle 3).

Der Richtungskoeffizient der Tangente im Äquivalenzpunkt wird durch eine Borsäurezugabe auf Werte von 10^{-5} bis 5×10^{-5} Äquivalent pro Liter erhöht. Die Änderung der Säurekonzentration c_t um etwa 10^{-6} Äquivalent pro Liter bewirkt in der Umgebung dieses Punktes eine pH-Änderung von 0,01. Deshalb ist bei Anwesenheit der Borsäure die theoretisch erreichbare Genauigkeit der Ammoniakbestimmung $10^{-6}M$ unter Verwendung der potentiometrischen Indikation bei pH-Ablesung auf Hundertstel. Bei pH-Ablesung auf Zehntel ist die erreichbare Genauigkeit $10^{-5}M$.

Ähnlich wie Borsäure verhält sich auch Kohlensäure, deren Wirkung aber deutlicher in Übereinstimmung mit der Größe ihrer Dissoziationskonstante ist. Bei dieser Säure ist ihre zweite Dissoziationsstufe zu beachten, erkennbar durch einen zweiten Wendepunkt, besonders eindeutig bei höheren CO_2-Konzentrationen. Bei niedrigen CO_2-Konzentrationen ist nur ein Wendepunkt deutlich, der aber stark vom Äquivalenzpunkt abweicht (Tabelle 3). Bei einer Kohlensäurekonzentration höher als $3 \times 10^{-4}M$,

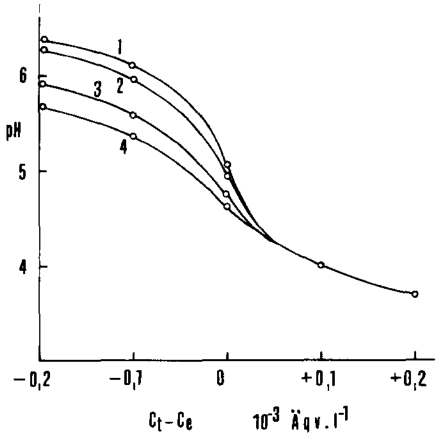

Abb. 2. Ammoniaktitrationskurven bei Anwesenheit von Borsäure und Kohlensäure $[NH_3] = 10^{-3}M$; $[H_3BO_3] = 10^{-1}M$

Kurve Nr.	$[CO_2]$	Kurve Nr.	$[CO_2]$
1	0	3	$5\ 10^{-4}M$
2	$10^{-4}M$	4	$10^{-3}M$

Tabelle 4. Die maximal zulässige CO_2-Konzentrationen (M) für die massanalytische Ammoniakbestimmung der verlangten Genauigkeit

	verlangte Genauigkeit der Bestimmung (in Mol NH_3 pro Liter)			
$[NH_3]$, M	10^{-4}	10^{-5}	10^{-6}	10^{-7}
(a) potentiometrische Indikation:				
für $[H_3BO_3] = 0$				
10^{-4}	10^{-3}	$2 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$2 \cdot 10^{-7}$
10^{-3}	10^{-3}	$3 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$3 \cdot 10^{-7}$
10^{-2}	10^{-3}	10^{-3}	10^{-5}	10^{-6}
für $[H_3BO_3] = 10^{-2}$–$10^{-1}M$				
10^{-4}–10^{-2}	10^{-3}	10^{-3}	$5 \cdot 10^{-5}$	—
(b) visuelle Indikation (im pH-Bereiche 5,7–4,1):				
für $[H_3BO_3] = 0$–$10^{-1}M$				
10^{-4}–10^{-2}	10^{-4}	—	—	—
(c) visuelle Indikation (im pH-Bereiche 5,0–4,8):				
für $[H_3BO_3] = 0$–$10^{-1}M$				
10^{-4}–10^{-2}	10^{-3}	10^{-4}	—	—

oder in Anwesenheit von Borsäure kann man den Wendepunkt der ersten Stufe, dessen Abweichung vom Äquivalenzpunkt kleiner ist, bestimmen. Liegt die CO_2-Konzentration höher als $10^{-3}M$ vor, wird die Titrationskurve so flach, daß die Ammoniakbestimmung sich nur mit einer Genauigkeit von $10^{-3}M$ durchführen läßt.

Die Angaben über den zulässigen CO_2-Konzentrationen bei der maßanalytischen Ammoniakbestimmung mit der verlangten Genauigkeit sind in Tabelle 4 verzeichnet. Sie gehen aus dem Verlauf der Titrationskurven und aus den in Tabellen 3 und 5 angeführten Werten hervor. Diese Angaben dokumentieren die Abhängigkeit der angeführten Grenzwerte von der Ammoniak- und Borsäurekonzentration in der analysierten Probe.

Von den azidobasischen Indikatoren, die bei der maßanalytischen Ammoniakbestimmung am häufig-

Tabelle 5. Die Differenz (mÄquiv./l.) der Konzentration der Normallösung in der titrierten Lösung beim Erreichen des angeführten pH-Wertes und des Äquivalenzpunktes ($c_t - c_e$)

		$[H_3BO_3] = 0$		$[H_3BO_3] = 10^{-1}M$	
$[NH_3]$, M	$[CO_2]$, M	pH 5,7	pH 4,1	pH 5,7	pH 4,1
10^{-2}	0	0	+0,079	−0,044	+0,078
	$5 \cdot 10^{-5}$	−0,010	+0,079	−0,054	+0,078
	10^{-4}	−0,020	+0,079	−0,064	+0,078
	$5 \cdot 10^{-4}$	−0,098	+0,076	−0,142	+0,075
	10^{-3}	−0,196	+0,073	−0,240	+0,072
	$5 \cdot 10^{-3}$	−0,981	+0,049	−1,025	+0,048
10^{-4}	0	+0,002	+0,079	−0,037	+0,078
	$5 \cdot 10^{-5}$	−0,006	+0,079	−0,045	+0,078
	10^{-4}	−0,015	+0,079	−0,054	+0,078
	$5 \cdot 10^{-4}$	−0,082	+0,077	−0,121	+0,076
	10^{-3}	−0,167	+0,074	−0,206	+0,073
	$5 \cdot 10^{-3}$	−0,845	+0,054	−0,884	+0,053
		pH 5,0	pH 4,8	pH 5,0	pH 4,8
10^{-2}	0	+0,010	+0,016	+0,001	+0,010
	$5 \cdot 10^{-5}$	+0,008	+0,015	−0,001	+0,009
	10^{-4}	+0,005	+0,013	−0,004	+0,007
	$5 \cdot 10^{-4}$	−0,013	+0,001	−0,001	−0,005
	10^{-3}	−0,036	−0,014	−0,045	−0,020
	$5 \cdot 10^{-3}$	−0,222	−0,133	−0,231	−0,139
10^{-4}	0	+0,010	+0,016	+0,003	+0,011
	$5 \cdot 10^{-5}$	+0,008	+0,015	+0,001	+0,010
	10^{-4}	+0,006	+0,014	+0,001	+0,009
	$5 \cdot 10^{-4}$	−0,010	+0,003	−0,017	−0,002
	10^{-3}	−0,029	−0,009	−0,036	−0,019
	$5 \cdot 10^{-3}$	−0,186	−0,109	−0,193	−0,114

stens verwendet werden, ist Methylrot oder seine Mischung mit Methylenblau (Indikator nach Taschiro) zu nennen. Die Indikatorkonstante ($pK_i = 4{,}9$) ist durch den ersten Bestandteil bestimmt. Methylenblau macht nur den Farbumschlag für das menschliche Auge deutlicher. Die Farbänderung des Indikators wird durch den Bereich von 10 bis 90% aus der erreichbaren Intensität der roten Farbe, die in diesem Falle maßgebend ist, bestimmt. Das entspricht dem pH-Bereiche 4,1–5,7. Eine genauere Unterscheidung kann man durch Verwendung einer auf den pH-Wert 4,9 gepufferten Vergleichslösung erreichen, In diesem Falle läßt sich in der Nähe von pK_{i1} die Farbintensität mit Genauigkeit auf ± 6% gegenüber ihrer maximaler Intensität, die bei einer extremen Azidität erreicht wird, zuverlässig unterscheiden. Dieses Farbintervall entspricht dem pH-Bereich 4,8–5,0.

Die Differenzen des Verbrauches an Normallösung der Säure beim Erreichen des gewünschten pH-Wertes und Äquivalenzpunktes im Verlaufe der Ammoniaktitration sind in Tabelle 5 angegeben. Diese Differenzen sind für die Beurteilung der erreichbaren Genauigkeit entscheidend.

Im ersten Falle, d.h. für den Farbumschlag, der durch den pH-Bereich 5,7–4,1 bestimmt wird, ist bei der Ammoniaktitration, auch in Anwesenheit der Borsäure, die maximal erreichbare Genauigkeit der Ammoniakbestimmung $10^{-4}M$. Durch das Verengen des pH-Intervalls, in dem der Farbumschlag wahrnehmbar ist, auf 5,0 bis 4,8, wird die Genauigkeit auf $10^{-5}M$ erhöht.

Bei Anwesenheit von Kohlendioxid wird die Titrationskurve flacher, wodurch die Indikation erschwert wird. Die erreichbare Genauigkeit der Ammoniakbestimmung ist bei der Indikation mit Methylrot $10^{-4}M$ unter Voraussetzung, daß die CO_2-Konzentration $10^{-4}M$ nicht übersteigt. Unter den gleichen Bedingungen kann man durch die Verwendung von Indikatorvergleichslösung eine Genauigkeit von $10^{-5}M$ erzielen. Liegt die CO_2-Konzentration höher als $10^{-4}M$ vor (bis ungefähr $2 \cdot 10^{-3}M$), läßt sich bei visueller Indikation nur eine Genauigkeit von $10^{-3}M$. bzw. unter Verwendung von Vergleichslösung $10^{-4}M$ erreichen.

Bei der genauen maßanalytischen Bestimmung muß man aber berücksichtigen, daß auch der Indikator beim Übergang von einer Form in die andere einen gewissen Verbrauch an Normallösung aufweist. Methylrot in der Menge von 0,1 ml 0,1%iger Lösung verbraucht bei dieser Umwandlung 0,003 ml 0,1N Normallösung.[2] Diese Tatsache wurde bei den in Tabelle 5 angegebenen Werten außer Acht gelassen.

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APPENDIX

Berechnung der Gleichung (8) aus der Gleichung (2): $c_t + \dfrac{c_b K_b}{K_b + [H^+]} = [H^+] + \dfrac{c_a K_a [H^+]}{K_a[H^+] + K_w} - \dfrac{K_w}{[H^+]}$

oder $F'(c_t, [H^+]) \equiv [H^+]^4 A + [H^+]^3 B + [H^+]^3 c_t D + [H^+]^2 E + [H^+]^2 c_t L + [H^+]P + [H^+] c_t S + T = 0$

wo $A = K_a$, $B = K_a K_b + K_a c_a + K_w$; $D = -K_a$; $E = K_a K_b c_a - K_a K_b c_b + K_b K_w - K_a K_w$, $L = -K_a K_b - K_w$.
$P = -K_a K_b K_w - K_b K_w c_b - K_w^2$; $S = -K_b K_w$; $T = -K_b K_w^2$

$$F'(c_t, 10^{-pH}) = F(c_t, pH)$$

$$\frac{\partial F(c_t, pH)}{\partial c_t} = 10^{-3pH} D + 10^{-2pH} L + 10^{-pH} S$$

$$\frac{\partial F(c_t, pH)}{\partial pH} = -\ln 10 \{4 \cdot 10^{-4pH} A + 3 \cdot 10^{-3pH}(B + c_t D) + 2 \cdot 10^{-2pH}(E + c_t L) + 10^{-pH}(P + c_t S)\}$$

aus der Gleichung (7):

$$-\frac{dc_t}{dpH} = \frac{\ln 10 \{4\; 10^{-3pH} A + 3 \cdot 10^{-2pH}(B + c_t D) + 2 \cdot 10^{-pH}(E + c_t L) + (P + c_t S)\}}{10^{-2pH} D + 10^{-pH} L + S}$$

für $c_t = c_a$ (Äquivalenzpunkt):

$$-\frac{dc_t}{dpH} = \frac{\begin{array}{r}\ln 10 \{4\; 10^{-3pH} K_a + 3 \cdot 10^{-2pH}(K_a K_b + K_w) + 2\; 10^{-pH}(K_b K_w - K_a K_w - K_a K_b c_b - K_w c_a) \\ - K_a K_b K_w - K_w^2 - K_b K_w c_b - K_b K_w c_a\}\end{array}}{10^{-2pH} K_a + 10^{-pH} K_a K_b + 10^{-pH} K_w + K_b K_w}$$

vereinfacht durch Vernachlässigung der kleinen Gliedern:

$$-\frac{dc_t}{dpH} = \frac{\ln 10 \{4\; 10^{-3pH} K_a - 2\; 10^{-pH}(K_a K_b c_b + K_w c_a)\}}{10^{-2pH} K_a}$$

daraus läßt sich schon leicht die Gleichung (8) ableiten.

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DIFFUSION-LAYER MODEL FOR COPPER SOLID-STATE CHALCOCITE MEMBRANE ELECTRODE; SENSITIVITY TO COPPER(II) IONS

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(*Received* 22 *July* 1975. *Revised* 20 *November* 1975. *Accepted* 29 *January* 1976)

Summary—The diffusion-layer model for the chalcocite (Cu_2S) membrane electrode is discussed. It is equivalent to a simpler model based on exchange reactions at the electrode surface. The chalcocite is sensitive to copper(I) and copper(II) ions and the theoretically predicted response is in good agreement with experimental data. The membrane is a conductor, but this does not significantly affect its function as an ion detector. The limitation of the electrode is the membrane solubility as shown when Cu(II) ions in contrast to copper(I) ions are strongly complexed.

The reason for the sensitivity to copper(II) ions of solid-state electrodes based on copper(I) chalcogenides[1–7] is not fully understood. Heerman and Rechnitz[6] have stated that the copper(I) ions should be considered as the significant ions for the copper(I) sulphide electrode and Hansen *et al.*[8] agree that the contribution of Cu(I) ions to the mechanism should be taken into account.

This paper proposes a model for the function of the chalcocite (Cu_2S) membrane electrode and its sensitivity to copper(II) ions.

EXPERIMENTAL

The indicator electrode with an internal solution containing copper(II) chloride was prepared as described previously.[7] The potential was measured with an N-512 meter (ELPO-Wrocław) and potentiograph E-336 (Metrohm). The saturated calomel electrode used as reference was connected through a salt bridge. The copper(I) solution was obtained by coulometric generation from the copper electrode in a chloride medium. The solutions were prepared from analytical grade reagents and doubly distilled water.

THEORETICAL

In various models of electrode action given by several authors[9–13] the potential E of the half-cell formed by the membrane electrode is given by

$$E = E_M + E_R \qquad (1)$$

where E_M is the membrane potential and E_R the internal reference potential.

Eisenman[9] and Buck[11] describe the membrane potential as the sum of the diffusion potential E_D in the membrane and the potential E_B on the phase boundaries, while the membrane is considered as an ionic conductor. In the Pungor and Tóth[12] model only the potential E_R is taken into account, while the condition concerning ionic conductance is not irremissible. Both models result in formally analogous equations relating the potential of the electrode to the ionic activity (where admissible, concentrations are used instead of activities). For the chalcocite electrode this may be expressed as

$$E = \text{const.} + \frac{RT}{F}\ln([Cu^+] + K^{pot}_{Cu^+,M_i}[M_i^{2+}]^{1/2}) \qquad (2)$$

where $[Cu^+]$, and $[M_i^{2+}]$ are the actual concentrations of the main (Cu^+) and interfering (M^{2+}) ions, and $K^{pot}_{Cu^+,M_i}$ is the corresponding potentiometric selectivity coefficient.

In the Eisenman[9] and Buck[11] models (for miscible salts) the selectivity coefficient is equal to the product of the ratio of the ionic mobilities U_{Cu^+}/U_{M_i} in the membrane and the equilibrium constant K of the exchange reaction

$$M^{2+} + Cu_2S \rightleftharpoons MS + 2Cu^+ \qquad (3)$$

In the Pungor–Tóth[12] and Buck[11] models (for immiscible salts) the selectivity coefficient is directly related to the same equilibrium constant, and equal to the ratio of the solubility products K_{so} of the corresponding sulphides (with an exponent which follows from the stoichiometry): $K_{so(Cu_2S)}/K_{so(MS)}$. When no other mechanism of interference is assumed, the exchange reaction provides some of the concentration of the main ion causing the electrode response.

In the electrode model discussed here we assume that the electrode response is caused by the main ion concentration at the electrode surface. Three contributions may be discussed: the first is due to the analytical concentration in solution $[Cu^+]^A$, the second to the finite solubility of the membrane $[Cu^+]^L$, and the last to the exchange reaction with interfering ions $[Cu^+]^I$. This is represented as:

$$[Cu^+]_0 = [Cu^+]_0^A + [Cu^+]_0^L + [Cu^+]_0^I \qquad (4)$$

where the suffix indicates concentrations at the electrode surface, in contrast to bulk concentrations.

The concentration $[Cu^+]_0^L$ is directly related to the conditional solubility product

$$K'_{so(Cu_2S)} = K_{so(Cu_2S)}\alpha_{S(H)}\alpha^2_{Cu^+} = [Cu(I)']^2\,[S']$$

of the electrode-active substance, *i.e.*, Cu_2S, where the α values represent the side-reaction coefficients. The $\alpha_{S(H)}$ and α_{Cu^+} values depend on pH and the chloride concentration, respectively. Since

$$[S'] = \tfrac{1}{2}[Cu(I)']$$

we obtain

$$[Cu^+]_0^L = \left[\frac{2K_{so(Cu_2S)}\alpha_{S(H)}}{\alpha_{Cu^+}}\right]^{1/3} \tag{5}$$

Perhaps in the limit the concentration of interstitial copper(I) ions may become important, as found by Morf, Kahr and Simon[14] for silver(I) and the Ag_2S electrode. In the present discussion this factor is not considered, but from our experiments its value is about $10^{-10}M$.

The relation (5) as a function of pH for two different chloride concentrations is graphically presented in Fig. 1. It can be seen that the value of $[Cu^+]_0^L$ is mostly well below $10^{-12}M$ and therefore this contribution is small compared to the others.

The concentration $[Cu^+]_0^E$ represents the contribution to the electrode response caused by the presence of interfering ions having particular selectivity coefficients. The coefficients are expected to be larger than unity for Ag^+ and Hg^{2+}, which interfere even in small concentrations by covering the membrane with their sulphides, preventing further contact of the chalcocite membrane with the solution. For other common ions, including Cu^{2+}, the selectivity coefficients are significantly less than unity.

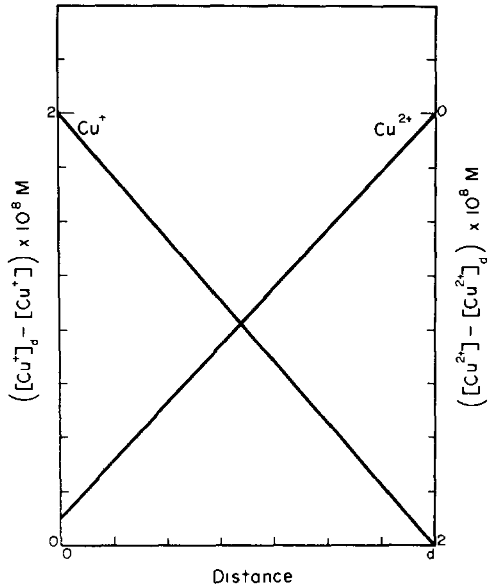

Fig. 2. Scheme for the diffusion layer $[Cu^+] = 1.6 \times 10^{-10}M$, $[Cu^{2+}] = 1.0 \times 10^{-3}M$ in bulk solution. $A = 2$, $K = 4 \times 10^{-13}$. [Calculated from equations (8) and (9).]

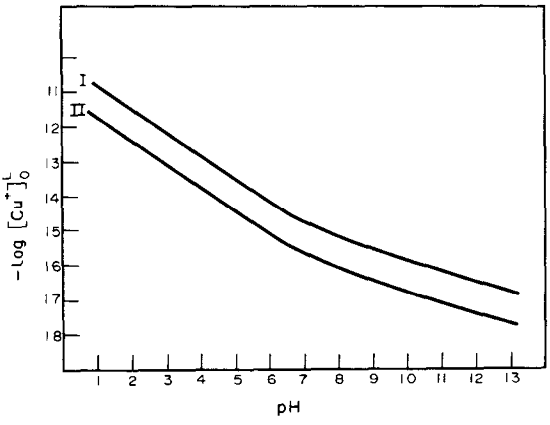

Fig. 1. Concentration of free copper(I) in equilibrium with the chalcocite membrane as a function of pH. Curve I—in 0.1*M* KCl, curve II—in 1*M* KCl.

For the equilibrium constant, K, of the reaction

$$Cu_2S + Cu^{2+} \rightleftharpoons CuS + 2Cu^+ \tag{6}$$

which is equal to the ratio of the solubility products, we obtain

$$K = ([Cu^+]_0)^2/[Cu^{2+}]_0 \tag{7}$$

where the concentrations are those at the electrode surface. When the reaction is sufficiently rapid and reversible a diffusion layer is formed, shown schematically in Fig. 2. Assuming diffusive transport at the electrode surface, linearity of the concentration gradients and independence of the diffusion coefficients on the diffusion layer thickness, we obtain from the mass balance

$$D_{Cu^+}([Cu^+]_0 - [Cu^+]) = 2D_{Cu^{2+}}([Cu^{2+}] - [Cu^{2+}]_0) \tag{8}$$

where D represents the diffusion coefficient of the ion indicated. From equations (7) and (8) the value of $[Cu^+]_0$ may be calculated as a function of the Cu^+ and Cu^{2+} concentrations:

$$[Cu^+]_0 = -\frac{AK}{4} + \frac{1}{2}\left(\frac{A^2K^2}{4} + 2AK[Cu^+] + 4K[Cu^{2+}]\right)^{1/2} \tag{9}$$

where $A = D_{Cu^+}/D_{Cu^{2+}}$, which has a numerical value of approximately 2, if the diffusion coefficient of Cu^+ (not reported in the literature) is taken as slightly smaller than that of Ag^+.

The value of $[Cu^+]_0$ should really be indicated as $[Cu^+]_0^E$, because it represents the contribution of the exchange reaction (interference) when the membrane solubility and analytical concentration contributions may be neglected. When the other contributions should be taken into account then the total concentration may be represented as:

$$[\mathrm{Cu}^+]_0 = [\mathrm{Cu}^+]_0^{\mathrm{A}} + [\mathrm{Cu}^+]_0^{\mathrm{L}} + \left\{ -\frac{AK}{4} + \frac{1}{2}\left(\frac{A^2K^2}{4} + 2AK[\mathrm{Cu}^+] + 4K[\mathrm{Cu}^{2+}] \right)^{1/2} \right\} \tag{10}$$

which enters into the equation for the potential:

$$E = \text{const.} + \frac{RT}{F}\ln[\mathrm{Cu}^+]_0. \tag{11}$$

This equation is valid for the intermediate range but no precise derivation of this equation can be presented. Nevertheless, from measurements in the concentration ranges used in our experiments, it evidently describes the behaviour of the electrode with enough accuracy for its practical use.

RESULTS AND DISCUSSION

The model described, in which the surface concentrations are different from those in the bulk of the solution, is similar to that given for the cyanide electrode.[13,15] The expanded form of equation (11):

$$E = \text{const.} + \frac{RT}{F}\ln\left\{ [\mathrm{Cu}^+]_0^{\mathrm{A}} + [\mathrm{Cu}^+]_0^{\mathrm{L}} + \left[-\frac{AK}{4} + \frac{1}{2}\left(\frac{A^2K^2}{4} + 2AK[\mathrm{Cu}^+] + 4K[\mathrm{Cu}^{2+}] \right)^{1/2} \right] \right\}, \tag{12}$$

may be simplified when some justifiable approximations are introduced. When $[\mathrm{Cu}^{2+}]$ is significantly greater than $4 \times 10^{-13}M$, *i.e.* $[\mathrm{Cu}^{2+}] \gg K$, then in equation (12) the total term corresponding to the exchange reaction is simplified to $K^{1/2}[\mathrm{Cu}^{2+}]^{1/2}$, and the equation is the same as given previously [(2)] on the basis of the Pungor–Tóth model.[12] The value of the constant $K = 4 \times 10^{-13}$ for reaction (6) is based on the solubility products,[19] and is an idealized approach. In real conditions the side-reaction coefficient effect of Cu^+ with chloride ions is much stronger than that of Cu^{2+}, shifting the reaction (6) towards the right-hand side. The dependence of pK' on the chloride concentration is shown in Fig. 3.

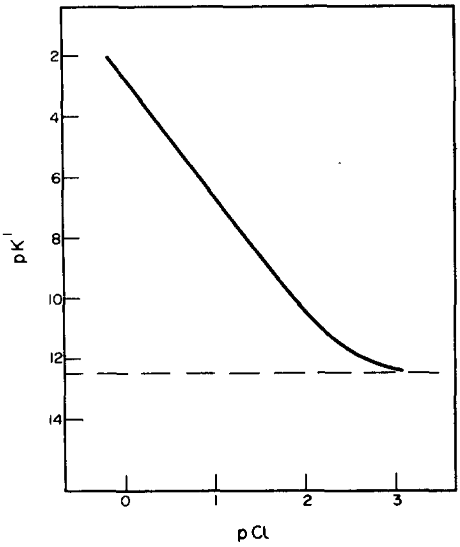

Fig. 3. Conditional constant of the exchange reaction $\mathrm{Cu}^{2+} + \mathrm{Cu_2S} \rightleftharpoons 2\mathrm{Cu}^+ + \mathrm{CuS}$ as a function of chloride concentration.

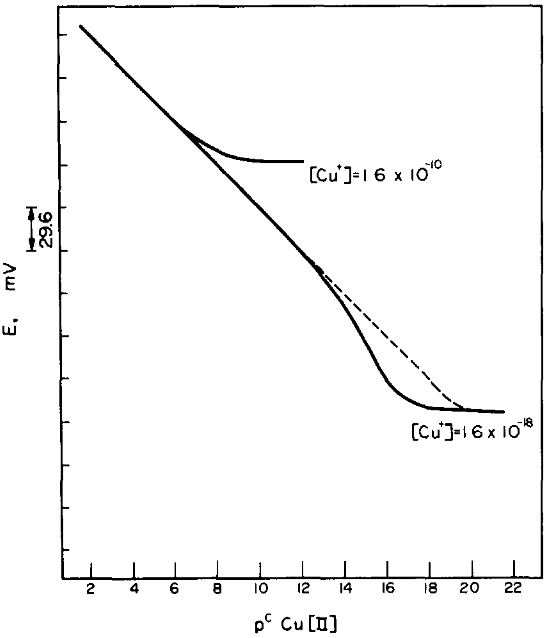

Fig. 4. Theoretical potential response curves calculated on the basis of the diffusion barrier model—solid line, and on the basis of the Pungor–Tóth model—dashed line.

For low concentrations of copper(I), *i.e.*, when $[\mathrm{Cu}^+] \ll K[\mathrm{Cu}^{2+}]^{1/2}$ the electrodes become sensitive to copper(II). In such conditions the chalcocite electrode may be treated as a copper(II) electrode, for which the copper(II) ions are the main ions. In this case the simplified model may be treated as a special case of the diffusion layer model. The potential response curves $E = f([\mathrm{Cu}^{2+}])$ have been calculated for several levels of concentration of copper(I) ions in solution (Fig. 4). It can be seen that only at the lowest levels is there departure from linearity.

The value of the selectivity coefficient of the chalcocite electrode is 4×10^{-13}, which is the equilibrium constant of the exchange reaction. The potentiometric selectivity coefficient, determined experimentally, $K^{\mathrm{pot}}_{\mathrm{Cu^+,Cu^{2+}}} = K^{1/2} = 6.3 \times 10^{-7}$, as described previously.[7] The magnitude of these values suggests that the extent of the exchange reaction is not large enough to allow the electrode to function according to the scheme $\mathrm{Cu_2S/CuS/Cu^{2+}}$ (external solution).

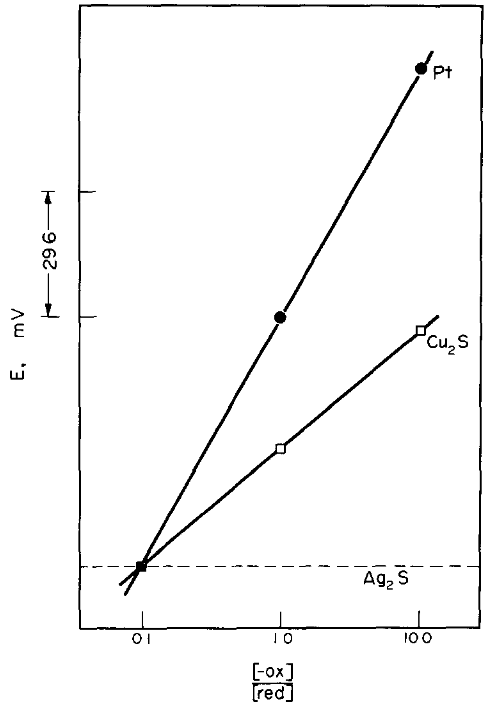

Fig. 5 Dependence of the electrode potential on the $[Fe(CN)_6^{3-}]$:$[Fe(CN)_6^{4-}]$ ratio at pH 5 The Ag_2S relationship is given according to Weser and Pungor [17]

It must be mentioned that the diffusion layer model does not specify the type of conductivity in the membrane. Because of the absence of β-Ag_2S, as the ionic conductor, one can expect for the chalcocite electrode a significant contribution of electron conductivity.[16] This has been confirmed experimentally by measuring the redox response of the electrode in comparison with that of the platinum electrode (Fig. 5).

Experimental potential response curves have been prepared for the chalcocite electrode in solutions containing both copper(I) and copper(II) ions. In the case of the copper(II) response (Fig. 6, curve I) the medium used was 1*M* potassium nitrate. The experimental points obtained by successive dilutions agree with those calculated on the assumption that $[Cu^+]$ is not greater than $1.6 \times 10^{-10}M$. As can be seen by comparison with Fig. 4 the curve is linear with the theoretical slope of 29.6 mV per decade. The slight curvature at low concentrations is due to $[Cu^+]_0^L$.

The response curve for copper(I) ions (Fig. 6, curve II) has been prepared on the basis of the analytical concentration of copper(I), generated coulometrically at pH 3 in 1*M* potassium chloride. The concentration of free (hydrated) Cu^+ ions is significantly lower. The constant degree of complexation due to the constant concentration of Cl^- as the predominant ligand, ensures that the slope has the theoretical value of 59.2 mV per decade, which is in good agreement with the calculated curve. Under these conditions the concentration of Cu^{2+} is insufficient for the formation of a CuS layer at the electrode surface. Therefore the contribution of the exchange concentration$[Cu^+]_0^L$ is negligible and except in a very low concentration range only the term $[Cu^+]_0^A$ is significant in equation (11).

In the presence of both copper(I) and copper(II) ions, at equal analytical concentrations, the potential response curve is influenced by both ions. The extent of complexation of copper(I) in 1*M* chloride solution is significantly greater ($\alpha_{Cu^+(Cl)} = 8.5 \times 10^4$)[18] than that of the copper(II). Therefore the α-value compensates partially for the small value of selectivity coefficient $K^{pot}_{Cu^+,Cu^{2+}}$. Both types of ion contribute to the slope, which in the range of concentrations indicated is approximately 55 mV per decade (Fig. 6, curve III).

The electrode limit, defined by $[Cu^+]_0^L$, may be reached under conditions where the copper(II) ions are more strongly complexed that the copper(I) ions. This happens, for example, in the potentiometric titration of copper(II) with EDTA. Because the copper(II) concentration drops significantly after the end-point, $[Cu^+]_0^L$ becomes the decisive factor influencing the potential response. From the potential limit the value of $[Cu^+]_0^L$ may be estimated and the α_{Cu} value calculated from equation (5). This makes it possible to estimate the stability constants of copper(I) complexes. In the case of the TETREN titration of copper it may be expected that both copper ions are complexed, therefore the limit is strongly suppressed, and the potentials after the end-point are much lower.[7]

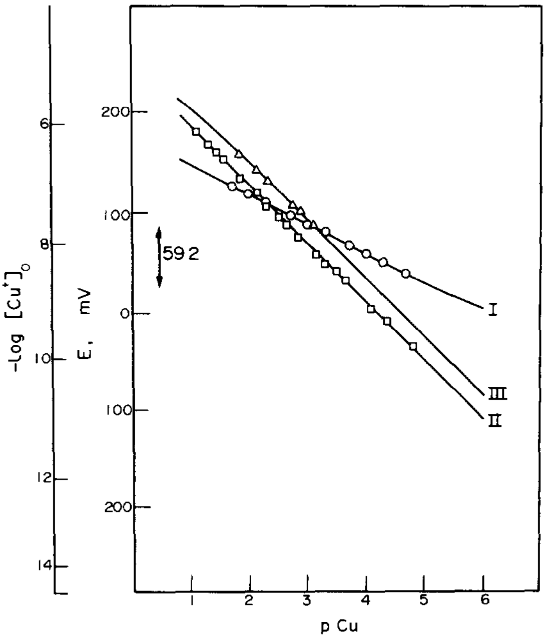

Fig. 6. Potential response curves of the chalcocite membrane electrode, in copper(II) solution (in 1*M* KNO_3). Curve I, Copper(II) solution in 1*M* KNO_3. Curve II, copper(I) solution in 1*M* KCl. Curve III, equivalent amounts of copper(I) and copper(II) in 1*M* KCl Experimental points are indicated on the theoretically calculated curves (solid lines).

The value of the stability constant of the copper(I)-TETREN complex calculated on this basis is approximately 10^8.

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In various models of electrode action given by several authors[9-13] the potential E of the half-cell formed by the membrane electrode is given by

$$E = E_M + E_R \tag{1}$$

where E_M is the membrane potential and E_R the internal reference potential.

Eisenman[9] and Buck[11] describe the membrane potential as the sum of the diffusion potential E_D in the membrane and the potential E_B on the phase boundaries, while the membrane is considered as an ionic conductor. In the Pungor and Tóth[12] model only the potential E_R is taken into account, while the condition concerning ionic conductance is not irremissible. Both models result in formally analogous equations relating the potential of the electrode to the ionic activity (where admissible, concentrations are used instead of activities). For the chalcocite electrode this may be expressed as

$$E = \text{const.} + \frac{RT}{F}\ln([\mathrm{Cu}^+] + K^{\mathrm{pot}}_{\mathrm{Cu}^+,\mathrm{M}_i}[\mathrm{M}_i^{2+}]^{1/2}) \tag{2}$$

where $[Cu^+]$, and $[M_i^{2+}]$ are the actual concentrations of the main (Cu^+) and interfering (M^{2+}) ions, and $K^{pot}_{Cu^+,M_i}$ is the corresponding potentiometric selectivity coefficient.

In the Eisenman[9] and Buck[11] models (for miscible salts) the selectivity coefficient is equal to the product of the ratio of the ionic mobilities U_{Cu^+}/U_{M_i} in the membrane and the equilibrium constant K of the exchange reaction

$$\mathrm{M}^{2+} + \mathrm{Cu_2S} \rightleftharpoons \mathrm{MS} + 2\mathrm{Cu}^+ \tag{3}$$

In the Pungor–Tóth[12] and Buck[11] models (for immiscible salts) the selectivity coefficient is directly related to the same equilibrium constant, and equal to the ratio of the solubility products K_{s0} of the corresponding sulphides (with an exponent which follows from the stoichiometry): $K_{s0(Cu_2S)}/K_{s0(MS)}$. When no other mechanism of interference is assumed, the exchange reaction provides some of the concentration of the main ion causing the electrode response.

In the electrode model discussed here we assume that the electrode response is caused by the main ion concentration at the electrode surface. Three contributions may be discussed: the first is due to the analytical concentration in solution $[Cu^+]^A$, the second to the finite solubility of the membrane $[Cu^+]^L$, and the last to the exchange reaction with interfering ions $[Cu^+]^I$. This is represented as:

$$[\mathrm{Cu}^+]_0 = [\mathrm{Cu}^+]_0^A + [\mathrm{Cu}^+]_0^L + [\mathrm{Cu}^+]_0^I \tag{4}$$

where the suffix indicates concentrations at the electrode surface, in contrast to bulk concentrations.

The concentration $[Cu^+]_0^L$ is directly related to the conditional solubility product

$$K'_{so(Cu_2S)} = K_{so(Cu_2S)}\alpha_{S(H)}\alpha^2_{Cu^+} = [Cu(I)']^2\,[S']$$

of the electrode-active substance, *i.e.*, Cu_2S, where the α values represent the side-reaction coefficients. The $\alpha_{S(H)}$ and α_{Cu^+} values depend on pH and the chloride concentration, respectively. Since

$$[S'] = \tfrac{1}{2}[Cu(I)']$$

we obtain

$$[Cu^+]_0^L = \left[\frac{2K_{so(Cu_2S)}\alpha_{S(H)}}{\alpha_{Cu^+}}\right]^{1/3} \qquad (5)$$

Perhaps in the limit the concentration of interstitial copper(I) ions may become important, as found by Morf, Kahr and Simon[14] for silver(I) and the Ag_2S electrode. In the present discussion this factor is not considered, but from our experiments its value is about $10^{-10}M$.

The relation (5) as a function of pH for two different chloride concentrations is graphically presented in Fig. 1. It can be seen that the value of $[Cu^+]_0^L$ is mostly well below $10^{-12}M$ and therefore this contribution is small compared to the others.

The concentration $[Cu^+]_0^E$ represents the contribution to the electrode response caused by the presence of interfering ions having particular selectivity coefficients. The coefficients are expected to be larger than unity for Ag^+ and Hg^{2+}, which interfere even in small concentrations by covering the membrane with their sulphides, preventing further contact of the chalcocite membrane with the solution. For other common ions, including Cu^{2+}, the selectivity coefficients are significantly less than unity.

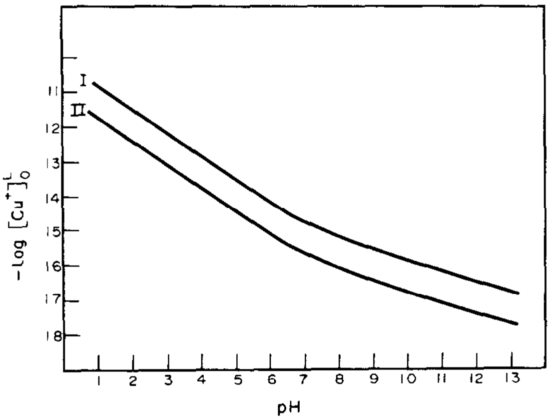

Fig. 1. Concentration of free copper(I) in equilibrium with the chalcocite membrane as a function of pH. Curve I—in 0.1*M* KCl, curve II—in 1*M* KCl.

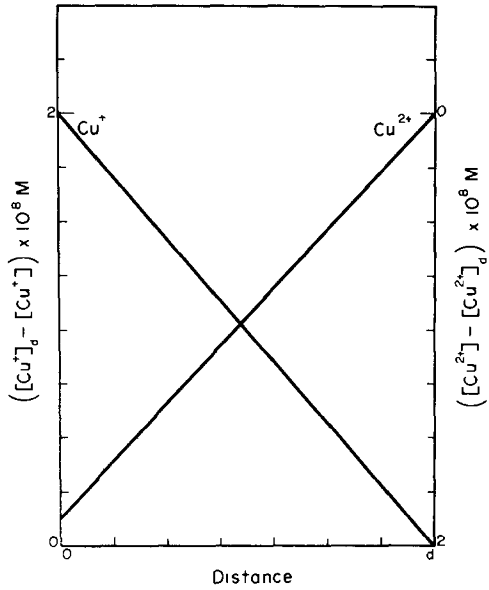

Fig. 2. Scheme for the diffusion layer $[Cu^+] = 1.6 \times 10^{-10}M$, $[Cu^{2+}] = 1.0 \times 10^{-3}M$ in bulk solution. $A = 2$, $K = 4 \times 10^{-13}$. [Calculated from equations (8) and (9).]

For the equilibrium constant, K, of the reaction

$$Cu_2S + Cu^{2+} \rightleftharpoons CuS + 2Cu^+ \qquad (6)$$

which is equal to the ratio of the solubility products, we obtain

$$K = ([Cu^+]_0)^2/[Cu^{2+}]_0 \qquad (7)$$

where the concentrations are those at the electrode surface. When the reaction is sufficiently rapid and reversible a diffusion layer is formed, shown schematically in Fig. 2. Assuming diffusive transport at the electrode surface, linearity of the concentration gradients and independence of the diffusion coefficients on the diffusion layer thickness, we obtain from the mass balance

$$D_{Cu^+}([Cu^+]_0 - [Cu^+]) = 2D_{Cu^{2+}}([Cu^{2+}] - [Cu^{2+}]_0) \qquad (8)$$

where D represents the diffusion coefficient of the ion indicated. From equations (7) and (8) the value of $[Cu^+]_0$ may be calculated as a function of the Cu^+ and Cu^{2+} concentrations:

$$[Cu^+]_0 = -\frac{AK}{4} + \frac{1}{2}\left(\frac{A^2K^2}{4} + 2AK[Cu^+] + 4K[Cu^{2+}]\right)^{1/2} \qquad (9)$$

where $A = D_{Cu^+}/D_{Cu^{2+}}$, which has a numerical value of approximately 2, if the diffusion coefficient of Cu^+ (not reported in the literature) is taken as slightly smaller than that of Ag^+.

The value of $[Cu^+]_0$ should really be indicated as $[Cu^+]_0^E$, because it represents the contribution of the exchange reaction (interference) when the membrane solubility and analytical concentration contributions may be neglected. When the other contributions should be taken into account then the total concentration may be represented as:

$$[\mathrm{Cu}^+]_0 = [\mathrm{Cu}^+]_0^{\mathrm{A}} + [\mathrm{Cu}^+]_0^{\mathrm{L}} + \left\{-\frac{AK}{4} + \frac{1}{2}\left(\frac{A^2K^2}{4} + 2AK[\mathrm{Cu}^+] + 4K[\mathrm{Cu}^{2+}]\right)^{1/2}\right\} \qquad (10)$$

which enters into the equation for the potential:

$$E = \mathrm{const.} + \frac{RT}{F}\ln[\mathrm{Cu}^+]_0. \qquad (11)$$

This equation is valid for the intermediate range but no precise derivation of this equation can be presented. Nevertheless, from measurements in the concentration ranges used in our experiments, it evidently describes the behaviour of the electrode with enough accuracy for its practical use.

RESULTS AND DISCUSSION

The model described, in which the surface concentrations are different from those in the bulk of the solution, is similar to that given for the cyanide electrode.[13,15] The expanded form of equation (11):

$$E = \mathrm{const.} + \frac{RT}{F}\ln\left\{[\mathrm{Cu}^+]_0^{\mathrm{A}} + [\mathrm{Cu}^+]_0^{\mathrm{L}} + \left[-\frac{AK}{4} + \frac{1}{2}\left(\frac{A^2K^2}{4} + 2AK[\mathrm{Cu}^+] + 4K[\mathrm{Cu}^{2+}]\right)^{1/2}\right]\right\}, \qquad (12)$$

may be simplified when some justifiable approximations are introduced. When $[\mathrm{Cu}^{2+}]$ is significantly greater than $4 \times 10^{-13}M$, *i.e.* $[\mathrm{Cu}^{2+}] \gg K$, then in equation (12) the total term corresponding to the exchange reaction is simplified to $K^{1/2}[\mathrm{Cu}^{2+}]^{1/2}$, and the equation is the same as given previously [(2)] on the basis of the Pungor–Tóth model.[12] The value of the constant $K = 4 \times 10^{-13}$ for reaction (6) is based on the solubility products,[19] and is an idealized approach. In real conditions the side-reaction coefficient effect of Cu^+ with chloride ions is much stronger than that of Cu^{2+}, shifting the reaction (6) towards the right-hand side. The dependence of pK' on the chloride concentration is shown in Fig. 3.

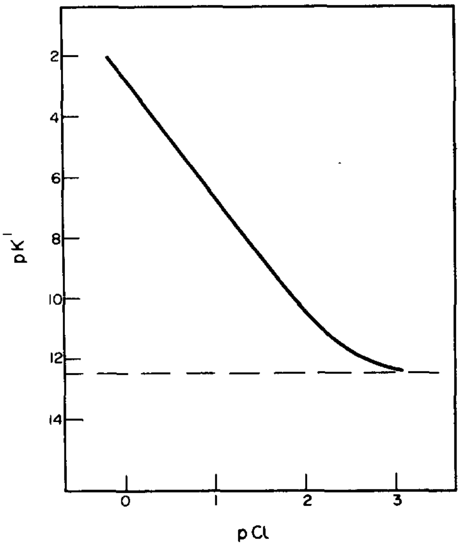

Fig. 3. Conditional constant of the exchange reaction $\mathrm{Cu}^{2+} + \mathrm{Cu_2S} \rightleftharpoons 2\mathrm{Cu}^+ + \mathrm{CuS}$ as a function of chloride concentration.

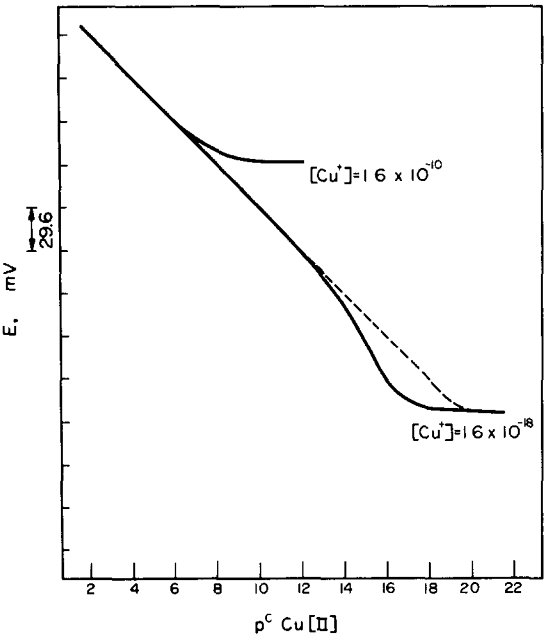

Fig. 4. Theoretical potential response curves calculated on the basis of the diffusion barrier model—solid line, and on the basis of the Pungor–Tóth model—dashed line.

For low concentrations of copper(I), *i.e.*, when $[\mathrm{Cu}^+] \ll K[\mathrm{Cu}^{2+}]^{1/2}$ the electrodes become sensitive to copper(II). In such conditions the chalcocite electrode may be treated as a copper(II) electrode, for which the copper(II) ions are the main ions. In this case the simplified model may be treated as a special case of the diffusion layer model. The potential response curves $E = f([\mathrm{Cu}^{2+}])$ have been calculated for several levels of concentration of copper(I) ions in solution (Fig. 4). It can be seen that only at the lowest levels is there departure from linearity.

The value of the selectivity coefficient of the chalcocite electrode is 4×10^{-13}, which is the equilibrium constant of the exchange reaction. The potentiometric selectivity coefficient, determined experimentally, $K^{\mathrm{pot}}_{\mathrm{Cu}^+,\mathrm{Cu}^{2+}} = K^{1/2} = 6.3 \times 10^{-7}$, as described previously.[7] The magnitude of these values suggests that the extent of the exchange reaction is not large enough to allow the electrode to function according to the scheme $\mathrm{Cu_2S/CuS/Cu}^{2+}$ (external solution).

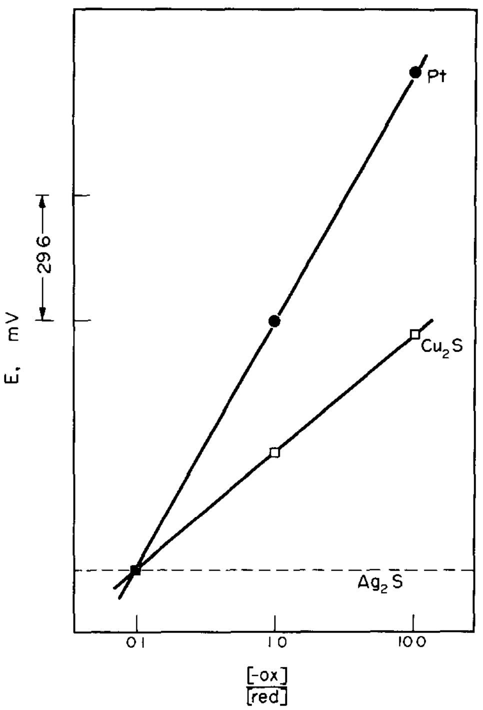

Fig. 5 Dependence of the electrode potential on the $[Fe(CN)_6^{3-}]:[Fe(CN)_6^{4-}]$ ratio at pH 5 The Ag_2S relationship is given according to Weser and Pungor[17]

It must be mentioned that the diffusion layer model does not specify the type of conductivity in the membrane. Because of the absence of β-Ag_2S, as the ionic conductor, one can expect for the chalcocite electrode a significant contribution of electron conductivity.[16] This has been confirmed experimentally by measuring the redox response of the electrode in comparison with that of the platinum electrode (Fig. 5).

Experimental potential response curves have been prepared for the chalcocite electrode in solutions containing both copper(I) and copper(II) ions. In the case of the copper(II) response (Fig. 6, curve I) the medium used was 1*M* potassium nitrate. The experimental points obtained by successive dilutions agree with those calculated on the assumption that $[Cu^+]$ is not greater than $1.6 \times 10^{-10}M$. As can be seen by comparison with Fig. 4 the curve is linear with the theoretical slope of 29.6 mV per decade. The slight curvature at low concentrations is due to $[Cu^+]_0^L$.

The response curve for copper(I) ions (Fig. 6, curve II) has been prepared on the basis of the analytical concentration of copper(I), generated coulometrically at pH 3 in 1*M* potassium chloride. The concentration of free (hydrated) Cu^+ ions is significantly lower. The constant degree of complexation due to the constant concentration of Cl^- as the predominant ligand, ensures that the slope has the theoretical value of 59.2 mV per decade, which is in good agreement with the calculated curve. Under these conditions the concentration of Cu^{2+} is insufficient for the formation of a CuS layer at the electrode surface. Therefore the contribution of the exchange concentration $[Cu^+]_0^L$ is negligible and except in a very low concentration range only the term $[Cu^+]_0^A$ is significant in equation (11).

In the presence of both copper(I) and copper(II) ions, at equal analytical concentrations, the potential response curve is influenced by both ions. The extent of complexation of copper(I) in 1*M* chloride solution is significantly greater ($\alpha_{Cu^+(Cl)} = 8.5 \times 10^4$)[18] than that of the copper(II). Therefore the α-value compensates partially for the small value of selectivity coefficient $K^{pot}_{Cu^+,Cu^{2+}}$. Both types of ion contribute to the slope, which in the range of concentrations indicated is approximately 55 mV per decade (Fig. 6, curve III).

The electrode limit, defined by $[Cu^+]_0^L$, may be reached under conditions where the copper(II) ions are more strongly complexed that the copper(I) ions. This happens, for example, in the potentiometric titration of copper(II) with EDTA. Because the copper(II) concentration drops significantly after the end-point, $[Cu^+]_0^L$ becomes the decisive factor influencing the potential response. From the potential limit the value of $[Cu^+]_0^L$ may be estimated and the α_{Cu} value calculated from equation (5). This makes it possible to estimate the stability constants of copper(I) complexes. In the case of the TETREN titration of copper it may be expected that both copper ions are complexed, therefore the limit is strongly suppressed, and the potentials after the end-point are much lower.[7]

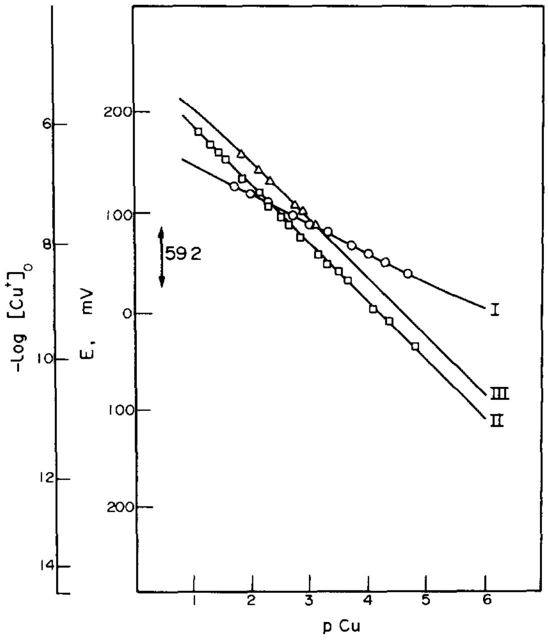

Fig. 6. Potential response curves of the chalcocite membrane electrode, in copper(II) solution (in 1*M* KNO_3). Curve I, Copper(II) solution in 1*M* KNO_3. Curve II, copper(I) solution in 1*M* KCl. Curve III, equivalent amounts of copper(I) and copper(II) in 1*M* KCl Experimental points are indicated on the theoretically calculated curves (solid lines).

The value of the stability constant of the copper(I)-TETREN complex calculated on this basis is approximately 10^8.

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SHORT COMMUNICATIONS

STUDIES ON THE ELECTROCAPILLARY CURVES OF ANIONIC SURFACTANTS IN PRESENCE OF NON-IONIC SURFACTANTS

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Polarographic maxima of simple and complex metal ions have been effectively suppressed by the use of surfactants[1–3]. In most cases, cationic soaps suppress the negative maxima while anionic soaps suppress the positive maxima.[1] However no such simple relation has been found for non-ionic surfactants. Studies have shown that weak positive charges may be associated with the micelles of polyoxyethyl non-ionic surfactants, but the sign of these charges is not definite. The changes in the electrocapillary curves of ionic surfactants on addition of non-ionic surfactants provide a means to assess the nature of the net effective charge on the latter (and hence their effectiveness in suppressing positive and/or negative polarographic maxima). Studies have, therefore, been carried out on the effect of four such non-ionic surfactants, *viz.* Tween 20, Tween 40, Nonidet P40, and Nonex 501 on the electrocapillary curves of three anionic surfactants, *viz.* Aerosol IB (di-isobutyl sodium sulphosuccinate, c.m.c. 0.20 *M*), Manaxol OT (dioctyl sodium sulphosuccinate, c.m.c. 6.8×10^{-4} *M*) and SLS (sodium lauryl sulphate, c.m.c. 8.2×10^{-3} *M*).

EXPERIMENTAL

The surfactants were B.D.H. products. Other reagents used were of analytical-reagent grade. All solutions were prepared in doubly-distilled water

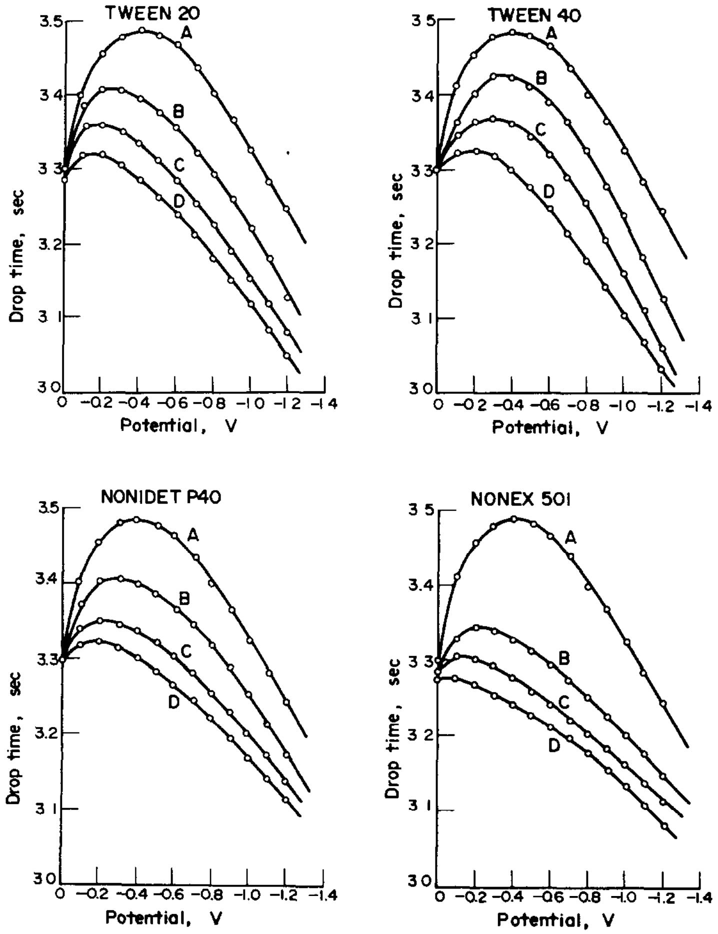

Fig. 1. Electrocapillary curves in 0.12 *M* Aerosol IB in the presence of *A* 0.0, *B* 0.01, *C* 0.04, *D* 0.08 g/100 ml concentrations of non-ionic surfactants.

Table 1. Potentials at the electrocapillary maxima in the presence of Aerosol IB, Manaxol OT and SLS alone and along with varying amounts of the non-ionic surfactants

Concentration of the non-ionic surfactant, *g*/100 *ml*	Potential at the electrocapillary maximum, *V*		
	Aerosol IB	Manaxol OT	SLS
0.0	−0.40	−0.54	−0.64
Tween 20			
0.01	−0.30	−0.42	−0 56
0 04	−0 18	−0.30	−0.48
0.08	−0.12	−0.20	−0.30
Tween 40			
0.01	−0.34	−0.48	−0.60
0.04	−0.30	−0.40	−0.52
0.08	−0.20	−0 32	−0.44
Nonidet P40			
0.01	−0.26	−0.40	−0.54
0.04	−0.16	−0 30	−0.42
0 08	−0.10	−0 18	−0.30
Nonex 501			
0 01	−0.22	−0.36	−0.50
0.04	−0.12	−0.24	−.040
0 08	−0.08	−0 18	−0.24

A Cambridge pen-recording polarograph was used for electrocapillary measurements The solutions were deaerated by bubbling purified nitrogen 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 reading being repeated at least three times. The electrocapillary measurements were carried out from 0.0 to −1.4 V at constant temperature (25 ± 1°). The concentration of the anionic surfactants was kept below their respective c m c's.

RESULTS AND DISCUSSION

Polyoxyethyl non-ionic surfactants may have cationic character. Chwala and Martina[4] have proposed the existence of anionic character for the ethylene oxide adducts. However, Wurzschmitt,[5] who studied the analytical behaviour of ethylene oxide adducts, concluded that in aqueous solutions they are present as cationic polyoxonium compounds

Wurzschmitt assumes that only a few of the ether oxygen atoms form oxonium ions and this fraction has been termed the degree of oxonium formation. Hsiao[6] and Scholler[7 8] have supported these views The present studies further confirm the existence of cation-active characteristics in these non-ionic surfactants.

Typical electrocapillary curves obtained by plotting drop-time against applied potential are depicted in Fig. 1. These curves, although parabolic, are marked by a lack of symmetry, indicating adsorption of the surfactant on the mercury–solution interface. Lipmann[9] has shown that mercury carries the positive charge (when the applied potential is zero), as a result of which the interfacial tension is decreased and a lower drop-time is observed. As the mercury is polarized to more negative potentials, the positive charge decreases and at a certain potential it disappears. At this point the interfacial tension is maximum and hence a maximum drop-time is recorded Further negative polarization results in a drop of interfacial tension and hence lower drop-times. An examination of the electrocapillary curves shows that the non-ionic surfactants, Tween 20, Tween 40, Nonidet P40 and Nonex 501 influence the electrocapillary curve of the anionic surfactants Aerosol IB, Manaxol OT and SLS in more or less the same manner The curves are shifted downwards and towards more positive potentials with increasing concentration of the non-ionic surfactant and they progressively lose their symmetry

The values of the electrocapillary maxima in the presence of the various anionic surfactants used (Table 1) show that their adsorbability at the mercury–solution interface follows the order: SLS > Manaxol OT > Aerosol IB.

The gradual shift in the electrocapillary maxima towards more positive potentials on addition of the non-ionic surfactants indicates neutralization of the adsorbed surface-active agent by the added non-ionic surfactant and its subsequent adsorption at the mercury–solution interface. The shift in electrocapillary maxima is then in the order. Aerosol IB ~ Manaxol OT > SLS. Thus the least shift occurs in the case of SLS which is the most strongly adsorbed anionic surfactant. These data provide evidence that the micelles of the polyoxyethylated non-ionic surfactants are associated with a net positive charge. The values of the electrocapillary maxima in presence of added non-ionic surfactants (Table 1) show that the shift caused by these surfactants follows the order: Nonex 501 > Nonidet P40 > Tween 20 > Tween 40. This may well be the order of the magnitude of positive charge carried by the micelles of these non-ionic surfactants.

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Summary—Polyoxyethylated non-ionic surfactants such as Tween 20, Tween 40, Nonidet P40 and Nonex 501 have been supposed to be associated with cationic characteristics. Studies on the effect of these surfactants on the electrocapillary curves of the anionic surfactants Aerosol IB, Manaxol OT and sodium lauryl sulphate (SLS), show that the electrocapillary maxima shift towards positive potentials. The order of adsorption of the anionic surfactants is SLS $>$ Manaxol OT $>$ Aerosol IB while the shift in maxima is in the order Aerosol IB $\sim$ Manaxol OT $>$ SLS which confirms association of cationic characteristics with the micelles of these non-ionic surfactants. The magnitude of the shift in electrocapillary maxima is Nonex 501 $>$ Nonidet P40 $>$ Tween 20 $>$ Tween 40 which may be the order of magnitude of the positive charge carried by these non-ionic surfactants.

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EFFECTS OF AUXILIARY COMPLEX-FORMING AGENTS ON THE RATE OF METALLOCHROMIC INDICATOR COLOUR CHANGE—IV*

MECHANISM OF THE COLOUR CHANGE OF XYLENOL ORANGE IN COPPER(II)—EDTA TITRATIONS

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In the copper(II)–EDTA titration with Xylenol Orange (XO) as indicator, hexamine slows down the rate of colour change of XO.[1,2] In the work described here, the rate of the substitution reaction of the copper(II)–XO chelate with EDTA was determined in MES buffer [2-(*N*-morpholino)ethanesulphonic acid] and in hexamine buffer, and the mechanism of the disturbing effect of hexamine on the colour change of the indicator discussed.

EXPERIMENTAL

XO was synthesized and purified in a manner similar to that in the literature.[3] The free acid form (H_6XO) was dissolved in water, and the solution stored in a refrigerator. Dissociation constants of XO determined by spectrophotometry and pH-titration were in good agreement with the values given by Murakami *et al.*[3]

A copper(II) solution was prepared from the reagent-grade nitrate.

Reagent-grade hexamine dried over phosphorus pentoxide was used without further purification. The purity was established as 99.0% by means of pH-titration with sodium hydroxide in the presence of excess of hydrochloric acid.

Other reagents and apparatus employed were the same as those reported previously.[4]

All experiments were carried out at 25 ± 1° and at ionic strength of 0.1 (KNO_3).

RESULTS AND DISCUSSION

The composition of copper(II)–XO chelates

From the results of the continuous variation method, the molar-ratio method by spectrophotometry and the potentiometric titration with use of a copper(II) ion-selective electrode, the ratio of copper to XO was essentially 2:1 in MES buffer. The pH-titration of a solution $3.76 \times 10^{-3}M$ in Cu and $0.934 \times 10^{-3}M$ in H_6XO with $0.198M$ sodium hydroxide shows the formation of Cu_2HXO^- at pH 2, and further release of one proton, which corresponds to the sixth proton of H_6XO, takes place in the pH-range from 3.5 to 5.5. In this pH-range the absorption maximum shifts from 440 to 574 nm, and an isosbestic point occurs at 487 nm. From these results the following equilibrium exists: $Cu_2XO^{2-} + H^+ \rightleftharpoons Cu_2HXO^-$. The equilibrium constant, $K^{H}_{Cu_2HXO} = [Cu_2HXO^-]/[Cu_2XO^{2-}][H^+]$, was evaluated as $10^{4.55}$ by spectrophotometry and pH-titration.

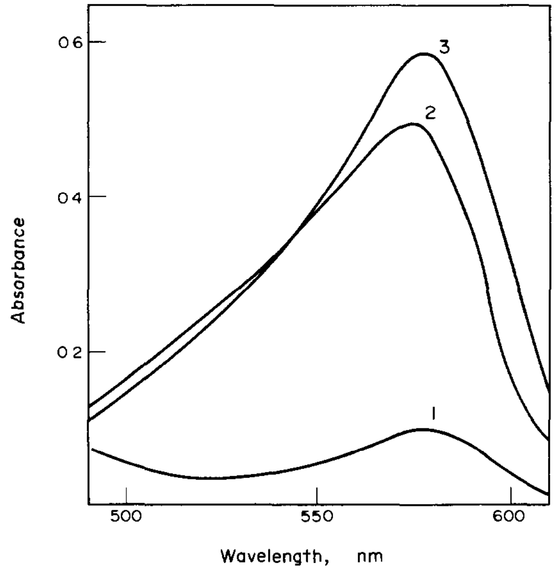

Fig. 1. Spectra of Cu–XO chelates. C_{Cu} $1.6 \times 10^{-4}M$, C_{XO} $1.1 \times 10^{-5}M$. 1, XO blank; 2, Cu_2XO^{2-}; 3, Cu_2XOL^{2-}, C_{hex} $2.0 \times 10^{-1}M$, pH 6.0.

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Polarographic maxima of simple and complex metal ions have been effectively suppressed by the use of surfactants[1-3]. In most cases, cationic soaps suppress the negative maxima while anionic soaps suppress the positive maxima.[1] However no such simple relation has been found for non-ionic surfactants. Studies have shown that weak positive charges may be associated with the micelles of polyoxyethyl non-ionic surfactants, but the sign of these charges is not definite. The changes in the electrocapillary curves of ionic surfactants on addition of non-ionic surfactants provide a means to assess the nature of the net effective charge on the latter (and hence their effectiveness in suppressing positive and/or negative polarographic maxima). Studies have, therefore, been carried out on the effect of four such non-ionic surfactants, *viz.* Tween 20, Tween 40, Nonidet P40, and Nonex 501 on the electrocapillary curves of three anionic surfactants, *viz.* Aerosol IB (di-isobutyl sodium sulphosuccinate, c.m.c. 0.20 *M*), Manaxol OT (dioctyl sodium sulphosuccinate, c.m.c. 6.8×10^{-4} *M*) and SLS (sodium lauryl sulphate, c.m.c. 8.2×10^{-3} *M*).

EXPERIMENTAL

The surfactants were B.D.H. products. Other reagents used were of analytical-reagent grade. All solutions were prepared in doubly-distilled water

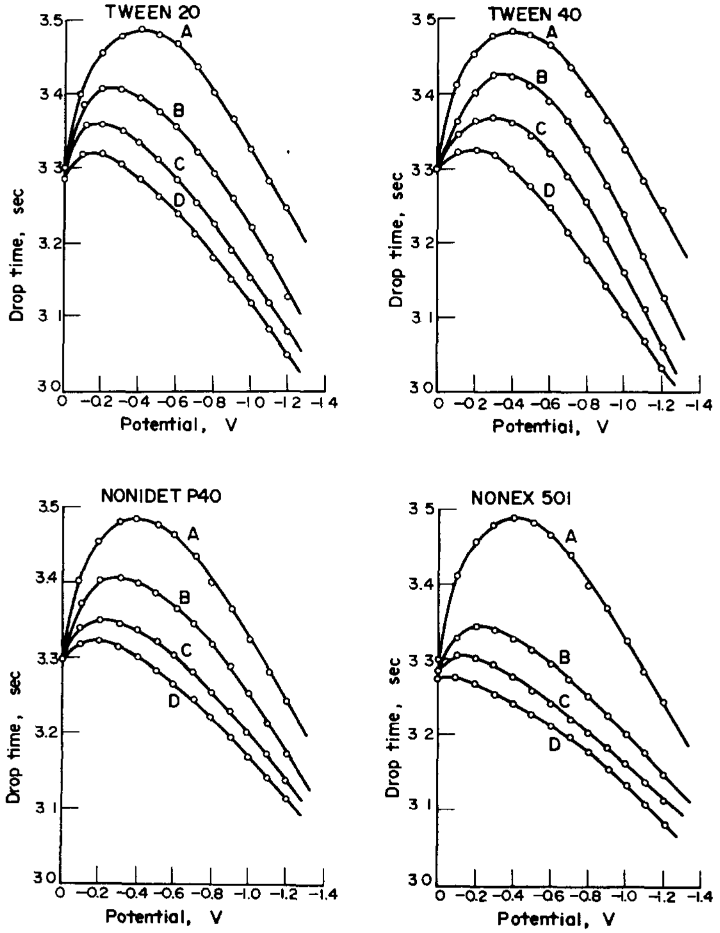

Fig. 1. Electrocapillary curves in 0.12 *M* Aerosol IB in the presence of *A* 0.0, *B* 0.01, *C* 0.04, *D* 0.08 g/100 ml concentrations of non-ionic surfactants.

Table 1. Potentials at the electrocapillary maxima in the presence of Aerosol IB, Manaxol OT and SLS alone and along with varying amounts of the non-ionic surfactants

Concentration of the non-ionic surfactant, *g*/100 *ml*	Potential at the electrocapillary maximum, *V*		
	Aerosol IB	Manaxol OT	SLS
0.0	−0.40	−0.54	−0.64
Tween 20			
0.01	−0.30	−0.42	−0 56
0 04	−0 18	−0.30	−0.48
0.08	−0.12	−0.20	−0.30
Tween 40			
0.01	−0.34	−0.48	−0.60
0.04	−0.30	−0.40	−0.52
0.08	−0.20	−0 32	−0.44
Nonidet P40			
0.01	−0.26	−0.40	−0.54
0.04	−0.16	−0 30	−0.42
0 08	−0.10	−0 18	−0.30
Nonex 501			
0 01	−0.22	−0.36	−0.50
0.04	−0.12	−0.24	−.040
0 08	−0.08	−0 18	−0.24

A Cambridge pen-recording polarograph was used for electrocapillary measurements The solutions were deaerated by bubbling purified nitrogen 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 reading being repeated at least three times. The electrocapillary measurements were carried out from 0.0 to −1.4 V at constant temperature (25 ± 1°). The concentration of the anionic surfactants was kept below their respective c m c's.

RESULTS AND DISCUSSION

Polyoxyethyl non-ionic surfactants may have cationic character. Chwala and Martina[4] have proposed the existence of anionic character for the ethylene oxide adducts. However, Wurzschmitt,[5] who studied the analytical behaviour of ethylene oxide adducts, concluded that in aqueous solutions they are present as cationic polyoxonium compounds

Wurzschmitt assumes that only a few of the ether oxygen atoms form oxonium ions and this fraction has been termed the degree of oxonium formation. Hsiao[6] and Scholler[7, 8] have supported these views The present studies further confirm the existence of cation-active characteristics in these non-ionic surfactants.

Typical electrocapillary curves obtained by plotting drop-time against applied potential are depicted in Fig. 1. These curves, although parabolic, are marked by a lack of symmetry, indicating adsorption of the surfactant on the mercury–solution interface. Lipmann[9] has shown that mercury carries the positive charge (when the applied potential is zero), as a result of which the interfacial tension is decreased and a lower drop-time is observed. As the mercury is polarized to more negative potentials, the positive charge decreases and at a certain potential it disappears. At this point the interfacial tension is maximum and hence a maximum drop-time is recorded Further negative polarization results in a drop of interfacial tension and hence lower drop-times. An examination of the electrocapillary curves shows that the non-ionic surfactants, Tween 20, Tween 40, Nonidet P40 and Nonex 501 influence the electrocapillary curve of the anionic surfactants Aerosol IB, Manaxol OT and SLS in more or less the same manner The curves are shifted downwards and towards more positive potentials with increasing concentration of the non-ionic surfactant and they progressively lose their symmetry

The values of the electrocapillary maxima in the presence of the various anionic surfactants used (Table 1) show that their adsorbability at the mercury–solution interface follows the order: SLS > Manaxol OT > Aerosol IB.

The gradual shift in the electrocapillary maxima towards more positive potentials on addition of the non-ionic surfactants indicates neutralization of the adsorbed surface-active agent by the added non-ionic surfactant and its subsequent adsorption at the mercury–solution interface. The shift in electrocapillary maxima is then in the order. Aerosol IB ~ Manaxol OT > SLS. Thus the least shift occurs in the case of SLS which is the most strongly adsorbed anionic surfactant. These data provide evidence that the micelles of the polyoxyethylated non-ionic surfactants are associated with a net positive charge. The values of the electrocapillary maxima in presence of added non-ionic surfactants (Table 1) show that the shift caused by these surfactants follows the order: Nonex 501 > Nonidet P40 > Tween 20 > Tween 40. This may well be the order of the magnitude of positive charge carried by the micelles of these non-ionic surfactants.

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Summary—Polyoxyethylated non-ionic surfactants such as Tween 20, Tween 40, Nonidet P40 and Nonex 501 have been supposed to be associated with cationic characteristics. Studies on the effect of these surfactants on the electrocapillary curves of the anionic surfactants Aerosol IB, Manaxol OT and sodium lauryl sulphate (SLS), show that the electrocapillary maxima shift towards positive potentials. The order of adsorption of the anionic surfactants is SLS $>$ Manaxol OT $>$ Aerosol IB while the shift in maxima is in the order Aerosol IB $\sim$ Manaxol OT $>$ SLS which confirms association of cationic characteristics with the micelles of these non-ionic surfactants. The magnitude of the shift in electrocapillary maxima is Nonex 501 $>$ Nonidet P40 $>$ Tween 20 $>$ Tween 40 which may be the order of magnitude of the positive charge carried by these non-ionic surfactants.

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EFFECTS OF AUXILIARY COMPLEX-FORMING AGENTS ON THE RATE OF METALLOCHROMIC INDICATOR COLOUR CHANGE—IV*

MECHANISM OF THE COLOUR CHANGE OF XYLENOL ORANGE IN COPPER(II)—EDTA TITRATIONS

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In the copper(II)–EDTA titration with Xylenol Orange (XO) as indicator, hexamine slows down the rate of colour change of XO.[1,2] In the work described here, the rate of the substitution reaction of the copper(II)–XO chelate with EDTA was determined in MES buffer [2-(*N*-morpholino)ethanesulphonic acid] and in hexamine buffer, and the mechanism of the disturbing effect of hexamine on the colour change of the indicator discussed.

EXPERIMENTAL

XO was synthesized and purified in a manner similar to that in the literature.[3] The free acid form (H_6XO) was dissolved in water, and the solution stored in a refrigerator. Dissociation constants of XO determined by spectrophotometry and pH-titration were in good agreement with the values given by Murakami *et al.*[3]

A copper(II) solution was prepared from the reagent-grade nitrate.

Reagent-grade hexamine dried over phosphorus pentoxide was used without further purification. The purity was established as 99.0% by means of pH-titration with sodium hydroxide in the presence of excess of hydrochloric acid.

Other reagents and apparatus employed were the same as those reported previously.[4]

All experiments were carried out at 25 ± 1° and at ionic strength of 0.1 (KNO_3).

RESULTS AND DISCUSSION

The composition of copper(II)–XO chelates

From the results of the continuous variation method, the molar-ratio method by spectrophotometry and the potentiometric titration with use of a copper(II) ion-selective electrode, the ratio of copper to XO was essentially 2:1 in MES buffer. The pH-titration of a solution $3.76 \times 10^{-3}M$ in Cu and $0.934 \times 10^{-3}M$ in H_6XO with $0.198M$ sodium hydroxide shows the formation of Cu_2HXO^- at pH 2, and further release of one proton, which corresponds to the sixth proton of H_6XO, takes place in the pH-range from 3.5 to 5.5. In this pH-range the absorption maximum shifts from 440 to 574 nm, and an isosbestic point occurs at 487 nm. From these results the following equilibrium exists: $Cu_2XO^{2-} + H^+ \rightleftharpoons Cu_2HXO^-$. The equilibrium constant, $K^{H}_{Cu_2HXO} = [Cu_2HXO^-]/[Cu_2XO^{2-}][H^+]$, was evaluated as $10^{4.55}$ by spectrophotometry and pH-titration.

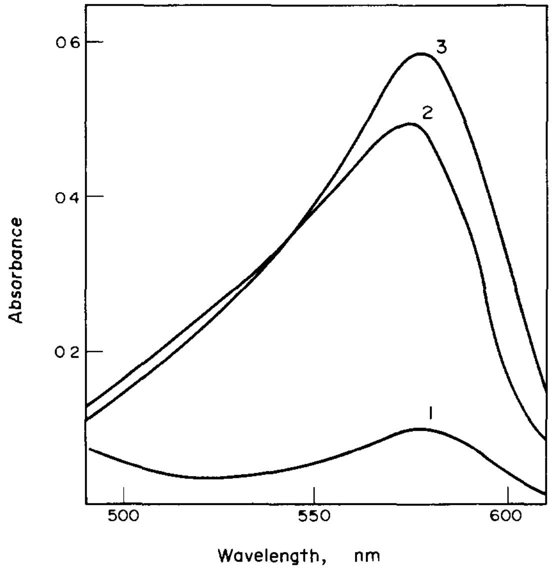

Fig. 1. Spectra of Cu–XO chelates. C_{Cu} $1.6 \times 10^{-4}M$, C_{XO} $1.1 \times 10^{-5}M$. 1, XO blank; 2, Cu_2XO^{2-}; 3, Cu_2XOL^{2-}, C_{hex} $2.0 \times 10^{-1}M$, pH 6.0.

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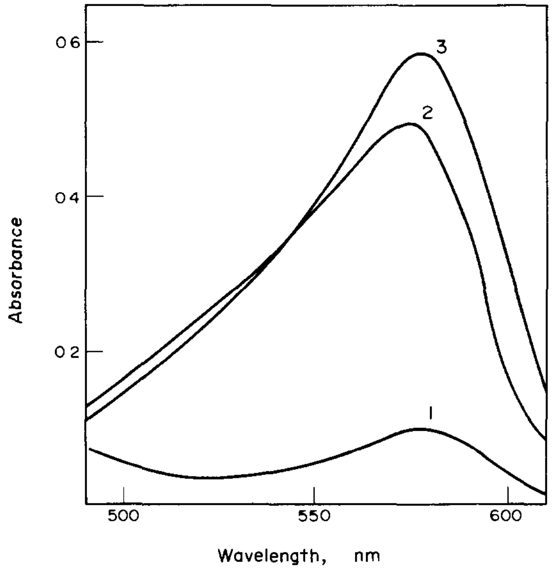

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At pH 6 in the presence of hexamine the absorption spectrum of Cu_2XO^{2-} shifts to longer wavelengths ($\lambda_{max} = 578$ nm) and the molar absorptivity increases with increase in the hexamine concentration (Fig. 1). This indicates the formation of a mixed-ligand complex of the copper–XO chelate with hexamine.

The formation constant of the mixed-ligand complex is defined as:

$$K^{nL}_{Cu_2XOL_n} = \frac{[Cu_2XOL_n^{2-}]}{[Cu_2XO^{2-}][L]^n} \qquad (1)$$

where L represents free hexamine. The absorbances of $Cu_2XOL_n^{2-}$ at 578 nm were measured for varying hexamine concentration from 10^{-3} to $10^{-1}M$ at pH 6.00–6.30. A plot of $\log[Cu_2XOL_n^{2-}]/[Cu_2XO^{2-}]$ *vs.* log[L] yielded a straight line with slope of 1. Therefore, one molecule of hexamine co-ordinates with Cu_2XO^{2-}. The value of $K^{L}_{Cu_2XOL}$ was evaluated as $10^{2.14}$. The dissociation constant of HL^+ was taken as $10^{-4.98}$.

The rate of substitution of Cu_2XO with EDTA

In MES buffer. A solution 2.10–5.25 × $10^{-5}M$ in XO, 3.87–7.74 × $10^{-5}M$ in Cu and 0.02*M* in MES–NaOH buffer (pH 4.82–6.00) and a solution 3.56–14.25 × $10^{-4}M$ in EDTA and 0.02*M* in MES–NaOH buffer (pH 4.82–6.00) were mixed, and the absorbance at 574 nm was measured as a function of the reaction time by the stopped-flow method.

Under these experimental conditions the substitution reaction of the Cu_2XO^{2-} chelate with EDTA proceeds to completion·

$$Cu_2XO + 2EDTA = 2Cu(EDTA) + XO \qquad (2)$$

The rate-law is expressed by

$$-\frac{d[Cu_2XO^{2-}]}{dt} = k_{0(H,R,M,Y)}[Cu_2XO^{2-}] \qquad (3)$$

where $k_{0(H,R,M,Y)}$ is the conditional rate-constant involving the concentrations of hydrogen ion, XO, Cu and EDTA. From equation (3) we obtain

$$\log(A_t - A_\infty) = -\frac{k_{0(H,R,M,Y)}}{2.303}t + \log(A_0 - A_\infty) \qquad (4)$$

where A_0, A_t and A_∞ represent the absorbances of the reaction system at $t = 0$, t and ∞, respectively. The plots of $\log(A_t - A_\infty)$ *vs.* t yielded straight lines up to 90% of the total reaction, and the conditional rate-constants $k_{0(H,R,M,Y)}$ were obtained from the slopes of the straight lines. The data in Table 1 indicate that the values of k_0 are proportional to the concentration of EDTA but are independent of hydrogen ion, XO and Cu concentrations. Hence,

$$-\frac{d[Cu_2XO^{2-}]}{dt} = k_1[Y'][Cu_2XO^{2-}] \qquad (5)$$

where [Y′] is the total concentration of EDTA ($[H_2Y^{2-}] + [HY^{3-}]$) not combined with copper ion, and the rate-constant k_1 was evaluated as 7.84 × 10^2 l.mole.sec^{-1}. The following reaction mechanism may be proposed.

$$Cu_2XO^{2-} + Y' \rightleftharpoons YCu(XO)Cu \xrightarrow{r\,d\,s}$$
$$CuY^{2-} + CuHXO^{3-} \quad \text{or} \quad CuH_2XO^{2-} \qquad (6)$$
$$CuHXO^{3-} \quad \text{or} \quad CuH_2XO^{2-} + Y' \xrightarrow{\text{fast}}$$
$$CuY^{2-} + H_3XO^{3-} \qquad (7)$$

The release of the first copper ion from the Cu_2XO^{2-} chelate may be the rate-determining step (r.d.s.). From the results of potentiometry with a copper(II) ion-selective electrode the resulting 1:1 chelate is in the form of $CuHXO^{3-}$ or CuH_2XO^{2-}, and the protonation of the 1:1 chelate may weaken the Cu–XO bonds. The high stability of the 2:1 chelate (Cu_2XO^{2-}) may support the mechanism proposed in equations (6) and (7).

In the presence of hexamine. A solution containing XO, Cu and hexamine (2.83 × 10^{-4}–2.19 × $10^{-1}M$) was mixed with a solution containing EDTA, and the absorbance at 578 nm was measured in the pH range from 5.77 to 6.24 (MES buffer) in the same way as for the MES buffer system.

The substitution reaction is written as:

$$Cu_2XOL + EDTA \rightleftharpoons 2Cu(EDTA) + XO + L \qquad (8)$$

The rate-law is

$$-\frac{d[Cu_2XOL^{2-}]}{dt} = k_{0(H,R,M,Y,L)}[Cu_2XOL^{2-}] \qquad (9)$$

The results are shown in Table 2. No dependence of $k_{0(H,R,M,Y,L)}$ on the concentrations of XO, Cu and hydrogen ion was observed, but there was a linear relation to EDTA concentration. With increasing concentration of hexamine the rate of the substitution reaction decreased. In the hexamine concentration range from 3.00 × 10^{-2} to 2.19 × $10^{-1}M$, where the mixed-ligand complex Cu_2XOL^{2-} forms quantitatively, k_0 was proportional to the reciprocal of the concentration of hexamine. Thus, the rate-law may be rewritten as

$$-\frac{d[Cu_2XOL^{2-}]}{dt} = k_2\frac{[Y'][Cu_2XOL^{2-}]}{[L']} \qquad (10)$$

The value of k_2 was evaluated as 5.39 sec^{-1}.

Therefore, the dissociation of hexamine from Cu_2XOL^{2-} takes place first:

$$Cu_2XOL^{2-} = Cu_2XO^{2-} + L \qquad (11)$$

The substitution mechanism of Cu_2XO^{2-} with EDTA may be the same as that in the absence of hexamine. From equations (1), (5) and (10):

$$k_1 = k_2K^{L}_{Cu_2XOL} = 5.39 \times 10^{2.14}$$
$$= 7.44 \times 10^2 \text{ l.mole}^{-1}.\text{sec}^{-1}$$

This value is in good agreement with that obtained in the absence of hexamine. This fact supports the reaction mechanism described above.

Table 1. First-order conditional rate constants $k_{0(H,R,M,Y)}$

25°C, μ = 0.1

$10^4 \times C_{EDTA}$, M	$10^5 \times C_{XO}$, M	$10^5 \times C_{Cu}$, M	pH	$10 \times k_{0(H,R,M,Y)}$ sec^{-1}
3.56	2.10	3.87	4.82	2.90
			5.59	2.65
			5.68	2.68
			5.80	2.46
			5.85	2.41
			6.00	2.30
	3.15		5.39	2.74
	4.20			2.78
	5.25			2.43
5.34	2.10		4.82	4.32
			5.51	4.03
			5.80	4.29
			5.85	4.22
			6.00	4.34
	3.15		5.39	4.09
	4.20			3.83
	2.10	5.42	5.68	4.09
		5.81	5.85	4.17
		7.74	5.68	4.09
7.12		3.87		5.21
			5.80	5.60
			5.85	5.10
			6.00	5.30
	3.15		5.39	5.47
	4.20			5.28
	5.25			5.89
10.7	2.10		4.82	8.64
			5.80	8.24
			5.85	7.90
			6.00	8.00
	3.15		5.39	8.46
	4.20			8.24
	5.25			8.59
14.3	2.10		5.80	10.3
			5.85	10.7
	3.15		5.39	11.7
	4.20			10.6
	5.25			11.7

Table 2. First-order conditional rate constants $k_{0(H,R,M,Y,L)}$

25°C, μ = 0.1

$10^5 \times C_{Cu}$, M	$10^5 \times C_{XO}$, M	$10^4 \times C_{EDTA}$, M	$10^3 \times C_L$, M	pH	$10 \times k_{0(H,R,M,Y,L)}$, sec^{-1}
3.87	2.10	3.56	0.283	5.84	2.15
			3.01		1.85
				6.00	1.85
			6.02	5.77	1.24
			12.0	5.92	0.973
			30.1	6.00	0.573
			42.1	6.03	0.456
		5.34	0.283	5.84	3.96
			3.01		2.85
				6.00	2.56
			6.02	5.77	2.23
			30.1	6.00	1.02
			60.2	5.94	0.308
		7.13	0.283	5.84	4.99
			3.01		3.80
				6.00	3.52
			6.02	5.77	2.82
			12.0	5.92	2.13
			30.1	6.00	1.22
			42.1	6.03	0.798
			60.2	5.94	0.638
		10.7	0.283	5.84	7.91
			3.01		5.81
				6.00	6.26
			6.02	5.77	4.10
			12.0	5.92	3.14
			30.1	6.00	1.92
			42.1	6.03	1.22
			60.2	5.94	1.01
		14.3	0.283	5.84	10.23
			3.01		9.10
				6.00	8.59
	3.15		6.02	5.77	5.36
			12.0	5.92	4.24
			30.1	6.00	2.66
			42.1	6.03	1.62
			60.2	5.94	1.30
3.09	1.32	108	43.2	6.16	10.5
			65.6		8.63
			87.4		6.57
			131		4.52
			219		2.52

At lower concentrations of hexamine Cu_2XO^{2-} and Cu_2XOL^{2-} complexes exist. Thus, the rate law can be expressed as

$$-\frac{d[(Cu_2XO)']}{dt} = k[Y'][(Cu_2XO)']$$

$$= \left(\frac{k_1}{1 + K^L_{Cu_2XOL}[L]}\right)[Y'][(Cu_2XO)'] \quad (12)$$

where $[(Cu_2XO)']$ represents the total concentration of Cu–XO chelates. The plot of log k *vs.* log[L] is shown in Fig. 2. The values of $K^L_{Cu_2XOL}$, k_1 and k_2 obtained by a curve-fitting method were $10^{2\ 18}$, 7.76×10^2 l.mole^{-1}.sec^{-1} and 5.13 sec^{-1}, respectively. These values agree well with those obtained above. The curve shows that the presence of more than $10^{-2}M$ hexamine markedly slows down the rate of colour change of the indicator.

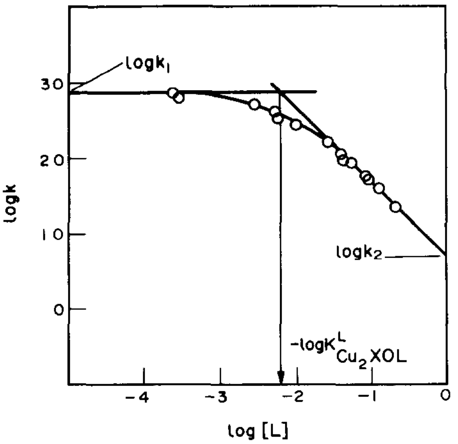

Fig. 2. Plot of log$k$ *vs.* log[L]. Solid line is the theoretical curve.

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Summary—The rate of ligand substitution of copper(II)-Xylenol Orange (XO) with EDTA (Y) has been determined spectrophotometrically over the pH range 4.8–6.0 at $\mu = 0.1$ (KNO_3) and at 25°. In 2-(*N*-morpholino)ethane sulphonic acid buffer, copper forms a 2:1 chelate (Cu_2XO^{2-}) with XO, and the rate-law is expressed as $-d[Cu_2XO^{2-}]/dt = 10^{2.89}[Cu_2XO^{2-}][Y']$. The release of the first copper ion from Cu_2XO^{2-} is the rate-determining step. The resulting $CuHXO^{3-}$ or CuH_2XO^{2-} may undergo fast substitution with EDTA. In the presence of hexamine, the copper(II)–XO chelate forms a mixed-ligand complex with hexamine (L). The formation constant $K^L_{Cu_2XOL} = [Cu_2XOL^{2-}]/[Cu_2XO^{2-}][L] = 10^{2\ 14}$ ($\mu = 0.1$, 25°). At 3×10^{-2}–$2 \times 10^{-1}M$ hexamine the rate-law is expressed as $-d[Cu_2XOL^{2-}]/dt = 5.39[Cu_2XOL^{2-}][Y']/[L']$. The dissociation of hexamine from Cu_2XOL^{2-} has to precede the substitution reaction of Cu_2XO^{2-} with EDTA. Hence, hexamine at higher concentrations than $10^{-3}M$ slows down the rate of colour change of XO in the copper–EDTA titration.

Summary—Polyoxyethylated non-ionic surfactants such as Tween 20, Tween 40, Nonidet P40 and Nonex 501 have been supposed to be associated with cationic characteristics. Studies on the effect of these surfactants on the electrocapillary curves of the anionic surfactants Aerosol IB, Manaxol OT and sodium lauryl sulphate (SLS), show that the electrocapillary maxima shift towards positive potentials. The order of adsorption of the anionic surfactants is SLS > Manaxol OT > Aerosol IB while the shift in maxima is in the order Aerosol IB ~ Manaxol OT > SLS which confirms association of cationic characteristics with the micelles of these non-ionic surfactants. The magnitude of the shift in electrocapillary maxima is Nonex 501 > Nonidet P40 > Tween 20 > Tween 40 which may be the order of magnitude of the positive charge carried by these non-ionic surfactants.

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EFFECTS OF AUXILIARY COMPLEX-FORMING AGENTS ON THE RATE OF METALLOCHROMIC INDICATOR COLOUR CHANGE—IV*

MECHANISM OF THE COLOUR CHANGE OF XYLENOL ORANGE IN COPPER(II)—EDTA TITRATIONS

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In the copper(II)–EDTA titration with Xylenol Orange (XO) as indicator, hexamine slows down the rate of colour change of XO.[1,2] In the work described here, the rate of the substitution reaction of the copper(II)–XO chelate with EDTA was determined in MES buffer [2-(*N*-morpholino)ethanesulphonic acid] and in hexamine buffer, and the mechanism of the disturbing effect of hexamine on the colour change of the indicator discussed.

EXPERIMENTAL

XO was synthesized and purified in a manner similar to that in the literature.[3] The free acid form (H_6XO) was dissolved in water, and the solution stored in a refrigerator. Dissociation constants of XO determined by spectrophotometry and pH-titration were in good agreement with the values given by Murakami *et al.*[3]

A copper(II) solution was prepared from the reagent-grade nitrate.

Reagent-grade hexamine dried over phosphorus pentoxide was used without further purification. The purity was established as 99.0% by means of pH-titration with sodium hydroxide in the presence of excess of hydrochloric acid.

Other reagents and apparatus employed were the same as those reported previously.[4]

All experiments were carried out at 25 ± 1° and at ionic strength of 0.1 (KNO_3).

RESULTS AND DISCUSSION

The composition of copper(II)–XO chelates

From the results of the continuous variation method, the molar-ratio method by spectrophotometry and the potentiometric titration with use of a copper(II) ion-selective electrode, the ratio of copper to XO was essentially 2:1 in MES buffer. The pH-titration of a solution $3.76 \times 10^{-3}M$ in Cu and $0.934 \times 10^{-3}M$ in H_6XO with $0.198M$ sodium hydroxide shows the formation of Cu_2HXO^- at pH 2, and further release of one proton, which corresponds to the sixth proton of H_6XO, takes place in the pH-range from 3.5 to 5.5. In this pH-range the absorption maximum shifts from 440 to 574 nm, and an isosbestic point occurs at 487 nm. From these results the following equilibrium exists: $Cu_2XO^{2-} + H^+ \rightleftharpoons Cu_2HXO^-$. The equilibrium constant, $K^{H}_{Cu_2HXO} = [Cu_2HXO^-]/[Cu_2XO^{2-}][H^+]$, was evaluated as $10^{4.55}$ by spectrophotometry and pH-titration.

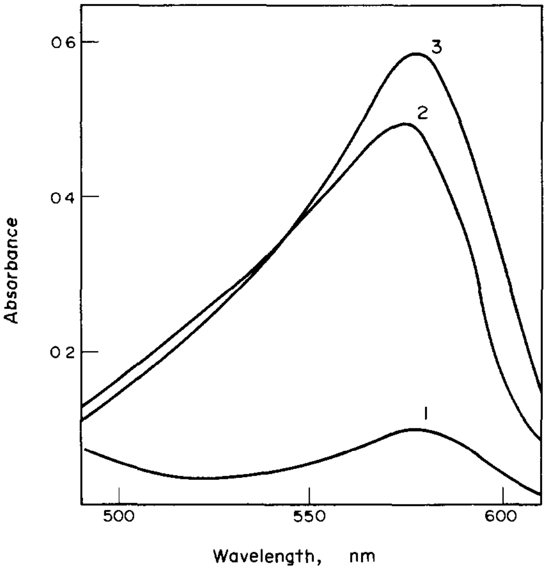

Fig. 1. Spectra of Cu–XO chelates. C_{Cu} $1.6 \times 10^{-4}M$, C_{XO} $1.1 \times 10^{-5}M$. 1, XO blank; 2, Cu_2XO^{2-}; 3, Cu_2XOL^{2-}, C_{hex} $2.0 \times 10^{-1}M$, pH 6.0.

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* Part III: *Talanta*, 1976, **23**, 155.

At pH 6 in the presence of hexamine the absorption spectrum of $\mathrm{Cu_2XO^{2-}}$ shifts to longer wavelengths ($\lambda_{\max} = 578$ nm) and the molar absorptivity increases with increase in the hexamine concentration (Fig. 1). This indicates the formation of a mixed-ligand complex of the copper–XO chelate with hexamine.

The formation constant of the mixed-ligand complex is defined as:

$$K^{nL}_{\mathrm{Cu_2XOL}_n} = \frac{[\mathrm{Cu_2XOL}_n^{2-}]}{[\mathrm{Cu_2XO^{2-}}][\mathrm{L}]^n} \qquad (1)$$

where L represents free hexamine. The absorbances of $\mathrm{Cu_2XOL}_n^{2-}$ at 578 nm were measured for varying hexamine concentration from 10^{-3} to $10^{-1}M$ at pH 6.00–6.30. A plot of $\log[\mathrm{Cu_2XOL}_n^{2-}]/[\mathrm{Cu_2XO^{2-}}]$ *vs.* $\log[\mathrm{L}]$ yielded a straight line with slope of 1. Therefore, one molecule of hexamine co-ordinates with $\mathrm{Cu_2XO^{2-}}$. The value of $K^{\mathrm{L}}_{\mathrm{Cu_2XOL}}$ was evaluated as $10^{2.14}$. The dissociation constant of $\mathrm{HL^+}$ was taken as $10^{-4.98}$.

The rate of substitution of Cu₂XO with EDTA

In MES buffer. A solution 2.10–5.25 × $10^{-5}M$ in XO, 3.87–7.74 × $10^{-5}M$ in Cu and 0.02*M* in MES–NaOH buffer (pH 4.82–6.00) and a solution 3.56–14.25 × $10^{-4}M$ in EDTA and 0.02*M* in MES–NaOH buffer (pH 4.82–6.00) were mixed, and the absorbance at 574 nm was measured as a function of the reaction time by the stopped-flow method.

Under these experimental conditions the substitution reaction of the $\mathrm{Cu_2XO^{2-}}$ chelate with EDTA proceeds to completion:

$$\mathrm{Cu_2XO + 2EDTA = 2Cu(EDTA) + XO} \qquad (2)$$

The rate-law is expressed by

$$-\frac{d[\mathrm{Cu_2XO^{2-}}]}{dt} = k_{0(\mathrm{H,R,M,Y})}[\mathrm{Cu_2XO^{2-}}] \qquad (3)$$

where $k_{0(\mathrm{H,R,M,Y})}$ is the conditional rate-constant involving the concentrations of hydrogen ion, XO, Cu and EDTA. From equation (3) we obtain

$$\log(A_t - A_\infty) = -\frac{k_{0(\mathrm{H,R,M,Y})}}{2.303}t + \log(A_0 - A_\infty) \qquad (4)$$

where A_0, A_t and A_∞ represent the absorbances of the reaction system at $t = 0$, t and ∞, respectively. The plots of $\log(A_t - A_\infty)$ *vs.* t yielded straight lines up to 90% of the total reaction, and the conditional rate-constants $k_{0(\mathrm{H,R,M,Y})}$ were obtained from the slopes of the straight lines. The data in Table 1 indicate that the values of k_0 are proportional to the concentration of EDTA but are independent of hydrogen ion, XO and Cu concentrations. Hence,

$$-\frac{d[\mathrm{Cu_2XO^{2-}}]}{dt} = k_1[\mathrm{Y'}][\mathrm{Cu_2XO^{2-}}] \qquad (5)$$

where [Y′] is the total concentration of EDTA ($[\mathrm{H_2Y^{2-}}] + [\mathrm{HY^{3-}}]$) not combined with copper ion, and the rate-constant k_1 was evaluated as 7.84 × 10^2 l.mole.sec^{-1}. The following reaction mechanism may be proposed.

$$\mathrm{Cu_2XO^{2-}} + \mathrm{Y'} \rightleftharpoons \mathrm{YCu(XO)Cu} \xrightarrow{\mathrm{r\,d\,s}}$$
$$\mathrm{CuY^{2-}} + \mathrm{CuHXO^{3-}} \text{ or } \mathrm{CuH_2XO^{2-}} \qquad (6)$$
$$\mathrm{CuHXO^{3-}} \text{ or } \mathrm{CuH_2XO^{2-}} + \mathrm{Y'} \xrightarrow{\mathrm{fast}}$$
$$\mathrm{CuY^{2-}} + \mathrm{H_3XO^{3-}} \qquad (7)$$

The release of the first copper ion from the $\mathrm{Cu_2XO^{2-}}$ chelate may be the rate-determining step (r.d.s.). From the results of potentiometry with a copper(II) ion-selective electrode the resulting 1:1 chelate is in the form of $\mathrm{CuHXO^{3-}}$ or $\mathrm{CuH_2XO^{2-}}$, and the protonation of the 1:1 chelate may weaken the Cu–XO bonds. The high stability of the 2:1 chelate ($\mathrm{Cu_2XO^{2-}}$) may support the mechanism proposed in equations (6) and (7).

In the presence of hexamine. A solution containing XO, Cu and hexamine (2.83 × 10^{-4}–2.19 × $10^{-1}M$) was mixed with a solution containing EDTA, and the absorbance at 578 nm was measured in the pH range from 5.77 to 6.24 (MES buffer) in the same way as for the MES buffer system.

The substitution reaction is written as:

$$\mathrm{Cu_2XOL + EDTA \rightleftharpoons 2Cu(EDTA) + XO + L} \qquad (8)$$

The rate-law is

$$-\frac{d[\mathrm{Cu_2XOL^{2-}}]}{dt} = k_{0(\mathrm{H,R,M,Y,L})}[\mathrm{Cu_2XOL^{2-}}] \qquad (9)$$

The results are shown in Table 2. No dependence of $k_{0(\mathrm{H,R,M,Y,L})}$ on the concentrations of XO, Cu and hydrogen ion was observed, but there was a linear relation to EDTA concentration. With increasing concentration of hexamine the rate of the substitution reaction decreased. In the hexamine concentration range from 3.00 × 10^{-2} to 2.19 × $10^{-1}M$, where the mixed-ligand complex $\mathrm{Cu_2XOL^{2-}}$ forms quantitatively, k_0 was proportional to the reciprocal of the concentration of hexamine. Thus, the rate-law may be rewritten as

$$-\frac{d[\mathrm{Cu_2XOL^{2-}}]}{dt} = k_2\frac{[\mathrm{Y'}][\mathrm{Cu_2XOL^{2-}}]}{[\mathrm{L'}]} \qquad (10)$$

The value of k_2 was evaluated as 5.39 sec^{-1}.

Therefore, the dissociation of hexamine from $\mathrm{Cu_2XOL^{2-}}$ takes place first:

$$\mathrm{Cu_2XOL^{2-} = Cu_2XO^{2-} + L} \qquad (11)$$

The substitution mechanism of $\mathrm{Cu_2XO^{2-}}$ with EDTA may be the same as that in the absence of hexamine. From equations (1), (5) and (10):

$$k_1 = k_2K^{\mathrm{L}}_{\mathrm{Cu_2XOL}} = 5.39 \times 10^{2.14}$$
$$= 7.44 \times 10^2\ \mathrm{l.mole^{-1}.sec^{-1}}$$

This value is in good agreement with that obtained in the absence of hexamine. This fact supports the reaction mechanism described above.

Table 1. First-order conditional rate constants $k_{0(\mathrm{H,R,M,Y})}$

25°C, μ = 0.1

$10^4 \times C_{\mathrm{EDTA}}$, *M*	$10^5 \times C_{\mathrm{XO}}$, *M*	$10^5 \times C_{\mathrm{Cu}}$, *M*	pH	$10 \times k_{0(\mathrm{H,R,M,Y})}$, sec^{-1}
3.56	2.10	3.87	4.82	2.90
			5.59	2.65
			5.68	2.68
			5.80	2.46
			5.85	2.41
			6.00	2.30
	3.15		5.39	2.74
	4.20			2.78
	5.25			2.43
5.34	2.10		4.82	4.32
			5.51	4.03
			5.80	4.29
			5.85	4.22
			6.00	4.34
	3.15		5.39	4.09
	4.20			3.83
	2.10	5.42	5.68	4.09
		5.81	5.85	4.17
		7.74	5.68	4.09
7.12		3.87		5.21
			5.80	5.60
			5.85	5.10
			6.00	5.30
	3.15		5.39	5.47
	4.20			5.28
	5.25			5.89
10.7	2.10		4.82	8.64
			5.80	8.24
			5.85	7.90
			6.00	8.00
	3.15		5.39	8.46
	4.20			8.24
	5.25			8.59
14.3	2.10		5.80	10.3
			5.85	10.7
	3.15		5.39	11.7
	4.20			10.6
	5.25			11.7

Table 2. First-order conditional rate constants $k_{0(H,R,M,Y,L)}$

25°C, μ = 0.1

$10^5 \times C_{Cu}$, M	$10^5 \times C_{XO}$, M	$10^4 \times C_{EDTA}$, M	$10^3 \times C_L$, M	pH	$10 \times k_{0(H,R,M,Y,L)}$, sec^{-1}
3.87	2.10	3.56	0.283	5.84	2.15
			3.01		1.85
				6.00	1.85
			6.02	5.77	1.24
			12.0	5.92	0.973
			30.1	6.00	0.573
			42.1	6.03	0.456
		5.34	0.283	5.84	3.96
			3.01		2.85
				6.00	2.56
			6.02	5.77	2.23
			30.1	6.00	1.02
			60.2	5.94	0.308
		7.13	0.283	5.84	4.99
			3.01		3.80
				6.00	3.52
			6.02	5.77	2.82
			12.0	5.92	2.13
			30.1	6.00	1.22
			42.1	6.03	0.798
			60.2	5.94	0.638
		10.7	0.283	5.84	7.91
			3.01		5.81
				6.00	6.26
			6.02	5.77	4.10
			12.0	5.92	3.14
			30.1	6.00	1.92
			42.1	6.03	1.22
			60.2	5.94	1.01
		14.3	0.283	5.84	10.23
			3.01		9.10
				6.00	8.59
	3.15		6.02	5.77	5.36
			12.0	5.92	4.24
			30.1	6.00	2.66
			42.1	6.03	1.62
			60.2	5.94	1.30
3.09	1.32	108	43.2	6.16	10.5
			65.6		8.63
			87.4		6.57
			131		4.52
			219		2.52

At lower concentrations of hexamine Cu_2XO^{2-} and Cu_2XOL^{2-} complexes exist. Thus, the rate law can be expressed as

$$-\frac{d[(Cu_2XO)']}{dt} = k[Y'][(Cu_2XO)']$$

$$= \left(\frac{k_1}{1 + K^L_{Cu_2XOL}[L]}\right)[Y'][(Cu_2XO)'] \quad (12)$$

where $[(Cu_2XO)']$ represents the total concentration of Cu–XO chelates. The plot of log k vs. log[L] is shown in Fig. 2. The values of $K^L_{Cu_2XOL}$, k_1 and k_2 obtained by a curve-fitting method were $10^{2.18}$, 7.76×10^2 l.mole^{-1}.sec^{-1} and 5.13 sec^{-1}, respectively. These values agree well with those obtained above. The curve shows that the presence of more than $10^{-2}M$ hexamine markedly slows down the rate of colour change of the indicator.

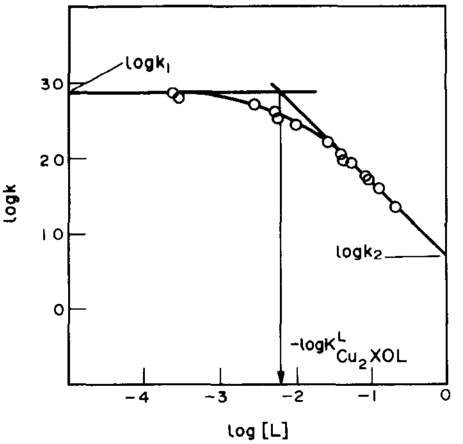

Fig. 2. Plot of log$k$ vs. log[L]. Solid line is the theoretical curve.

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Summary—The rate of ligand substitution of copper(II)-Xylenol Orange (XO) with EDTA (Y) has been determined spectrophotometrically over the pH range 4.8–6.0 at μ = 0.1 (KNO_3) and at 25°. In 2-(*N*-morpholino)ethane sulphonic acid buffer, copper forms a 2:1 chelate (Cu_2XO^{2-}) with XO, and the rate-law is expressed as $-d[Cu_2XO^{2-}]/dt = 10^{2.89}[Cu_2XO^{2-}][Y']$. The release of the first copper ion from Cu_2XO^{2-} is the rate-determining step. The resulting $CuHXO^{3-}$ or CuH_2XO^{2-} may undergo fast substitution with EDTA. In the presence of hexamine, the copper(II)-XO chelate forms a mixed-ligand complex with hexamine (L). The formation constant $K^L_{Cu_2XOL} = [Cu_2XOL^{2-}]/[Cu_2XO^{2-}][L] = 10^{2.14}$ (μ = 0.1, 25°). At 3×10^{-2}–$2 \times 10^{-1}M$ hexamine the rate-law is expressed as $-d[Cu_2XOL^{2-}]/dt = 5.39[Cu_2XOL^{2-}][Y']/[L']$. The dissociation of hexamine from Cu_2XOL^{2-} has to precede the substitution reaction of Cu_2XO^{2-} with EDTA. Hence, hexamine at higher concentrations than $10^{-3}M$ slows down the rate of colour change of XO in the copper–EDTA titration.

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CONTROLLED POTENTIAL IODOMETRIC DETERMINATION OF IRON AFTER EXTRACTION WITH DI-ISOPROPYL ETHER

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The main difficulty arising in the determination of the iron in samples with complex matrices, is the separation of the iron from the other constituents in the sample. This is necessary to prevent any interference with the analysis. The lower the concentration of iron in the sample the better the separation required for its accurate determination.

Solvent extraction has been found to be one of the most efficient ways of separating iron from other constituents and several papers have described analytical applications of such methods.[1–3] The ferric chloride–hydrochloric acid–ether system is probably the most studied, and according to Dodson *et al.*[4] the use of di-isopropyl ether offers the greatest advantages. Nachtrieb *et al.*[5–6] have investigated this system and have stated the optimal conditions for such extractions.

An iodometric method for the determination of iron (III), based on the reaction

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \qquad (1)$$

was originally proposed by Mohr,[7] and later Kolthoff[8] and Swift[9] worked out the best conditions for its analytical application.

The extraction procedures outlined in the methods above will give a tetrachloroferrate(III) complex in acid solution and an acidic ferric chloride solution is to be preferred for the iodometric determination of iron(III). Consequently, a combination of the extraction procedure and iodometric analysis seems rather attractive. The present work describes the development of a di-isopropyl ether extraction procedure for micro amounts of iron(III) and an iodometric method for the determination of the iron(III), based on a modification of the apparatus used previously for the investigation of controlled potential coulometry in the iodine–iodide system [10,11]

EXPERIMENTAL

Apparatus

The controlled-potential coulometric circuit and the electrolysis cell used were constructed on the principles applied for the apparatus used in our laboratory and described previously.[10,11] However, the recent rapid development in electronic components has made it possible to choose better components and modify the circuit to achieve 100% higher current capacity in the controlled-potential apparatus used in this study.

Separatory funnel. The separatory funnel is made of Pyrex glass and connected to a Teflon tube (see Fig. 1) which can be pushed up and down, and is closed by the sealed-in glass plug when pushed up. A series of five identical funnels was used during the analyses.

Reagents

Cell solutions. The counter-electrode compartment and the bridge compartment are filled with 1*M* sodium perchlorate and the working electrode compartment with equal volumes of 1*M* sodium iodide and 1*M* sodium perchlorate.

Ether for extraction. Di-isopropyl ether of *p.a.* quality was used. Redistillation of this ether did not give significantly better results. The ether was treated before use by shaking with appropriate concentrations of hydrochloric acid (usually 8*M*). The occurrence of peroxide in the ether will interfere with the iodometric analysis and therefore the ether was regularly tested for peroxide content by the method proposed by Fiedler.[12]

Iron stock solutions. Stock solutions of ferrous and ferric iron were prepared from ferrous and ferric ammonium sulphate of p.a. quality. All solutions were prepared with distilled water that had been boiled and then cooled under nitrogen. The solutions were standardized with 1,10-phenanthroline (Fe^{2+}) and EDTA with sulphosalicylic acid as indicator (Fe^{3+}).

Extraction

A suitable aliquot of the sample was made to be 8*M* in hydrochloric acid, placed in the separatory funnel, and shaken with di-isopropyl ether (generally 2.0 ml), pre-equilibrated with hydrochloric acid. After the phases had separated the aqueous phase was discarded and the ether phase shaken with three 1-ml portions of distilled water. The

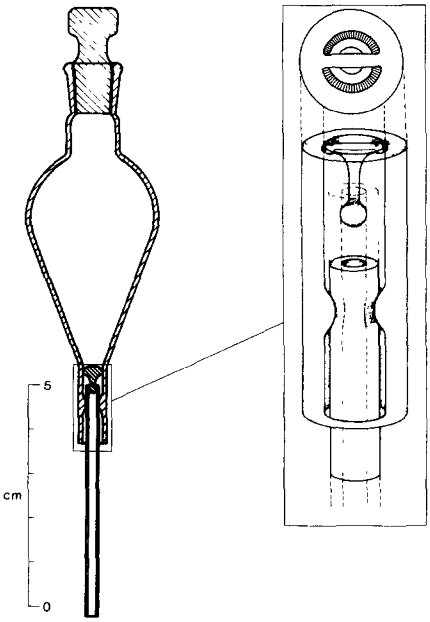

Fig. 1. Separatory funnel.

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aqueous fractions were retained for further analysis in the electrolysis cell, the ether phase was discarded. For more complex samples it is recommended that the first aqueous fraction is re-extracted by the same procedure, but generally, this step has been found to be unnecessary. The volume of the extraction solutions used can be varied, within rather wide limits, in order to obtain suitable concentrations of iron(III) for the coulometric step. However, from a practical point of view, volumes in the range 1–5 ml are preferred.

Preparation of sample

Blood serum. Serum sample (1–4 ml) was mixed with an equal amount of 10% trichloroacetic acid solution in a 10-ml test-tube. The test-tube was then covered, shaken and centrifuged. As much as possible of the clear supernatant was then transferred with a graduated pipette to a second test-tube, and the solution made 8*M* in hydrochloric acid.

Tablets. An appropriate number of tablets, depending on their iron content, was powdered in a mortar and dissolved in 8*M* hydrochloric acid.

Cocoa powder The sample was heated in a furnace at 600° for 2 hr and then the residue was dissolved in 8*M* hydrochloric acid. This method may also be used for analysis of tablets.

After the samples have been prepared, all the iron present must be oxidized to the ferric state before the extraction step. Either oxygen can be bubbled through the sample solution for 30 min, or an excess of bromine can be added and the excess reduced with formic acid.

Procedure

After the electrolysis cell had been filled with the appropriate solutions, a stream of nitrogen (15 ml/min) was allowed to pass through the solution in the working compartment for 10 min, after which the coulometric system was checked. The system was standardized with reagent blank solutions. A suitable amount of iodine was generated coulometrically at 350 mV *vs.* SCE and then immediately reduced at 0 mV *vs.* SCE and any discrepancies arising from the calculated blank value, background current or time of analysis were corrected for before the analyses of iron. After this standardization a sample containing iron(III) was added and the iodine formed according to reaction (1) reduced, and from the integrator read-out the iron content in the sample was calculated.

RESULTS AND DISCUSSION

The extraction procedure is critically dependent on the concentration of hydrochloric acid used and to some extent on the concentration of iron to be extracted. Therefore it was necessary to determine the best conditions for quantitative extraction of iron.

From a 0.050*M* stock solution of Fe(III) in 12*M* hydrochloric acid, 1.0-ml aliquots were pipetted into each of 15 volumetric flasks (10 ml) and made up to volume with 2.5–12*M* hydrochloric acid. With an Agla microsyringe, a 0.5-ml portion was then transferred from each flask to different separatory funnels and extracted with 2.0 ml of di-isopropyl ether which had previously been shaken once with the corresponding concentration of hydrochloric acid. The extraction procedure and coulometric analysis steps described above were then performed, and the results are shown in Fig. 2. It can be seen that in order to obtain quantitative extraction, the concentration of the acid must be within the limits 7.5–8.5*M*.

The method investigated is only valid for ferric iron, and any ferrous iron must be oxidized if the total iron concentration is to be determined. This can very easily be done by means of the two methods outlined above.

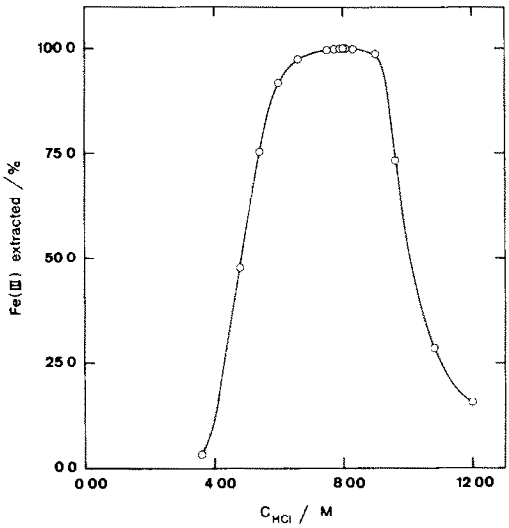

Fig. 2. Extraction of Fe(III) from hydrochloric acid by di-isopropyl ether.

The dependence of the oxidation of ferrous to ferric iron on the hydrochloric acid concentration is shown in Fig. 3. In this experiment a 0.005*M* ferrous solution was oxidized by allowing oxygen to bubble through the solution for 30 min. The higher the concentration of the hydrochloric acid the more efficient was the oxidation, because the formation of ferric chloride complexes decreases the formal potential for the ferrous–ferric couple, and the oxidizing power of oxygen increases with increasing acidity. However, with a hydrochloric acid concentration of just over 8*M* the oxidation is quantitative, as can be seen from Fig. 3, and this concentration has also been shown to be the most favourable for the extraction procedure. Thus dilution of the sample is not necessary. A drawback is the rather time-consuming oxidation procedure. The bromine–formic acid method of oxidation is rapid and does not interfere with either the extraction or the coulometric steps, but the concomitant dilution of the sample may be a source of error when only small samples are available for analysis.

The iron contents of several different samples have been determined and in Tables 1 and 2 some of the more interesting results are collected. Because both the extraction and the coulometric steps are quite selective for ferric iron,

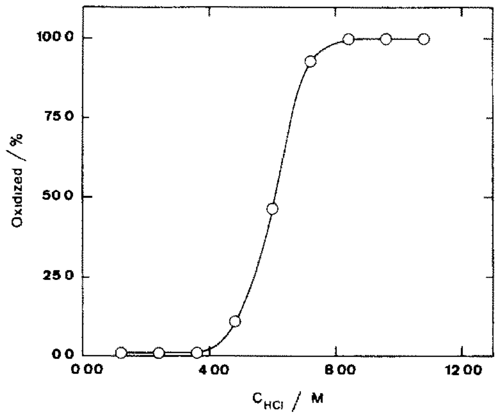

Fig. 3. Oxidation of 0.005*M* Fe(II) by oxygen at varying concentrations of HCl.

Table 1

Substance	Iron, *μg/ml* Added	Present*	Found	Recovery, %
Tap water A		0.33	0.33	100.0
Tap water B		0.56	0.55	98.2
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Blood serum A	0.50	1.34	1.32	98.5
Blood serum B		0.63	0.64	101.6
Blood serum B	0.50	1.13	1.10	97.3

* Determined spectrophotometrically.

Table 2

Substance	Iron, *mg* Calc.	Found	Standard deviation, *mg*
Tablet A[1]	15*	15.09	0.05
Tablet B[2]	60*	62.12	0.08
Tablet B[3]	60*	0.2	0.05
Cocoa powder	85*	86.5	0.1

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Department of Chemistry, University of Rajasthan, Jaipur, India

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$$H_4P_2O_8 + Fe(II) \rightarrow H_3PO_4 + HPO_4^- + Fe(III) \quad (1)$$

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The limiting value of the induction factor, the ratio of the number of equivalents of H_3PO_2 oxidized to the number of equivalents of iron(II) oxidized, was found to be one,

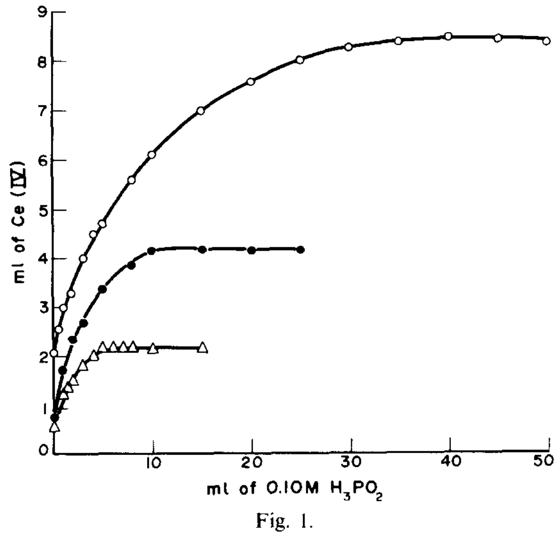

Fig. 1.

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CONTROLLED POTENTIAL IODOMETRIC DETERMINATION OF IRON AFTER EXTRACTION WITH DI-ISOPROPYL ETHER

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(*Received* 23 *December* 1975. *Accepted* 1 *February* 1976)

The main difficulty arising in the determination of the iron in samples with complex matrices, is the separation of the iron from the other constituents in the sample. This is necessary to prevent any interference with the analysis. The lower the concentration of iron in the sample the better the separation required for its accurate determination.

Solvent extraction has been found to be one of the most efficient ways of separating iron from other constituents and several papers have described analytical applications of such methods.[1–3] The ferric chloride–hydrochloric acid–ether system is probably the most studied, and according to Dodson *et al.*[4] the use of di-isopropyl ether offers the greatest advantages. Nachtrieb *et al.*[5–6] have investigated this system and have stated the optimal conditions for such extractions.

An iodometric method for the determination of iron (III), based on the reaction

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2 \qquad (1)$$

was originally proposed by Mohr,[7] and later Kolthoff[8] and Swift[9] worked out the best conditions for its analytical application.

The extraction procedures outlined in the methods above will give a tetrachloroferrate(III) complex in acid solution and an acidic ferric chloride solution is to be preferred for the iodometric determination of iron(III). Consequently, a combination of the extraction procedure and iodometric analysis seems rather attractive. The present work describes the development of a di-isopropyl ether extraction procedure for micro amounts of iron(III) and an iodometric method for the determination of the iron(III), based on a modification of the apparatus used previously for the investigation of controlled potential coulometry in the iodine–iodide system.[10,11]

EXPERIMENTAL

Apparatus

The controlled-potential coulometric circuit and the electrolysis cell used were constructed on the principles applied for the apparatus used in our laboratory and described previously.[10,11] However, the recent rapid development in electronic components has made it possible to choose better components and modify the circuit to achieve 100% higher current capacity in the controlled-potential apparatus used in this study.

Separatory funnel. The separatory funnel is made of Pyrex glass and connected to a Teflon tube (see Fig. 1) which can be pushed up and down, and is closed by the sealed-in glass plug when pushed up. A series of five identical funnels was used during the analyses.

Reagents

Cell solutions. The counter-electrode compartment and the bridge compartment are filled with 1*M* sodium perchlorate and the working electrode compartment with equal volumes of 1*M* sodium iodide and 1*M* sodium perchlorate.

Ether for extraction. Di-isopropyl ether of *p.a.* quality was used. Redistillation of this ether did not give significantly better results. The ether was treated before use by shaking with appropriate concentrations of hydrochloric acid (usually 8*M*). The occurrence of peroxide in the ether will interfere with the iodometric analysis and therefore the ether was regularly tested for peroxide content by the method proposed by Fiedler.[12]

Iron stock solutions. Stock solutions of ferrous and ferric iron were prepared from ferrous and ferric ammonium sulphate of p.a. quality. All solutions were prepared with distilled water that had been boiled and then cooled under nitrogen. The solutions were standardized with 1,10-phenanthroline (Fe^{2+}) and EDTA with sulphosalicylic acid as indicator (Fe^{3+}).

Extraction

A suitable aliquot of the sample was made to be 8*M* in hydrochloric acid, placed in the separatory funnel, and shaken with di-isopropyl ether (generally 2.0 ml), pre-equilibrated with hydrochloric acid. After the phases had separated the aqueous phase was discarded and the ether phase shaken with three 1-ml portions of distilled water. The

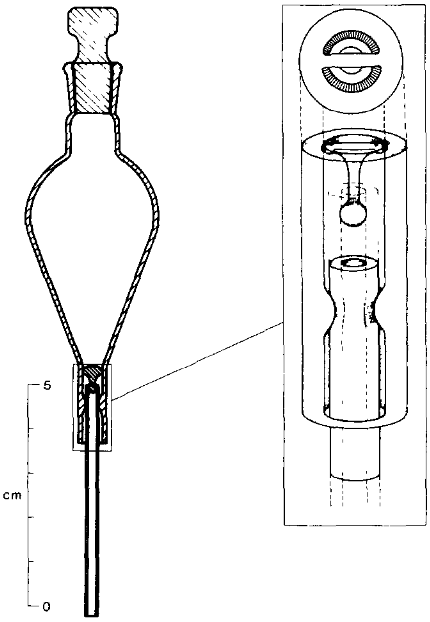

Fig. 1. Separatory funnel.

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* Present address: Boliden Aktiebolag, Chemicals Division, Research and Development, Analytical Section, S-251 00 Helsingborg, Sweden.

aqueous fractions were retained for further analysis in the electrolysis cell, the ether phase was discarded. For more complex samples it is recommended that the first aqueous fraction is re-extracted by the same procedure, but generally, this step has been found to be unnecessary. The volume of the extraction solutions used can be varied, within rather wide limits, in order to obtain suitable concentrations of iron(III) for the coulometric step. However, from a practical point of view, volumes in the range 1–5 ml are preferred.

Preparation of sample

Blood serum. Serum sample (1–4 ml) was mixed with an equal amount of 10% trichloroacetic acid solution in a 10-ml test-tube. The test-tube was then covered, shaken and centrifuged. As much as possible of the clear supernatant was then transferred with a graduated pipette to a second test-tube, and the solution made 8*M* in hydrochloric acid.

Tablets. An appropriate number of tablets, depending on their iron content, was powdered in a mortar and dissolved in 8*M* hydrochloric acid.

Cocoa powder The sample was heated in a furnace at 600° for 2 hr and then the residue was dissolved in 8*M* hydrochloric acid. This method may also be used for analysis of tablets.

After the samples have been prepared, all the iron present must be oxidized to the ferric state before the extraction step. Either oxygen can be bubbled through the sample solution for 30 min, or an excess of bromine can be added and the excess reduced with formic acid.

Procedure

After the electrolysis cell had been filled with the appropriate solutions, a stream of nitrogen (15 ml/min) was allowed to pass through the solution in the working compartment for 10 min, after which the coulometric system was checked. The system was standardized with reagent blank solutions. A suitable amount of iodine was generated coulometrically at 350 mV *vs.* SCE and then immediately reduced at 0 mV *vs.* SCE and any discrepancies arising from the calculated blank value, background current or time of analysis were corrected for before the analyses of iron. After this standardization a sample containing iron(III) was added and the iodine formed according to reaction (1) reduced, and from the integrator read-out the iron content in the sample was calculated.

RESULTS AND DISCUSSION

The extraction procedure is critically dependent on the concentration of hydrochloric acid used and to some extent on the concentration of iron to be extracted. Therefore it was necessary to determine the best conditions for quantitative extraction of iron.

From a 0.050*M* stock solution of Fe (III) in 12*M* hydrochloric acid, 1.0-ml aliquots were pipetted into each of 15 volumetric flasks (10 ml) and made up to volume with 2.5–12*M* hydrochloric acid. With an Agla microsyringe, a 0.5-ml portion was then transferred from each flask to different separatory funnels and extracted with 2.0 ml of di-isopropyl ether which had previously been shaken once with the corresponding concentration of hydrochloric acid. The extraction procedure and coulometric analysis steps described above were then performed, and the results are shown in Fig. 2. It can be seen that in order to obtain quantitative extraction, the concentration of the acid must be within the limits 7.5–8.5*M*.

The method investigated is only valid for ferric iron, and any ferrous iron must be oxidized if the total iron concentration is to be determined. This can very easily be done by means of the two methods outlined above.

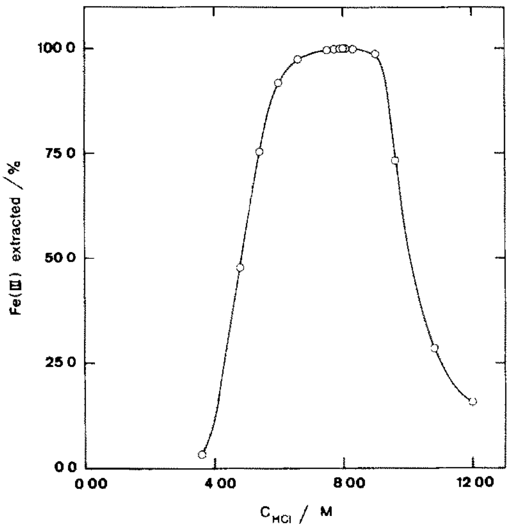

Fig. 2. Extraction of Fe(III) from hydrochloric acid by di-isopropyl ether.

The dependence of the oxidation of ferrous to ferric iron on the hydrochloric acid concentration is shown in Fig. 3. In this experiment a 0.005*M* ferrous solution was oxidized by allowing oxygen to bubble through the solution for 30 min. The higher the concentration of the hydrochloric acid the more efficient was the oxidation, because the formation of ferric chloride complexes decreases the formal potential for the ferrous–ferric couple, and the oxidizing power of oxygen increases with increasing acidity. However, with a hydrochloric acid concentration of just over 8*M* the oxidation is quantitative, as can be seen from Fig. 3, and this concentration has also been shown to be the most favourable for the extraction procedure. Thus dilution of the sample is not necessary. A drawback is the rather time-consuming oxidation procedure. The bromine–formic acid method of oxidation is rapid and does not interfere with either the extraction or the coulometric steps, but the concomitant dilution of the sample may be a source of error when only small samples are available for analysis.

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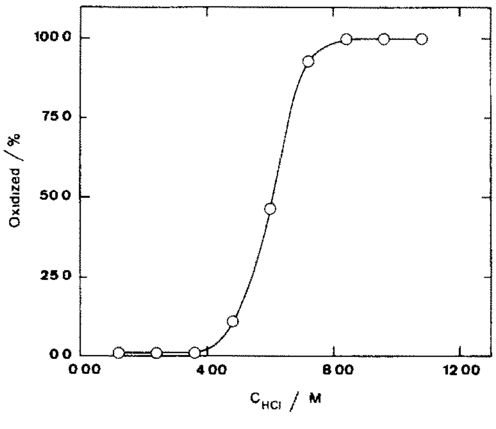

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* Determined spectrophotometrically.

Table 2

Substance	Iron, *mg*		Standard deviation, *mg*
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Tablet B[2]	60*	62.12	0.08
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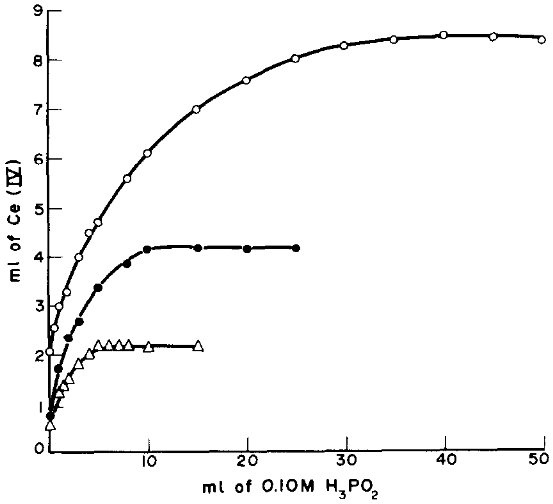

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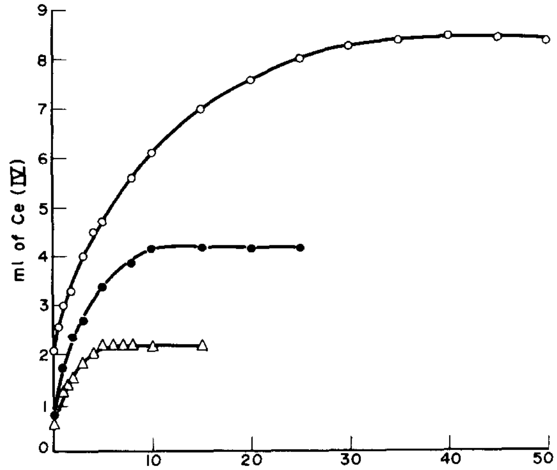

Fig. 1.

Table 1. [Fe(II)] = 1.0 × $10^{-2}M$; [$K_4P_2O_8$] = 8.53 × $10^{-3}M$; [H_3PO_2] = 1.0 × $10^{-1}M$

Set	ml of Ce(IV) for A	 B	 C	 D	 E	Induction factor
1	5 ml Fe(II)	A + 2.5 ml $K_4P_2O_8$	B + excess H_3PO_2 (>4 ml)	$K_4P_2O_8$ A − B	Oxidation of H_3PO_2, A − C	$\frac{[H_3PO_2]_{oxidized}}{[Fe(II)]_{oxidized}}$
	3.75	0.55	2.15	3.20	1.60	1.0
2	10 ml Fe(II)	A + 5 ml $K_4P_2O_8$	B + excess H_3PO_2 (>10 ml)	$K_4P_2O_8$, A − B	Oxidation of H_3PO_2, A − C	
	7.55	0 85	4.25	6.70	3.30	0.97
3	20 ml Fe(II)	A + 10 ml $K_4P_2O_8$	B + excess H_3PO_2 (>40 ml)	$K_4P_2O_8$, A − B	Oxidation of H_3PO_2, A − C	
	14.85	2.05	8.40	12.8	6.45	1.01

consistent with a two electron-change of the peroxydiphosphate.

Stock solutions of 0 0083M $K_4P_2O_8$, 0.01M iron(II) ammonium sulphate, 0.1M sodium hypophosphite, 0.4M iron(III) sulphate, and *ca* 0.01M cerium(IV) nitrate were prepared. Sulphuric acid was added wherever necessary to check hydrolysis of the solution. The indicator was *N*-phenylanthranilic acid.

Ten ml of iron(II) solution were titrated with cerium(IV). Next 5 ml of $K_4P_2O_8$ solution were added to 10 ml of iron(II) solution and the excess of the latter was titrated with cerium(IV). Then 10 ml of iron(II) solution were mixed with 25 ml of iron(III) solution and varying amounts of hypophosphite, 10 ml of peroxydiphosphate solution were added, and the whole was titrated with cerium(IV). The iron(III) solution was added to remove interference[2] of hypophosphite in the cerimetric determination of excess of iron(II).

These sets of titrations were repeated with 5 ml of iron(II) solution and 2.5 ml of $K_4P_2O_8$ solution, and with 20 ml of iron(II) solution and 10 ml of $K_4P_2O_8$ solution. All the results are shown in Fig. 1. It is obvious from the limiting titration values that when excess of hypophosphite is present, half the amount of peroxydiphosphate is consumed by iron(II) and half by hypophosphite (Table 1). Although it has been possible to identify this induced reaction by the titration of iron(II) with Ce(IV), it is not possible to determine hypophosphite or phosphite under the conditions of the experiment.

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1. S. Kapoor and Y. K. Gupta, unpublished work.
2. *Idem*, unpublished work.

Summary—It is shown that when peroxydiphosphate reacts with excess of iron(II) an induced oxidation of hypophosphite occurs if any is present.

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REMARQUES SUR LE MICRODOSAGE DU SELENIUM DANS LES COMPOSES ORGANIQUES

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2 rue Henry Dunant, 94320 Thiais, France

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La demande croissante de dosage du sélénium dans les composés organiques nous a conduit à éprouver différentes méthodes en vue de leur application dans le domaine microanalytique et à choisir, entre elles, la plus appropriée. Cette étude est l'objet de la présente note.

PARTIE EXPERIMENTALE

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Table 1

Substance	Iron, $\mu g/ml$ Added	Present*	Found	Recovery, %
Tap water A		0.33	0.33	100.0
Tap water B		0.56	0.55	98.2
Blood serum A		0.84	0.83	98.8
Blood serum A	0.50	1.34	1.32	98.5
Blood serum B		0.63	0.64	101.6
Blood serum B	0.50	1.13	1.10	97.3

* Determined spectrophotometrically.

Table 2

Substance	Iron, mg Calc.	Found	Standard deviation, mg
Tablet A[1]	15*	15.09	0.05
Tablet B[2]	60*	62.12	0.08
Tablet B[3]	60*	0.2	0.05
Cocoa powder	85*	86.5	0.1

[1] Multivitamin preparation with Fe^{2+}.
[2] Fe^{2+} as the only active substance.
[3] Analysed before oxidation.
* According to the manufacturer.

the distribution between ferrous and ferric iron in a sample can be readily determined (see Table 2, tablet B[3]). Analyses before and after oxidation will give the amount of ferric iron and the total amount of iron in the sample, and from these results the amount of ferrous iron can be readily determined.

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Summary—A selective method for the determination of small amounts of iron in different kinds of samples with complex matrices has been developed. The iron in a sample is converted into the ferric state and after extraction with di-isopropyl ether the ferric iron is iodometrically determined with a controlled-potential apparatus previously described. Iron concentrations lower than 1 ppm can be determined.

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IRON(II)-INDUCED OXIDATION OF HYPOPHOSPHITE BY PEROXYDIPHOSPHATE IN ACID MEDIUM

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An induced reaction was discovered while attempting to determine peroxydiphosphate cerimetrically in the presence of hypophosphite. Peroxydiphosphate is added to excess of iron(II), the surplus of which is back-titrated with cerium(IV) However, in the presence of hypophosphite the method fails. The reaction of peroxydiphosphate with iron(II) is fast, but with hypophosphite[1] it is slow. However, if iron(II) and hypophosphite are present together, both are oxidized comparably. Peroxydiphosphate, iron(II) and hypophosphite are respectively the *actor*, *inductor* and *acceptor*. The induced reaction suggests an intermediate species derived from peroxydiphosphate, possibly a free radical HPO_4^-:

$$H_4P_2O_8 + Fe(II) \rightarrow H_3PO_4 + HPO_4^- + Fe(III) \quad (1)$$

$$HPO_4^- + Fe(II) \rightarrow HPO_4^{2-} + Fe(III) \quad (2)$$

$$2HPO_4^- + H_3PO_2 + H_2O \rightarrow 2H_2PO_4^{2-} + H_3PO_3 \quad (3)$$

The limiting value of the induction factor, the ratio of the number of equivalents of H_3PO_2 oxidized to the number of equivalents of iron(II) oxidized, was found to be one,

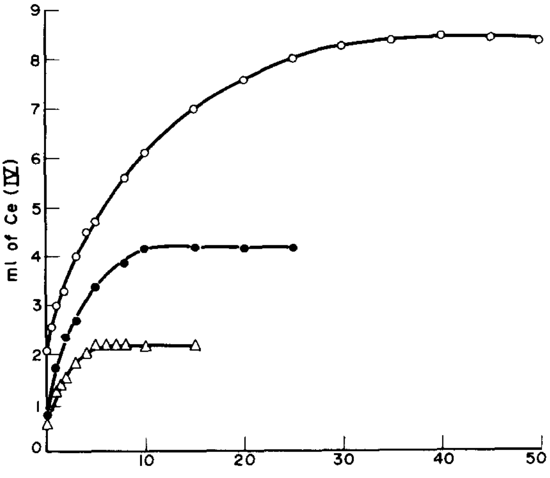

Fig. 1.

Table 1. $[Fe(II)] = 1.0 \times 10^{-2}M; [K_4P_2O_8] = 8.53 \times 10^{-3}M; [H_3PO_2] = 1.0 \times 10^{-1}M$

	ml of Ce(IV) for					
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	3.75	0.55	2.15	3.20	1.60	1.0
2	10 ml Fe(II)	A + 5 ml $K_4P_2O_8$	B + excess H_3PO_2 (>10 ml)	$K_4P_2O_8$, A − B	Oxidation of H_3PO_2, A − C	
	7.55	0 85	4.25	6.70	3.30	0.97
3	20 ml Fe(II)	A + 10 ml $K_4P_2O_8$	B + excess H_3PO_2 (>40 ml)	$K_4P_2O_8$, A − B	Oxidation of H_3PO_2, A − C	
	14.85	2.05	8.40	12.8	6.45	1.01

consistent with a two electron-change of the peroxydiphosphate.

Stock solutions of 0 0083M $K_4P_2O_8$, 0.01M iron(II) ammonium sulphate, 0.1M sodium hypophosphite, 0.4M iron(III) sulphate, and *ca* 0.01M cerium(IV) nitrate were prepared. Sulphuric acid was added wherever necessary to check hydrolysis of the solution. The indicator was *N*-phenylanthranilic acid.

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Deux conditions sont très importantes en vue de l'obtention de résultats corrects : la destruction totale du brome résiduel et la limitation du volume de solution à titrer. Un trop grand excès de brome, s'il est mal détruit, donne lieu à l'obtention de résultats erronés par excès. Le volume total de solution obtenu après rinçage de la fiole ne doit pas dépasser 21 ml (10 ml de solution absorbante + 11 ml d'eau de rinçage) afin que la concentration d'acide chlorhydrique reste appropriée.

Les sélénites ou séléniates trouvés dans le commerce ne possèdent pas, en général, les caractéristiques requises pour préparer une solution de titre exactement connu par simple pesage de ces produits; il est possible de préparer une solution de séléniate de sodium approximativement titrée et de déterminer son titre exact par réduction du séléniate en sélénium rouge par l'acide chlorhydrique et l'iodure de potassium. La distillation de l'iode libéré et son titrage permettent d'obtenir la titre exact du séléniate.[5] Le titre de thiosulfate utilisé pour le titrage après minéralisation en fiole de Schöniger est alors déterminé par rapport au séléniate dans les conditions décrites pour ce titrage (méthode A).

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Quelques résultats significatifs obtenus par la méthode préconisée sont reportés dans le tableau ci-dessous.

De nombreux hétéroéléments métalliques tels que Co, Cr, *etc.* sont souvent responsables d'une combustion et mise en solution du sélénium incomplètes.

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Des essais d'emploi de l'urée,[9] à cette fin, n'ont pas conduit à l'obtention de résultats iodométriques reproductibles.

Tableau 1

Composé de recherche*	Masse du prélèvement, *mg*	Teneur en élément, %	
		trouvée	calculée
A	2,693	$27{,}3_7$	26,93
	3,077	$26{,}6_5$	—
	2,960	$27{,}2_3$	—
B	3,104	$32{,}5_6$	32,61
	2,252	$32{,}2_0$	—
	2,987	$32{,}4_0$	—
C	1,260	$33{,}9_3$	33,60
	3,816	$33{,}1_8$	—
	3,008	$33{,}7_2$	—

* Il est difficile de se procurer dans le commerce des substances pures et stables. La composé A est un dérivé de l'α sélénonaphtol , le composé B est un dérivé du sélénacyclopentadiène ; le composé C est un dérivé du diséléniure de diphényle

Conclusion

La méthode retenue pour la mise en oeuvre du microdosage du sélénium est la combustion en fiole de Schöniger associée à une iodométrie.

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Résumé—Les auteurs exposent quelques remarques relatives à la minéralisation des composés organiques séléniés en vue du dosage microanalytique du sélénium Ils mettent en oeuvre la combustion en fiole remplie d'oxygène suivie d'un dosage iodométrique. Les masses des prélèvements sont de 2 à 3 mg.

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	2,960	27,2$_3$	—
B	3,104	32,5$_6$	32,61
	2,252	32,2$_0$	—
	2,987	32,4$_0$	—
C	1,260	33,9$_3$	33,60
	3,816	33,1$_8$	—
	3,008	33,7$_2$	—

* Il est difficile de se procurer dans le commerce des substances pures et stables. La composé A est un dérivé de l'α sélénonaphtol , le composé B est un dérivé du sélénacyclopentadiène ; le composé C est un dérivé du diséléniure de diphényle

Conclusion

La méthode retenue pour la mise en oeuvre du microdosage du sélénium est la combustion en fiole de Schöniger associée à une iodométrie.

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Résumé—Les auteurs exposent quelques remarques relatives à la minéralisation des composés organiques séléniés en vue du dosage microanalytique du sélénium Ils mettent en oeuvre la combustion en fiole remplie d'oxygène suivie d'un dosage iodométrique. Les masses des prélèvements sont de 2 à 3 mg.

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A LIQUID STATE Hg^{2+}-SENSITIVE ELECTRODE

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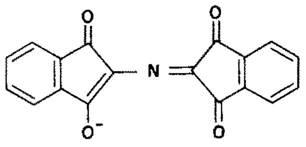
DYDA is formed in the reaction between ninhydrin (triketohydrindene hydrate) with amino-acids[3] and is more commonly known under the name of "Ruhemann's Purple":



DYDA

This reaction has been studied from the mechanistic point of view by many authors, starting with Ruhemann. On the basis of this reaction some methods were developed for the determination of amino-acids.[4–8]

EXPERIMENTAL

Preparation of the electroactive substance (the liquid membrane)

In order to obtain the liquid membrane, the procedure is as follows: 10 ml of $10^{-2}M$ glycine and 10 ml of $5 \times 10^{-2}M$ ninhydrin are introduced into a U-shaped glass tube with stop-cocks at both ends. One of the stop-cocks is kept closed, while the other is connected with a rubber tube to a water-filled graduated cylinder. The U-tube is placed in a bath of boiling water. The reaction is finished when no more CO_2 evolves from the U-shaped tube. The product is a solution of the ammonium salt of DYDA. It is transferred to a 100-ml separating funnel, then 3 ml of $0{\cdot}1M$ nitric acid are added. DYDA (the free acid) is precipitated and is extracted with 25 ml of chloroform by shaking for 2 min. The organic layer (solution A) is transferred to another separating funnel containing 25 ml of $10^{-2}M$ mercuric nitrate. The acidity of the solution is adjusted to pH 6 with hexamine and the two phases are shaken for 2 min. The aqueous phase is transferred to another separating funnel and shaken with 25 ml of chloroform The organic phases are combined, dried by passage through anhydrous sodium sulphate and transferred to a 100-ml flask. This is solution B, the liquid membrane with a mercury(II) concentration of $5 \times 10^{-4}M$. The absorption spectra of solutions A and B have peaks at 480 and 520 nm respectively.

Construction of the electrode

This is done as described previously[9–11] by impregnating the support material (a hydrophobized graphite rod) with solution B. The internal reference electrode is eliminated by use of a stainless-steel wire introduced into the graphite rod. The electrode is stored in solution B.

RESULTS AND DISCUSSIONS

The electrode function

The emf measurements were made with the electrochemical cell

$$\begin{array}{c|c|c|c} \text{Hg}^{2+}\text{-sensitive electrode} & \text{Hg}^{2+}(C_{\text{Hg}^{2+}}),\ \mu = 0.4\ (\text{KNO}_3) & \text{KNO}_3\ \text{std.} & \text{SCE} \end{array} \qquad \text{(I)}$$

where $C_{Hg^{2+}}$ represents the Hg^{2+} concentration, varying from 10^{-1} to $10^{-6}M$. The emf of cell (I) is given by

$$E_1 = E'_0 + 0.031 \log [\text{Hg}^{2+}] \qquad (1)$$

in the range 10^{-1}–$10^{-5}M$ Hg^{2+} concentration; E'_0 represents the conditional standard potential of the electrode. The measurements were carried out at constant ionic strength ($\mu = 0.4$, KNO_3), and the junction potential was kept constant.

The fact that we cannot obtain better sensitivities for this electrode is probably due to the absorption of Hg^{2+} at the end of the electrolyte bridge and on the surface of the glass vessel.

Influence of pH

In Fig. 1 we show the effect of pH on the response of the electrode at different mercury(II) concentrations.

The pH range in which the potential remains constant is relatively narrow because of the hydrolysis of Hg^{2+}. The direct potential measurements for calibration of the electrode were done at pH 1 (adjusted with nitric acid).

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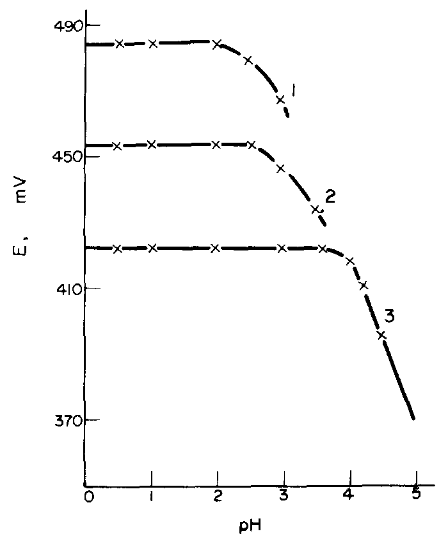
The response characteristics of the electrode were evaluated by introducing the electrode into mercuric nitrate solutions of different concentrations but of identical acidity (pH 1) and noting the emf values as a function of time. A Servogor^S potentiometric recorder (Goerz Electro, Vienna) was used. The response time of the electrode is



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where E_I is the emf of cell I for $C_{\mathrm{Hg}^{2+}} = 10^{-1}M$, and E_{II} is the emf of an electrochemical cell of type (II):

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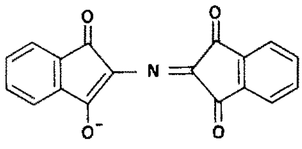

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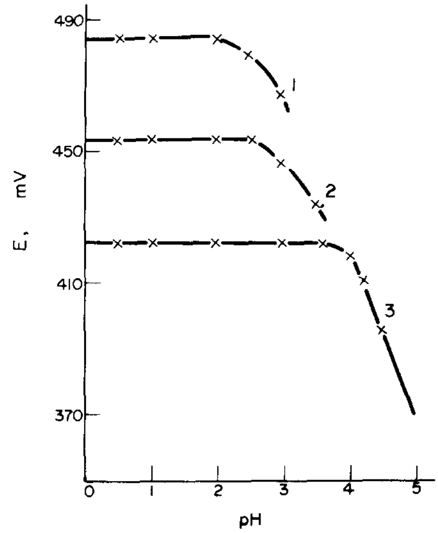

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF ZINC(II) WITH 4-(2-PYRIDYLAZO)-RESORCINOL AND A QUATERNARY AMMONIUM SALT

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The object of this study was to develop a new, simple and highly sensitive spectrophotometric method for zinc determination. Recent studies have shown that the quaternary ammonium salts, when used to extract chelates in the form of an ion-association complex, improve the quality of spectrophotometric methods.[1–7] Accordingly we decided to investigate whether the sensitive reaction between zinc(II) and 4-(2-pyridylazo)-resorcinol (PAR),[8] could be enhanced by extraction in the presence of cetyldimethylbenzylammonium chloride (CDBA), just as the determination of zinc with PAN is improved by addition of the surfactant Triton-X-100.[9]

EXPERIMENTAL

Apparatus

A Carl Zeiss VSU-1 universal spectrophotometer was used for the accurate absorbance measurements and a Zeiss SPECORD-UV-VIS spectrophotometer for recording the spectra.

The precise pH values were measured with a digital Radiometer pH-meter PHM 52; A Seibold pH-meter, type GLD was used for analytical purposes.

Reagents

Standard zinc solution A known weight of pure zinc was dissolved in hydrochloric acid[10] or 0.1*M* perchloric acid and diluted to known volume.

4-(2-Pyridylazo)-resorcinol, monosodium salt. A $10^{-4}M$ solution was standardized by spectrophotometric titration with copper(II) nitrate solution at pH 5 and 520 nm.[11] More dilute solutions ($10^{-5}M$) were also used. An aqueous 0.01% (w/v) solution was used for the analytical studies.

Cetyldimethylbenzylammonium chloride. A 0.002*M* solution was prepared by dissolving 0.082 g of the quaternary salt in 100 ml of distilled water

Buffer solutions pH 9.5–11.5. Mixtures of 0.2*M* sodium bicarbonate and 0 2*M* sodium carbonate[12] were used. At pH above, 11.5, 0.1*M* sodium hydroxide was used.

Standard cadmium solution. A 0.01*M* stock solution was standardized complexometrically and diluted as required.

Sodium diethyldithiocarbamate. A 0.1% (w/v) aqueous solution.

All other chemicals used were of analytical-reagent grade.

Extraction procedure

Place an aliquot of the sample solution containing not more than 50 μg of zinc in a 50-ml volumetric flask, add 10 ml of 0.01% PAR solution, 5 ml of bicarbonate–carbonate buffer solution (pH 9.7) and dilute to the mark. Pipette into a 100-ml separatory funnel an aliquot of this solution containing up to 5 μg of zinc. Add 1 ml of 0.002*M* CDBA solution and 5.00 ml of chloroform. Dilute with a little water (5–6 ml) and shake for about 1 min. Allow the layers to separate and run the pink chloroform extract into a 10-mm glass cell containing, if necessary, a small amount of anhydrous sodium sulphate crystals to remove the droplets of water. Measure the absorbance at 505 nm against a reagent blank as reference solution (the excess of PAR is also extracted).

RESULTS AND DISCUSSION

Absorption spectra sensitivity and accuracy

The absorption spectra of the zinc(II)–PAR complex and PAR in water, as well as their ion-association compounds in chloroform, were recorded. The extraction with the quaternary ammonium salt produces a small bathochromic shift for the metal complex (10 nm) and a hypsochromic shift for the chromogenic reagent (15 nm) but otherwise the spectra in the two phases are virtually identical. Thus the long-chain cation favourably influences the optical characteristics of the analytical system.

The colour appears immediately after shaking and the absorbance remains constant for at least 1 hr. Beer's law is valid up to an absorbance of 1.4, corresponding to a range of 0.2–1.2 ppm zinc. Two quite different standard zinc solutions ($10^{-5}M$ and 1 ppm) were used to calculate the conditional molar absorptivity, giving $9.14 \pm 0.21 \times 10^4$ and $9.21 \pm 0.26 \times 10^4$ $\text{l.mole}^{-1}.\text{cm}^{-1}$ respectively compared with 8.68×10^4 and 8.3×10^4 for aqueous solutions. This is an improvement over the dithizone procedure.

A series of solutions containing 0.129–0.645 ppm zinc were subjected to the procedure. Recoveries ranged from 99.2 to 101.1% with a standard deviation[13] of 0.0056 ppm.

Nature of the reaction

The reaction between zinc(II) and PAR in aqueous solution has been investigated in detail by several workers.[14–18] Kitano and Ueda[8] have discussed the analytical aspects of the reaction, and confirmed the composition of the chelate in alkaline medium to be Zn.PAR = 1:2. We verified the anionic nature of the chelate complex by determining the number of protons released during the complexation in equimolar solutions, using the following equation[19,20]

$$\log \beta_2' = \log K_{eq} + n\text{pH} \qquad (1)$$

The conditional stability constants β_2' were calculated and plotted against corresponding pH values. The plot gave a straight line with a slope $n = 2$ which led to $\log \beta_2 = 21.7 \pm 0.3$. This is in agreement with the results of Tanaka *et al.*[18] ($\log \beta_2 = 22.2 \pm 0.2$) and Corsini *et al.*[16] ($n = 2$), so in the pH range studied the reaction is

$$Zn^{2+} + 2HL^- = ZnL_2^{2-} + 2H^+ \qquad (2)$$

where L denotes PAR.

Effect of pH, and concentrations of PAR and CDBA

The absorbance depends on pH, but is constant over the range 9.5–11.5 (Fig. 1). Several standard buffer solutions were examined, but only with carbonate/bicarbonate was a clean separation of the layers obtained.

The amount of PAR added in aqueous solution was varied and the absorbance of the organic phase measured

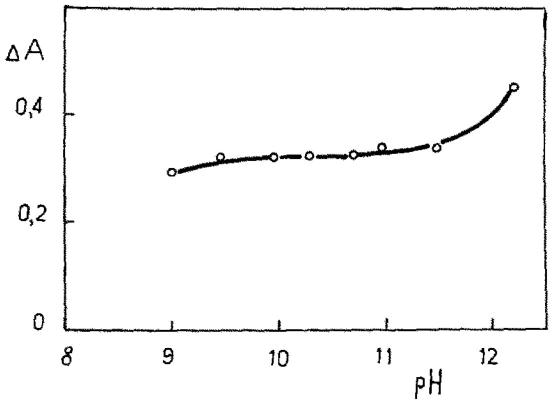

Fig. 1. Effect of pH (series of bicarbonate-carbonate buffer solutions). $C_{Zn} = 0.3$ ppm.

The results obtained are shown in Fig. 2. The absorbance increases rapidly on addition of the reagent to a mole-ratio of Zn:PAR = 1:4, whereas beyond this value the colour intensity is independent of the reagent concentration.

In the presence of a quaternary ammonium salt PAR is also extracted. Thus, the excess of both PAR and CDBA needed to ensure that PAR will always be extracted and transferred completely into the chloroform layer, must be established.

The extraction also depends on the excess of cationic surfactant, which affects the rate at which the two phases separate and remain clear. A very large excess of CDBA produces a stable emulsion on shaking so that the two liquids do not separate quickly. One ml of $2 \times 10^{-3}M$ CDBA solution proved adequate for the extraction and permitted satisfactory separation (Fig. 3).

Composition of the ion-association complexes

(*a*) The composition of the zinc(II)-PAR chelate in the organic phase was determined by the Job method.[21] This was done by extracting into the same volume of chloroform (5 ml) various ratios of the two equimolar solutions ($1.01 \times 10^{-5}M$) added to the aqueous phase in presence of a small excess of the quaternary ammonium salt and a buffer solution, which also kept the ionic strength constant. The molar ratio thus found was the same as in aqueous solution, 1:2.

(*b*) The composition of the Zn-PAR-CDBA ion-association compound was determined by extracting the three-component isomolar series prepared by varying the volumes of the three equimolar solutions ($1.01 \times 10^{-5}M$) of zinc, PAR and CDBA in such a way that the molar ratio of zinc:PAR was always 1:2 and the total volume was always the same (20 ml). The results obtained show that the stoichiometry of the complex is Zn:PAR:CDBA = 1:2:2, suggesting that the extracted species is $[Zn(PAR)_2](CDBA)_2$. The results were confirmed by other standard methods.

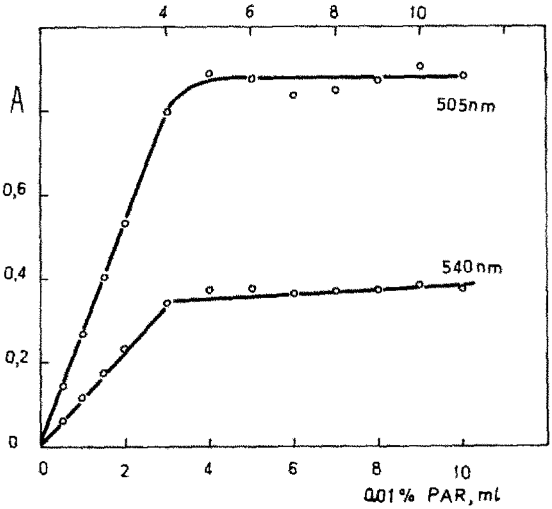

Fig. 2. Effect of PAR concentration on the absorbance of the complex in chloroform. $C_{Zn} = 0.5$ ppm (*vs.* water).

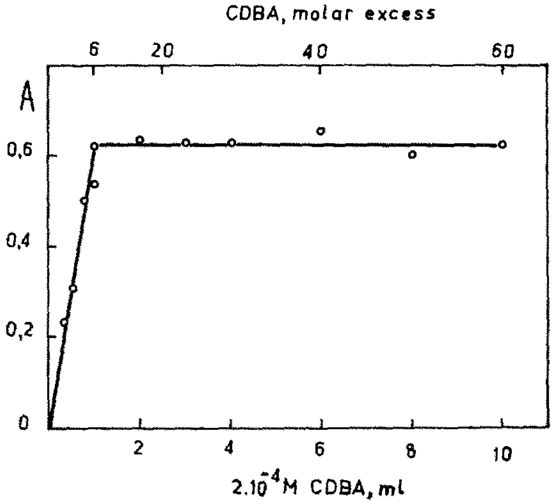

Fig. 3. Effect of CDBA concentration on the extractability of the system $C_{Zn} = 0.4$ ppm (*vs* water)

Effect of cadmium

Preliminary tests with several kinds of masking reagents for cadmium showed that only sodium diethyldithiocarbamate (DDTC) was satisfactory. In order to find the optimum conditions for determination of zinc without cadmium being simultaneously extracted, the mutual dependence of the DDTC and CDBA concentrations was studied. For these experiments [Cd] = [Zn] = 0.26 ppm. First [CDBA] was held constant (1 ml of $2 \times 10^{-3}M$ solution) and the volume of 0.01% DDTC varied, with the following results:

DDTC, *ml*:	0	0.1	0.25	0.5	1.0	1.5
Absorbance.	0.364	0.352	0.365	0.345	0.348	0.327

Then the level of DDTC was fixed at 0.25 ml whilst the volume of CDBA was varied:

CDBA, *ml*.	0	0.1	0.25	0.5	1.0
Absorbance:	0.364	0.269	0.353	0.372	0.365

These results enable optimum concentrations of DDTC and CDBA to be selected. The zinc solution should be diluted to at least 20 ml before the extraction, otherwise zinc will be partially masked, and the buffer solution should be added after the reagent to prevent the precipitation of cadmium. The results obtained by the modified procedure are given in Table 1.

It is evident that cadmium can be tolerated in up to 50-fold w/w ratio. This is a better selectivity than that of the dithizone method.

Preliminary investigations on the influence of DDTC on strongly interfering cations such as cobalt(II), nickel and copper(II) were also performed It was found that these metals are masked when present in the same amount as the zinc Cobalt and nickel can be tolerated up to a weight ratio Zn:Me = 1:10, while copper is tolerated at a ratio 1:2.5. These investigations will be extended to other interfering ions. Further work on the analytical application of the method will also be carried out and presented later

Table 1. Effect of cadmium(II) on the determination of zinc(II) with DDTC as masking agent (0.26 ppm Zn, 505 nm, 10-mm cell)

Weight ratio Zn:Cd	Absorbance	Zn found, *ppm*
1:0	0.364	
1:1	0.364	0.260
	0.367	0.263
1:10	0.360	0.258
	0.345	0.247
	0.355	0.254
	0.362	0.259
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Summary—A simple and selective extraction spectrophotometric determination of zinc is described. The complex $[Zn(PAR)_2](CDBA)_2$, where PAR is the 4-(2-pyridylazo)resorcinol anion and CDBA is cetyldimethylbenzylammonium ion, is extracted from a solution buffered at pH 9.7 with carbonate/bicarbonate. Beer's law is obeyed over the range 0.2–1.2 ppm zinc, the molar absorptivity being 9.2×10^4 $l.mole^{-1}.cm^{-1}$. The precision in this range is 0.0056 ppm. Cadmium in up to a 50-fold w/w ratio may be masked with diethyldithiocarbamate.

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DETERMINATION OF BARIUM AND STRONTIUM PEROXIDES (ACTIVE OXYGEN) IN IGNITERS IN SMALL-ARMS TRACER AMMUNITION

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(*Received* 24 *October* 1975. *Accepted* 15 *December* 1975)

Tracer ammunition for both small arms and artillery is used for determining range and for directing fire. The tracer compositions in such ammunition are set off by igniters which may contain barium or strontium peroxide (oxidizers), calcium resinate, "Parlon" and zinc stearate (binders and fuels), magnesium powder (fuel), and Toluidine Red toner (identifying colouring agent and fuel). It has been noted by ammunition experts for many years that the igniters (and consequently the rounds of tracer ammunition) are inclined to lose their effectiveness with time and it has been suggested that this deterioration is caused by decomposition of the peroxide. However, this has never been proved, because of the lack of satisfactory analytical methods.

In view of the need, this arsenal undertook an investigation to develop a method for determining peroxide (active oxygen) in igniters in small-arms tracer ammunition. Many methods that had been previously used for determining peroxide in various materials were considered. The most common method for determining peroxide is the titrimetric permanganate method.[1–5] Other titrimetric methods that have been used involve ceric sulphate, potassium iodide, sodium thiosulphate, titanous chloride, and sodium nitrite.[1,5,6] Another method for peroxide is the eudiometric method whereby the volume of oxygen generated on decomposition is measured.[6] Spectrophotometric methods that have been proposed include the use of the titanium–peroxide complex,[5–9] permanganate decolorization,[5,6] ferric thiocyanate,[6] starch–iodide,[6–10] and ferroin[11] reactions.

The permanganate titrimetric method was found to be unreliable for the determination of peroxides in igniters because of interference from organic matter and magnesium powder. It is possible that some other titrimetric reagent could be used, but this approach was not pursued because a titrimetric method would not be applicable in any case to the accurate determination of the small amount of igniter to be found in ammunition. The eudiometer method was not applicable because of interference from hydrogen generated by the magnesium. It seemed, therefore, that a spectrophotometric technique would be the most feasible means for determining peroxide in igniters. The titanium–peroxide method was selected as the most useful.

EXPERIMENTAL

Reagents

Titanium solution. Weigh 2.00 g of titanium sponge into

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF ZINC(II) WITH 4-(2-PYRIDYLAZO)-RESORCINOL AND A QUATERNARY AMMONIUM SALT

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(*Received* 19 *November* 1975. *Accepted* 23 *February* 1976)

The object of this study was to develop a new, simple and highly sensitive spectrophotometric method for zinc determination. Recent studies have shown that the quaternary ammonium salts, when used to extract chelates in the form of an ion-association complex, improve the quality of spectrophotometric methods.[1–7] Accordingly we decided to investigate whether the sensitive reaction between zinc(II) and 4-(2-pyridylazo)-resorcinol (PAR),[8] could be enhanced by extraction in the presence of cetyldimethylbenzylammonium chloride (CDBA), just as the determination of zinc with PAN is improved by addition of the surfactant Triton-X-100.[9]

EXPERIMENTAL

Apparatus

A Carl Zeiss VSU-1 universal spectrophotometer was used for the accurate absorbance measurements and a Zeiss SPECORD-UV-VIS spectrophotometer for recording the spectra.

The precise pH values were measured with a digital Radiometer pH-meter PHM 52; A Seibold pH-meter, type GLD was used for analytical purposes.

Reagents

Standard zinc solution A known weight of pure zinc was dissolved in hydrochloric acid[10] or $0.1M$ perchloric acid and diluted to known volume.

4-(2-Pyridylazo)-resorcinol, monosodium salt. A $10^{-4}M$ solution was standardized by spectrophotometric titration with copper(II) nitrate solution at pH 5 and 520 nm.[11] More dilute solutions ($10^{-5}M$) were also used. An aqueous 0.01% (w/v) solution was used for the analytical studies.

Cetyldimethylbenzylammonium chloride. A $0.002M$ solution was prepared by dissolving 0.082 g of the quaternary salt in 100 ml of distilled water

Buffer solutions pH 9.5–11.5. Mixtures of $0.2M$ sodium bicarbonate and $0.2M$ sodium carbonate[12] were used. At pH above, 11.5, $0.1M$ sodium hydroxide was used.

Standard cadmium solution. A $0.01M$ stock solution was standardized complexometrically and diluted as required.

Sodium diethyldithiocarbamate. A 0.1% (w/v) aqueous solution.

All other chemicals used were of analytical-reagent grade.

Extraction procedure

Place an aliquot of the sample solution containing not more than 50 μg of zinc in a 50-ml volumetric flask, add 10 ml of 0.01% PAR solution, 5 ml of bicarbonate–carbonate buffer solution (pH 9.7) and dilute to the mark. Pipette into a 100-ml separatory funnel an aliquot of this solution containing up to 5 μg of zinc. Add 1 ml of $0.002M$ CDBA solution and 5.00 ml of chloroform. Dilute with a little water (5–6 ml) and shake for about 1 min. Allow the layers to separate and run the pink chloroform extract into a 10-mm glass cell containing, if necessary, a small amount of anhydrous sodium sulphate crystals to remove the droplets of water. Measure the absorbance at 505 nm against a reagent blank as reference solution (the excess of PAR is also extracted).

RESULTS AND DISCUSSION

Absorption spectra sensitivity and accuracy

The absorption spectra of the zinc(II)–PAR complex and PAR in water, as well as their ion-association compounds in chloroform, were recorded. The extraction with the quaternary ammonium salt produces a small bathochromic shift for the metal complex (10 nm) and a hypsochromic shift for the chromogenic reagent (15 nm) but otherwise the spectra in the two phases are virtually identical. Thus the long-chain cation favourably influences the optical characteristics of the analytical system.

The colour appears immediately after shaking and the absorbance remains constant for at least 1 hr. Beer's law is valid up to an absorbance of 1.4, corresponding to a range of 0.2–1.2 ppm zinc. Two quite different standard zinc solutions ($10^{-5}M$ and 1 ppm) were used to calculate the conditional molar absorptivity, giving $9.14 \pm 0.21 \times 10^4$ and $9.21 \pm 0.26 \times 10^4$ $l.mole^{-1}.cm^{-1}$ respectively compared with 8.68×10^4 and 8.3×10^4 for aqueous solutions. This is an improvement over the dithizone procedure.

A series of solutions containing 0.129–0.645 ppm zinc were subjected to the procedure. Recoveries ranged from 99.2 to 101.1% with a standard deviation[13] of 0.0056 ppm.

Nature of the reaction

The reaction between zinc(II) and PAR in aqueous solution has been investigated in detail by several workers.[14–18] Kitano and Ueda[8] have discussed the analytical aspects of the reaction, and confirmed the composition of the chelate in alkaline medium to be Zn.PAR = 1:2. We verified the anionic nature of the chelate complex by determining the number of protons released during the complexation in equimolar solutions, using the following equation[19,20]

$$\log \beta'_2 = \log K_{eq} + n\text{pH} \qquad (1)$$

The conditional stability constants β'_2 were calculated and plotted against corresponding pH values. The plot gave a straight line with a slope $n = 2$ which led to $\log \beta_2 = 21.7 \pm 0.3$. This is in agreement with the results of Tanaka *et al.*[18] ($\log \beta_2 = 22.2 \pm 0.2$) and Corsini *et al.*[16] ($n = 2$), so in the pH range studied the reaction is

$$Zn^{2+} + 2HL^- = ZnL_2^{2-} + 2H^+ \qquad (2)$$

where L denotes PAR.

Effect of pH, and concentrations of PAR and CDBA

The absorbance depends on pH, but is constant over the range 9.5–11.5 (Fig. 1). Several standard buffer solutions were examined, but only with carbonate/bicarbonate was a clean separation of the layers obtained.

The amount of PAR added in aqueous solution was varied and the absorbance of the organic phase measured

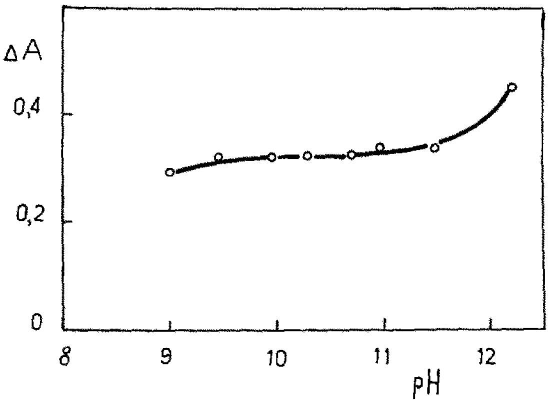


Fig. 1. Effect of pH (series of bicarbonate-carbonate buffer solutions). $C_{Zn} = 0.3$ ppm.

The results obtained are shown in Fig. 2. The absorbance increases rapidly on addition of the reagent to a mole-ratio of Zn:PAR = 1:4, whereas beyond this value the colour intensity is independent of the reagent concentration.

In the presence of a quaternary ammonium salt PAR is also extracted. Thus, the excess of both PAR and CDBA needed to ensure that PAR will always be extracted and transferred completely into the chloroform layer, must be established.

The extraction also depends on the excess of cationic surfactant, which affects the rate at which the two phases separate and remain clear. A very large excess of CDBA produces a stable emulsion on shaking so that the two liquids do not separate quickly. One ml of $2 \times 10^{-3}M$ CDBA solution proved adequate for the extraction and permitted satisfactory separation (Fig. 3).

Composition of the ion-association complexes

(*a*) The composition of the zinc(II)–PAR chelate in the organic phase was determined by the Job method.[21] This was done by extracting into the same volume of chloroform (5 ml) various ratios of the two equimolar solutions ($1.01 \times 10^{-5}M$) added to the aqueous phase in presence of a small excess of the quaternary ammonium salt and a buffer solution, which also kept the ionic strength constant. The molar ratio thus found was the same as in aqueous solution, 1:2.

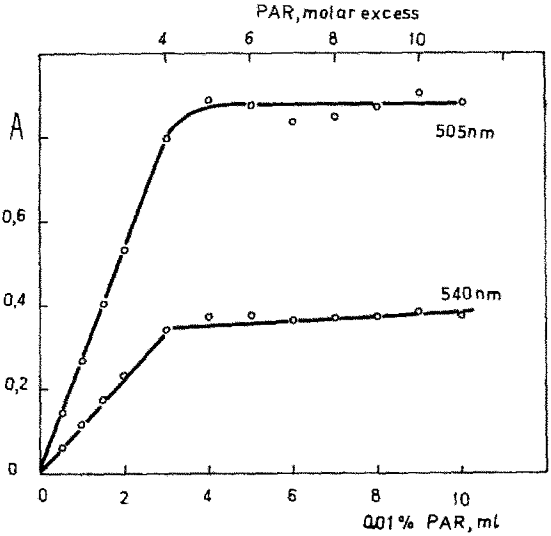
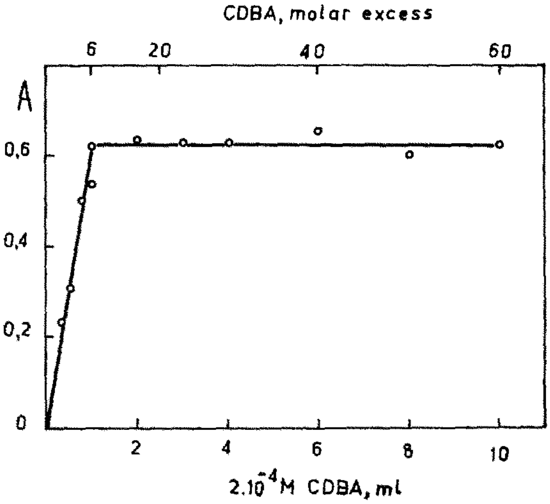


Fig. 2. Effect of PAR concentration on the absorbance of the complex in chloroform. $C_{Zn} = 0.5$ ppm (*vs.* water).



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(*b*) The composition of the Zn–PAR–CDBA ion-association compound was determined by extracting the three-component isomolar series prepared by varying the volumes of the three equimolar solutions ($1.01 \times 10^{-5}M$) of zinc, PAR and CDBA in such a way that the molar ratio of zinc:PAR was always 1:2 and the total volume was always the same (20 ml). The results obtained show that the stoichiometry of the complex is Zn:PAR:CDBA = 1:2:2, suggesting that the extracted species is $[Zn(PAR)_2](CDBA)_2$. The results were confirmed by other standard methods.

Effect of cadmium

Preliminary tests with several kinds of masking reagents for cadmium showed that only sodium diethyldithiocarbamate (DDTC) was satisfactory. In order to find the optimum conditions for determination of zinc without cadmium being simultaneously extracted, the mutual dependence of the DDTC and CDBA concentrations was studied. For these experiments [Cd] = [Zn] = 0.26 ppm. First [CDBA] was held constant (1 ml of $2 \times 10^{-3}M$ solution) and the volume of 0.01% DDTC varied, with the following results:

DDTC, *ml*:	0	0.1	0.25	0.5	1.0	1.5
Absorbance.	0.364	0.352	0.365	0.345	0.348	0.327

Then the level of DDTC was fixed at 0.25 ml whilst the volume of CDBA was varied:

CDBA, *ml*.	0	0.1	0.25	0.5	1.0
Absorbance:	0.364	0.269	0.353	0.372	0.365

These results enable optimum concentrations of DDTC and CDBA to be selected. The zinc solution should be diluted to at least 20 ml before the extraction, otherwise zinc will be partially masked, and the buffer solution should be added after the reagent to prevent the precipitation of cadmium. The results obtained by the modified procedure are given in Table 1.

It is evident that cadmium can be tolerated in up to 50-fold w/w ratio. This is a better selectivity than that of the dithizone method.

Preliminary investigations on the influence of DDTC on strongly interfering cations such as cobalt(II), nickel and copper(II) were also performed. It was found that these metals are masked when present in the same amount as the zinc. Cobalt and nickel can be tolerated up to a weight ratio Zn:Me = 1:10, while copper is tolerated at a ratio 1:2.5. These investigations will be extended to other interfering ions. Further work on the analytical application of the method will also be carried out and presented later

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Summary—A simple and selective extraction spectrophotometric determination of zinc is described. The complex $[Zn(PAR)_2](CDBA)_2$, where PAR is the 4-(2-pyridylazo)resorcinol anion and CDBA is cetyldimethylbenzylammonium ion, is extracted from a solution buffered at pH 9.7 with carbonate/bicarbonate. Beer's law is obeyed over the range 0.2–1.2 ppm zinc, the molar absorptivity being 9.2×10^4 l.mole^{-1}.cm^{-1}. The precision in this range is 0.0056 ppm. Cadmium in up to a 50-fold w/w ratio may be masked with diethyldithiocarbamate.

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DETERMINATION OF BARIUM AND STRONTIUM PEROXIDES (ACTIVE OXYGEN) IN IGNITERS IN SMALL-ARMS TRACER AMMUNITION

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(*Received* 24 *October* 1975. *Accepted* 15 *December* 1975)

Tracer ammunition for both small arms and artillery is used for determining range and for directing fire. The tracer compositions in such ammunition are set off by igniters which may contain barium or strontium peroxide (oxidizers), calcium resinate, "Parlon" and zinc stearate (binders and fuels), magnesium powder (fuel), and Toluidine Red toner (identifying colouring agent and fuel). It has been noted by ammunition experts for many years that the igniters (and consequently the rounds of tracer ammunition) are inclined to lose their effectiveness with time and it has been suggested that this deterioration is caused by decomposition of the peroxide. However, this has never been proved, because of the lack of satisfactory analytical methods.

In view of the need, this arsenal undertook an investigation to develop a method for determining peroxide (active oxygen) in igniters in small-arms tracer ammunition. Many methods that had been previously used for determining peroxide in various materials were considered. The most common method for determining peroxide is the titrimetric permanganate method.[1–5] Other titrimetric methods that have been used involve ceric sulphate, potassium iodide, sodium thiosulphate, titanous chloride, and sodium nitrite.[1,5,6] Another method for peroxide is the eudiometric method whereby the volume of oxygen generated on decomposition is measured.[6] Spectrophotometric methods that have been proposed include the use of the titanium–peroxide complex,[5–9] permanganate decolorization,[5,6] ferric thiocyanate,[6] starch–iodide,[6–10] and ferroin[11] reactions.

The permanganate titrimetric method was found to be unreliable for the determination of peroxides in igniters because of interference from organic matter and magnesium powder. It is possible that some other titrimetric reagent could be used, but this approach was not pursued because a titrimetric method would not be applicable in any case to the accurate determination of the small amount of igniter to be found in ammunition. The eudiometer method was not applicable because of interference from hydrogen generated by the magnesium. It seemed, therefore, that a spectrophotometric technique would be the most feasible means for determining peroxide in igniters. The titanium–peroxide method was selected as the most useful.

EXPERIMENTAL

Reagents

Titanium solution. Weigh 2.00 g of titanium sponge into

a 250-ml beaker, add 90 ml of concentrated hydrochloric acid, cover with a watch-glass, and warm on the hot-plate to dissolve. Maintain the volume of hydrochloric acid at 75–90 ml during the dissolution process. After the metal has completely dissolved, add 1 ml of concentrated nitric acid and boil for 1 min Cool and dilute to 200 ml in a volumetric flask

Barium peroxide, MIL-B-153A, Grade B,[2] or equivalent (the sample used in this work contained 8.9% active oxygen).

Strontium peroxide, MIL-S-612B, Grade B,[3] or equivalent (the sample used in this work contained 12.7% active oxygen).

Magnesium powder, MIL-M-382B, Type III, Granulation 12, nominal mesh size 120–200,[12] or equivalent.

Calcium resinate, MIL-C-20470A, Type II.[13]

"Parlon" (chlorinated rubber), MIL-R-60671 [14]

Zinc stearate, USP [15]

Toluidine Red toner, TT-P-445.[16]

Preparation of calibration curves

Barium peroxide. Transfer 0.20–0 21 g of barium peroxide (weighed to 0.1 mg) to a 150-ml beaker. Add 100 ml of dilute hydrochloric acid (1 + 9) and allow to stand with occasional stirring until the sample has dissolved (10–30 min) Dilute to 250 ml in a volumetric flask. Transfer 5.0, 10 0, 15.0, 20.0, and 25.0-ml aliquots to 100-ml volumetric flasks and dilute to about 35 ml with water. Add sufficient concentrated hydrochloric acid to bring its total content in each flask to 5 ml Dilute to about 75 ml with water and add 5.0 ml of titanium solution. Dilute to the mark and within 1 hr measure the absorbance at 410 nm against the reagent blank. Plot mg of barium peroxide (per 100 ml) against absorbance.

Strontium peroxide. Transfer 0.15–0.16 g of strontium peroxide (weighed to 0.1 mg) to a 150-ml beaker and proceed as described for the calibration curve for barium peroxide, but use 5.0, 10.0, 15.0, 17.5, and 20.0-ml aliquots. Plot mg of strontium peroxide (per 100 ml) against absorbance

Procedure

Igniter mixes. Transfer about 0.20 g of sample (weighed to 0 1 mg) to a 150-ml beaker. Add 100 ml of dilute hydrochloric acid (1 + 9) all at once. Allow to stand with occasional stirring until the barium or strontium peroxide has dissolved (10–30 min). Within 30 min after dissolution, filter through a Whatman No. 41 filter paper, wash with water, and dilute to the mark in a 250 ml volumetric flask. Transfer an aliquot, containing 13–20 mg of barium peroxide or 10–15 mg of strontium peroxide, to a 100-ml volumetric flask and dilute to about 35 ml. Add sufficient concentrated hydrochloric acid to bring its total content in the flask to 5 ml, dilute to about 75 ml with water, add 5 ml of titanium solution, dilute to the mark, and within 1 hr measure the absorbance at 410 nm against a reagent blank Find the number of mg of barium or strontium peroxide from the calibration curve and calculate the barium or strontium peroxide content as follows:

$$\% \, BaO_2 \text{ or } SrO_2 = \frac{\text{mg of } BaO_2 \text{ or } SrO_2 \text{ read from curve}}{\text{g of sample in aliquot}} \times 0{\cdot}101$$

Igniters contained in small-arms tracer ammunition. Remove the bullet from the round Working behind a safety shield, cut through the exterior of the bullet jacket lengthwise on both sides with a handsaw to just sufficient depth to be able to reach the tracer and igniter. Take care not to overheat the bullet during cutting, since overheating might cause some decomposition of the peroxide and constitute a hazard. Pull off one side of the jacket with a suitable instrument. Remove the igniter mix and store it in a closed bottle. Transfer a weighed sample to a 150-ml beaker, add 35–100 ml of dilute hydrochloric acid (1 + 9), allow to stand until the barium or strontium peroxide has dissolved, filter, wash, and dilute to volume in a volumetric flask (the amount of hydrochloric acid and the volume of the flask will depend on the amount of sample). Transfer an appropriate aliquot to a 100-ml volumetric flask and proceed as described for barium and strontium peroxides in igniter mixes.

DISCUSSION AND RESULTS

The magnesium metal dissolves almost instantaneously on adding 100 ml of hydrochloric acid (1 + 9) at room temperature and all at once; then the barium or strontium peroxide dissolves slowly in 10–30 min The extremely rapid dissolution of the magnesium minimizes the interference of magnesium If a more concentrated hydrochloric acid solution were used, the barium and strontium peroxides would dissolve simultaneously with the magnesium, causing lower results. The acid dissolution process must be conducted at room temperature. If the solutions were cooled, the magnesium would not dissolve instantly, causing lower results. The organic matter contained in the igniters does not dissolve in the acid and is filtered off and does not seem to interfere. In spite of all precautions, however, preliminary work with synthetic samples showed that the recoveries for peroxides were slightly low; therefore, it was decided on the basis of the preliminary work to multiply the calculated result by the empirical factor 1·01.

Hydrochloric acid is used rather than sulphuric acid because the latter would precipitate barium and strontium sulphates.

The acidity of the solution in which the titanium peroxide colour is developed is about 1.8*N*. This acidity is not critical since the permissible range is about 1·5–3·5*N* [17]

Full colour development was achieved with 5 ml of the titanium solution. Our titanium solution was prepared from the metal because that could be readily obtained in high purity. Nitric acid must be used in oxidizing Ti(III) to Ti(IV); oxidizing with hydrogen peroxide and subsequent boiling to destroy the peroxide caused hydrolysis of the titanium. The calibration curves followed Beer's law.

All the calculations for the barium and strontium peroxides in igniters were relative to the original barium and strontium peroxides which were arbitrarily taken to be 100% pure. This mode of calculation was chosen because the prime aim of the investigation was to determine whether there had been degradation of the barium or strontium peroxide in the igniters

If it were desired to make the calculation for the igniters in terms of active oxygen it would first be necessary to determine the active oxygen content of the barium and strontium peroxides used for preparing the calibration curves and then plot mg of active oxygen (per 100 ml) against absorbance. This would be a relatively simple matter.

The active oxygen of barium and strontium peroxide can be defined as the per cent oxygen (by weight) released when the peroxide reverts to the simple oxide (*e.g.*, $2BaO_2 \rightarrow 2BaO + O_2$). The active oxygen content of these materials is best determined by titration with permanganate in a perchloric–phosphoric acid medium.[2,3] The theoretical oxygen contents of barium and strontium peroxide are 9.45% and 13.38%, respectively The military specifications for barium and strontium peroxides[2,3] call for a minimum active oxygen content of 8.5% and 12 3%, respectively. However, according to the experience of this arsenal over many years, the active oxygen content of the barium peroxide and strontium peroxide used in the preparation of igniters varies from 8.8 to 9.0% for barium peroxide and from 12 5 to 12.8% for strontium peroxide (and does not change significantly for 2 or 3 years if the two

Table 1. Nominal composition of igniters used in small-arms tracer ammunition

Igniter	Nominal composition
I-280	76.5 SrO_2, 15.0 Mg, 8.5 Ca resinate
I-276	83.5 BaO_2, 15.0 Mg, 1.0 Zn stearate, 0.5 Toluidine Red toner
I-508	79.0 BaO_2, 14.1 Mg, 5.5 "Parlon", 0.9 Zn stearate, 0.5 Toluidine Red toner

materials are stored in air-tight containers). The cited ranges for active oxygen are equivalent to 93.1–95.2% pure barium peroxide and 93.4–95.7% pure strontium peroxide, respectively. Rosin[4] and the Fisher Scientific Co.[18] specify a minimum barium peroxide content of 88% and 85%, respectively, for reagent-grade barium peroxide. There is no specification for reagent-grade strontium peroxide.

The nominal compositions of the common igniter mixes used in small-arms tracer ammunition by the U.S. Army are shown in Table 1.

The results obtained for barium and strontium peroxides in synthetic igniter mixes are shown in Table 2. The recoveries were satisfactory (the average for all the runs was 100.2%).

The results obtained for peroxide in three actual production igniter mixes stored in closed containers for about a year are shown in Table 3. The results obtained for an igniter in a batch of ammunition several years old were 57.0, 49.0 and 53.3% BaO_2, the nominal content being 79.0% BaO_2 (each result represents an individual round). It is seen that two of three actual igniter mixes showed some deterioration while the igniter in the ammunition showed marked deterioration.

Table 2. Results for barium and stronium peroxides in synthetic igniter mixes

Present, *g*	Found, *g*	Recovery, %
BaO_2 + 25 mg Mg		
0.1514	0.1523 BaO_2	100.6
0.1518	0.1523 BaO_2	100.3
0.1519	0.1534 BaO_2	101.0
0.1479	0.1474 BaO_2	99.7
0.1484	0.1482 BaO_2	99.9
SrO_2 + 25 mg Mg + 15 mg Ca resinate		
0.1523	0.1507 SrO_2	99.0
0.1585	0.1555 SrO_2	98.1
0.1590	0.1602 SrO_2	100.9
0.1624	0.1613 SrO_2	99.3
0.1509	0.1518 SrO_2	100.6
BaO_2 + 30 mg Mg + 5 mg Z^a + 5 mg T^b		
0.1642	0.1632 BaO_2	99.4
0.1683	0.1679 BaO_2	99.8
0.1684	0.1679 BaO_2	99.7
0.1663	0.1682 BaO_2	101.1
0.1514	0.1548 BaO_2	102.2
BaO_2 + 30 mg Mg + 15 mg P^c + 5 mg Z^a + 5 mg T^b		
0.1545	0.1553 BaO_2	100.5
0.1583	0.1590 BaO_2	100.4
0.1587	0.1589 BaO_2	100.1
0.1566	0.1581 BaO_2	101.0
0.1567	0.1578 BaO_2	100.7

[a]Z = zinc stearate
[b]T = Toluidine Red toner
[c]P = "Parlon"

Table 3. Results for strontium and barium peroxides in actual igniter mixes

Igniter	Nominal, %	Results, %
I-280	76.5 SrO_2	67.5
		66.7
		67.5
		67.4
		67.0
		Ave. 67.2
		Std. dev 0.36
I-276	83.5 BaO_2	88.4
		88.4
		90.0
		88.7
		90.0
		88.8
		Ave. 89.1
		Std. dev. 0.75
I-508	79.0 BaO_2	72.7
		71.2
		72.7
		72.9
		73.3
		73.3
		Ave. 72.7
		Std. dev. 1.00

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Summary—A method is proposed for the determination of barium and strontium peroxides (active oxygen) in igniters in small-arms tracer ammunition. The sample is treated with dilute hydrochloric acid (1 + 9) which dissolves the magnesium powder almost instantaneously and then dissolves the barium or strontium peroxides within 10–30 min. The solution is then filtered to remove the organic substances (calcium resinate, "Parlon". Toluidine Red toner, and zinc stearate) and the peroxide is determined by means of the colour of the titanium–peroxide complex. It is shown that igniter mixes and igniters used in small-arms tracer ammunition deteriorate on storage.

Table 1. Effect of cadmium(II) on the determination of zinc(II) with DDTC as masking agent (0.26 ppm Zn, 505 nm, 10-mm cell)

Weight ratio Zn:Cd	Absorbance	Zn found, *ppm*
1:0	0.364	
1:1	0.364	0.260
	0.367	0.263
1:10	0.360	0.258
	0.345	0.247
	0.355	0.254
	0.362	0.259
1:50	0.366	0.262
	0.356	0.254
	0.400	0.283

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EXPERIMENTAL

Reagents

Titanium solution. Weigh 2.00 g of titanium sponge into

a 250-ml beaker, add 90 ml of concentrated hydrochloric acid, cover with a watch-glass, and warm on the hot-plate to dissolve. Maintain the volume of hydrochloric acid at 75–90 ml during the dissolution process. After the metal has completely dissolved, add 1 ml of concentrated nitric acid and boil for 1 min Cool and dilute to 200 ml in a volumetric flask

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Barium peroxide. Transfer 0.20–0.21 g of barium peroxide (weighed to 0.1 mg) to a 150-ml beaker. Add 100 ml of dilute hydrochloric acid (1 + 9) and allow to stand with occasional stirring until the sample has dissolved (10–30 min) Dilute to 250 ml in a volumetric flask. Transfer 5.0, 10.0, 15.0, 20.0, and 25.0-ml aliquots to 100-ml volumetric flasks and dilute to about 35 ml with water. Add sufficient concentrated hydrochloric acid to bring its total content in each flask to 5 ml Dilute to about 75 ml with water and add 5.0 ml of titanium solution. Dilute to the mark and within 1 hr measure the absorbance at 410 nm against the reagent blank. Plot mg of barium peroxide (per 100 ml) against absorbance.

Strontium peroxide. Transfer 0.15–0.16 g of strontium peroxide (weighed to 0.1 mg) to a 150-ml beaker and proceed as described for the calibration curve for barium peroxide, but use 5.0, 10.0, 15.0, 17.5, and 20.0-ml aliquots. Plot mg of strontium peroxide (per 100 ml) against absorbance

Procedure

Igniter mixes. Transfer about 0.20 g of sample (weighed to 0.1 mg) to a 150-ml beaker. Add 100 ml of dilute hydrochloric acid (1 + 9) all at once. Allow to stand with occasional stirring until the barium or strontium peroxide has dissolved (10–30 min). Within 30 min after dissolution, filter through a Whatman No. 41 filter paper, wash with water, and dilute to the mark in a 250 ml volumetric flask. Transfer an aliquot, containing 13–20 mg of barium peroxide or 10–15 mg of strontium peroxide, to a 100-ml volumetric flask and dilute to about 35 ml. Add sufficient concentrated hydrochloric acid to bring its total content in the flask to 5 ml, dilute to about 75 ml with water, add 5 ml of titanium solution, dilute to the mark, and within 1 hr measure the absorbance at 410 nm against a reagent blank Find the number of mg of barium or strontium peroxide from the calibration curve and calculate the barium or strontium peroxide content as follows:

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All the calculations for the barium and strontium peroxides in igniters were relative to the original barium and strontium peroxides which were arbitrarily taken to be 100% pure. This mode of calculation was chosen because the prime aim of the investigation was to determine whether there had been degradation of the barium or strontium peroxide in the igniters

If it were desired to make the calculation for the igniters in terms of active oxygen it would first be necessary to determine the active oxygen content of the barium and strontium peroxides used for preparing the calibration curves and then plot mg of active oxygen (per 100 ml) against absorbance. This would be a relatively simple matter.

The active oxygen of barium and strontium peroxide can be defined as the per cent oxygen (by weight) released when the peroxide reverts to the simple oxide (*e.g.*, $2BaO_2 \rightarrow 2BaO + O_2$). The active oxygen content of these materials is best determined by titration with permanganate in a perchloric–phosphoric acid medium.[2,3] The theoretical oxygen contents of barium and strontium peroxide are 9.45% and 13.38%, respectively The military specifications for barium and strontium peroxides[2,3] call for a minimum active oxygen content of 8.5% and 12.3%, respectively. However, according to the experience of this arsenal over many years, the active oxygen content of the barium peroxide and strontium peroxide used in the preparation of igniters varies from 8.8 to 9.0% for barium peroxide and from 12.5 to 12.8% for strontium peroxide (and does not change significantly for 2 or 3 years if the two

Table 1. Nominal composition of igniters used in small-arms tracer ammunition

Igniter	Nominal composition
I-280	76.5 SrO_2, 15.0 Mg, 8.5 Ca resinate
I-276	83.5 BaO_2, 15.0 Mg, 1.0 Zn stearate, 0.5 Toluidine Red toner
I-508	79.0 BaO_2, 14.1 Mg, 5.5 "Parlon", 0.9 Zn stearate, 0.5 Toluidine Red toner

materials are stored in air-tight containers). The cited ranges for active oxygen are equivalent to 93.1–95.2% pure barium peroxide and 93.4–95.7% pure strontium peroxide, respectively. Rosin[4] and the Fisher Scientific Co.[18] specify a minimum barium peroxide content of 88% and 85%, respectively, for reagent-grade barium peroxide. There is no specification for reagent-grade strontium peroxide.

The nominal compositions of the common igniter mixes used in small-arms tracer ammunition by the U.S. Army are shown in Table 1.

The results obtained for barium and strontium peroxides in synthetic igniter mixes are shown in Table 2. The recoveries were satisfactory (the average for all the runs was 100.2%).

The results obtained for peroxide in three actual production igniter mixes stored in closed containers for about a year are shown in Table 3. The results obtained for an igniter in a batch of ammunition several years old were 57.0, 49.0 and 53.3% BaO_2, the nominal content being 79.0% BaO_2 (each result represents an individual round). It is seen that two of three actual igniter mixes showed some deterioration while the igniter in the ammunition showed marked deterioration.

Table 2. Results for barium and stronium peroxides in synthetic igniter mixes

Present, *g*	Found, *g*	Recovery, %
BaO_2 + 25 mg Mg		
0.1514	0.1523 BaO_2	100.6
0.1518	0.1523 BaO_2	100.3
0.1519	0.1534 BaO_2	101.0
0.1479	0.1474 BaO_2	99.7
0.1484	0.1482 BaO_2	99.9
SrO_2 + 25 mg Mg + 15 mg Ca resinate		
0.1523	0.1507 SrO_2	99.0
0.1585	0.1555 SrO_2	98.1
0.1590	0.1602 SrO_2	100.9
0.1624	0.1613 SrO_2	99.3
0.1509	0.1518 SrO_2	100.6
BaO_2 + 30 mg Mg + 5 mg Z[a] + 5 mg T[b]		
0.1642	0.1632 BaO_2	99.4
0.1683	0.1679 BaO_2	99.8
0.1684	0.1679 BaO_2	99.7
0.1663	0.1682 BaO_2	101.1
0.1514	0.1548 BaO_2	102.2
BaO_2 + 30 mg Mg + 15 mg P[c] + 5 mg Z[a] + 5 mg T[b]		
0.1545	0.1553 BaO_2	100.5
0.1583	0.1590 BaO_2	100.4
0.1587	0.1589 BaO_2	100.1
0.1566	0.1581 BaO_2	101.0
0.1567	0.1578 BaO_2	100.7

[a] Z = zinc stearate

[b] T = Toluidine Red toner

[c] P = "Parlon"

Table 3. Results for strontium and barium peroxides in actual igniter mixes

Igniter	Nominal, %	Results, %
I-280	76.5 SrO_2	67.5
		66.7
		67.5
		67.4
		67.0
		Ave. 67.2
		Std. dev 0.36
I-276	83.5 BaO_2	88.4
		88.4
		90.0
		88.7
		90.0
		88.8
		Ave. 89.1
		Std. dev. 0.75
I-508	79.0 BaO_2	72.7
		71.2
		72.7
		72.9
		73.3
		73.3
		Ave. 72.7
		Std. dev. 1.00

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Summary—A method is proposed for the determination of barium and strontium peroxides (active oxygen) in igniters in small-arms tracer ammunition. The sample is treated with dilute hydrochloric acid (1 + 9) which dissolves the magnesium powder almost instantaneously and then dissolves the barium or strontium peroxides within 10–30 min. The solution is then filtered to remove the organic substances (calcium resinate, "Parlon", Toluidine Red toner, and zinc stearate) and the peroxide is determined by means of the colour of the titanium–peroxide complex. It is shown that igniter mixes and igniters used in small-arms tracer ammunition deteriorate on storage.

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DOSAGE PAR SPECTROMETRIE GAMMA NON DESTRUCTIVE DU MERCURE ET DE L'OR DANS L'EAU DE MER APRES PRECONCENTRATION PAR LE SULFURE DE PLOMB

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A l'heure actuelle, le dosage du mercure dans l'eau est un problème étroitement lié au problème de la pollution de l'environnement. Par exemple, le mercure s'accumule dans le corps des poissons et peut mener à des empoisonnements graves. Dans une revue récente, Chilov[1] discute les méthodes de détermination de petites quantités de mercure. Quelques recherches importantes ont été consacrées au dosage du mercure dans l'eau.[2–6]

L'intérêt du dosage de l'or dans l'eau de mer provient des nombreuses tentatives d'extraction industrielle. Différentes méthodes de dosage de petites quantités d'or dans l'eau de mer sont connues.[7–26]

L'application des sorbants inorganiques dans la radiochimie analytique, en particulier dans l'analyse par activation, devient de plus en plus fréquente. Nous présentons ci-dessous nos résultats sur la rétention du mercure et de l'or de l'eau de mer par le sulfure de plomb en colonne, ainsi qu'une nouvelle méthode de dosage de ces éléments par analyse par activation sans séparation radiochimique.

PARTIE EXPERIMENTALE

Colonne

La colonne consiste en un tube de verre, dont la partie inférieure est rétrécie (0,3 cm de diamètre et 3 cm de hauteur). On y introduit 0,5 g de PbS sur un tampon de laine de verre. Le PbS est d'abord dégazé dans 25 ml de HNO_3 0,1 *N* à la température de 20 ± 2° pendant 15 mn, puis versé dans la colonne qu'on relie à un récipient contenant l'eau de mer (Fig. 1).

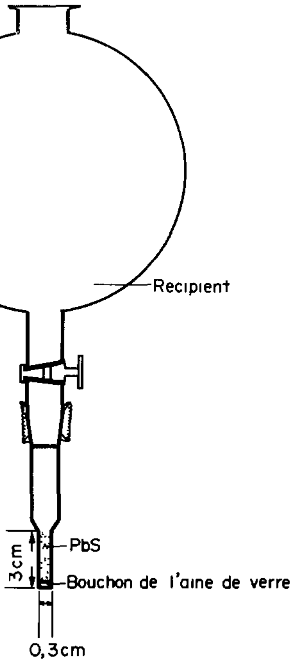

Fig. 1. Appareil utilisé pour la rétention du mercure et de l'or de l'eau de mer sur le PbS.

Reactifs et solutions

Le sulfure de plomb utilisé a été préparé à partir de plomb 99,9999% (Lead-Zinc Plant, Kirdzali, Bulgaria) ne contenant pas de mercure, d'argent et d'or en quantités détectables par radioactivation par neutrons thermiques. Le plomb a été dissous à l'aide de HNO_3 *p.a.* (2 + 1), puis PbS a été précipité par chauffage lent en présence de thioacétamide. Après 24 h de repos et centrifugation, le PbS a été seché a 50°. Le spectre de diffraction X a montré que le produit a la même structure que la galène. Il présente une granulométrie de l'ordre de 0,1 à 0,4 mm, permettant l'emploi facile en colonne. L'analyse par radioactivation par neutrons thermiques a indiqué que, dans le spectre gamma du PbS irradié pendant 6 h et mesuré 6 jours après la fin de l'irradiation, il n'y a pas de pics photoélectriques du mercure et de l'or (Fig. 2*a*).

La solution étalon de mercure a été preparée à partir de $Hg(NO_3)_2$, *p a.* La concentration précise a été déterminée par la méthode gravimétrique après précipitation du HgS[27]

La solution étalon d'or a été préparée par dissolution d'or métallique, *p.a.*

Les deux solutions étalons contenaient 10^{-3} g/ml de mercure et d'or. Les solutions diluées—$1 \cdot 10^{-6}$–$1 \cdot 10^{-8}$ g/ml de mercure et $1 \cdot 10^{-8}$–$1 \cdot 10^{-10}$ g/ml d'or—ont été préparées le jour de l'utilisation. Les solutions des traceurs ^{203}Hg et ^{198}Au ont été obtenues par radioactivation d'or en poudre et de $HgCl_2$ au réacteur suivie de la dissolution de l'or dans l'eau régale et du $HgCl_2$ dans l'eau. La concentration des solutions utilisées était de $1 \cdot 10^{-8}$–$1 \cdot 10^{-9}$ g/ml pour Au et de $1 \cdot 10^{-6}$–$1 \cdot 10^{-8}$ g/ml pour Hg.

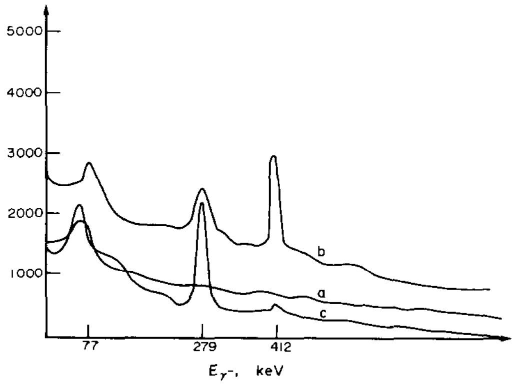

Fig. 2. Spectres gamma: (*a*) de 0,5 g du précipité de PbS irradié pendant 6 h dans un flux de $1{,}2 \cdot 10^{12}$ $n.cm^{-2}.sec^{-1}$, mesuré 6 jours après la fin de l'irradiation; (*b*) de l'étalon (0,5 g PbS + $1 \cdot 10^{-6}$ g Hg + $1 \cdot 10^{-8}$ g Au) irradié pendant 6 h, mesuré 6 jours après la fin de l'irradiation; (*c*) du même étalon, mesuré 15 jours après la fin de l'irradiation. Temps de comptage 15 mn

Irradiation des echantillons

Les échantillons ont été irradiés au réacteur IRT-2000 de FI ANEB, Sofia (Bulgarie) dans un flux de l'ordre de 10^{12} n.cm^{-2}.sec^{-1}. On a mis les échantillons dans de petits cachets de polyéthylène et ceux-ci dans de petites boites de polyéthylène. L'irradiation de PbS, contenant Hg et Au, donne ^{197}Hg, ^{203}Hg et ^{198}Au selon les réactions ^{196}Hg (n,γ) ^{197}Hg, ^{202}Hg (n,γ) ^{203}Hg, ^{197}Au (n,γ) ^{198}Au. Les pics photoélectriques ont des énergies de 77, 288, et 412 keV respectivement et des périodes de 2,7, 47 et 2,7 jours.

Moyens de mesure

Les activités gamma tant en phase solide (PbS) qu'en phase liquide ont été mesurées au moyen d'un analyseur à 100 canaux équipé d'une sonde NaI (Tl) 4,5 × 4,5 cm. Les activités mises en jeu assurent une précision statistique des comptages de ^{203}Hg et ^{198}Au de l'ordre de $\pm 2\%$ (temps de comptage 15 mn).

Mode opératoire

Pour étudier la rétention du mercure et de l'or contenus dans l'eau de mer sur PbS en colonne, on a utilisé les traceurs ^{203}Hg et ^{198}Au. On a fait d'abord des essais pour déterminer le rendement (R) de fixation sur PbS du mercure et de l'or. A un litre d'eau de mer, on ajoute $HNO_3 + H_2SO_4$ (1:1) pour obtenir le pH désiré et 1 ml de la solution contenant les traceurs Après une semaine, on fait passer cet échantillon d'eau de mer sur la colonne. La vitesse d'écoulement (0,2–0,5 ml/mn) dépend des dimensions des grains On lave le PbS sur la colonne avec 100 ml de la solution $HNO_3 + H_2SO_4$, ayant la même valeur de pH que la solution étudiée. On sèche doucement le PbS dans la colonne, puis on le récupère. On mesure la radioactivité gamma du PbS. On mesure aussi la radioactivité des étalons qui representent 0,5 g PbS sur lequel on a séché 1 ml de la solution des traceurs. On calcule $R\%$.

$$R\% = (A_e/A_0)\cdot 100$$

ou A_e = l'activité (cpm) de PbS en colonne, A_0 = l'activité de l'étalon.

Aux échantillons d'eau de mer qu'on utilise pour le dosage de l'or et du mercure, on ajoute $HNO_3 + H_2SO_4$ (1:1) au moment même où l'on prélève les échantillons de la mer, jusqu'a ce qu'on obtienne pH = 1. Après passage de la solution à travers la colonne, le PbS est lavé avec 100 ml de la solution $HNO_3 + H_2SO_4$ à pH = 1, séché à 50° et transféré dans un cachet de polyéthylène. On prépare deux étalons en séchant à 50° 1 ml de la solution étalon de mercure et d'or sur 0,5 g de PbS. L'un des étalons contient $1\cdot10^{-6}$ g Hg et $1\cdot10^{-8}$ g Au et l'autre $1\cdot10^{-8}$ g Hg et $1\cdot10^{-10}$ g Au.

Trois des échantillons et les deux étalons sont irradiés simultanément pendant 6 h au réacteur dans une boîte de polyéthylène. Après 6 jours, le pic photoélectrique du ^{198}Au est mesuré. On procède de même avec de ^{203}Hg, mais après 15 jours. On mesure des étalons dans les mêmes conditions.

RESULTATS ET DISCUSSION

A l'aide des traceurs ^{203}Hg et ^{198}Au, on a constaté que la quantité de PbS dans la colonne doit être d'environ 0,5 g. Cette quantité assure la rétention complète du mercure et de l'or contenus en petites quantités dans les solutions. Si la quantité du PbS est inférieure à 0,4 g, la vitesse d'écoulement est élevée et le temps de contact n'est pas suffisant pour la rétention complète du mercure et de l'or. Si la quantité est supérieure à 0,5 g la vitesse d'écoulement est très lente. A l'aide de ^{203}Hg et ^{198}Au, on a constaté aussi que le séchage à 50° n'entraine pas de pertes notables de Hg et Au par suite de l'évaporation.

Tableau 1.

pH	R, % Hg	Au
0	87	86
0,5	91	94
1	98	97
1,5	98	96
2	91	88

Les résultats, présentés dans le Tableau 1, indiquent que dans l'intervalle de pH 0,5–1,5 et à la température de 20 ± 2°, le rendement de la fixation du mercure et de l'or sur le PbS dépasse 90% (les chiffres donnés sont des valeurs moyennes pour trois essais).

On peut supposer que, après une semaine, les traceurs ^{203}Hg et ^{198}Au ajoutés à l'échantillon d'eau de mer sont dans le même état que le mercure et l'or contenus dans l'eau des mers et des océans. (A pH 1, la fixation du mercure et de l'or sur le verre est insignifiante.)[28–30] Des études antérieures[31–34] ont permis de constater que l'or est fixé au mieux sur le PbS en milieu acide sulfurique à pH 0,5–1,5 et le mercure en acide nitrique a pH = 1. Dans le mélange $H_2SO_4 + HNO_3$ a pH 1, les rendements de fixation sont de 98 et 97% pour le mercure et l'or respectivement (Tableau 1).

La Fig. 2*a* présente le spectre gamma de 0,5 g de PbS irradié pendant 6 h et mesuré 6 jours après la fin de l'irradiation. On n'y voit pas de pics photoélectriques gênants. La Fig. 2 présente aussi le spectre gamma de l'étalon, mesuré 6 jours (2*b*) et 15 jours (2*c*) après la fin de l'irradiation. La Fig. 3 montre le spectre gamma de 0,5 g de PbS utilisé en colonne pour retenir le mercure et l'or d'un échantillon d'un litre d'eau de la Mer Noire. Le PbS est irradié dans les conditions mentionnées ci-dessus; ^{198}Au est mesuré 6 jours après la fin de l'irradiation (3*a*) et ^{203}Hg 15 jours après la fin de l'irradiation (3*b*).

Après 6 jours, le bruit de fond provenant du PbS et la radioactivité-gamma des éléments à courte durée de vie qui se trouvent sur le PbS diminuent. Les éléments les plus gênants sont ^{24}Na et ^{64}Cu. Leurs quantités dans le PbS sont telles que les pics photoélectriques de ^{203}Hg et de ^{198}Au sont à peine visibles dans leur "compton". Après 15 jours, le pic de ^{198}Au n'empêche plus la mesure de ^{203}Hg. Le pic photoélectrique de ^{197}Hg ne convient pas pour le dosage, car le bruit de fond provenant du PbS est très élevé. Les spectres gamma ont été traités par la méthode de Covell.[35]

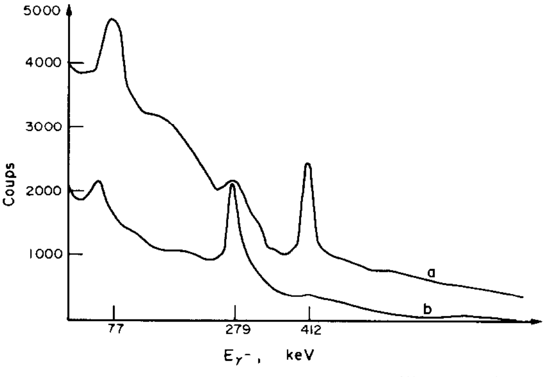

Fig. 3. Spectres gamma de 0,5 g de PbS utilisé en colonne pour retenir Hg et Au dans l'eau de la Mer Noire, irradié pendant 6 h et mesuré (*a*) 6 jours après la fin de l'irradiation; (*b*) 15 jours après la fin de l'irradiation. Temps de comptage 15 mn.

La Fig. 3 indique aussi qu'il suffit d'irradier les échantillons pendant 6 h pour déterminer avec une précision suffisante le mercure et l'or contenus dans 1 litre d'eau de la Mer Noire. Une série de mesures effectuées sur 10 échantillons de 1 litre de la même region de la Mer Noire a donné les résultats suivants: $(8 \pm 2)\cdot 10^{-7}$ g/l. Hg et $(6 \pm 3)\cdot 10^{-9}$ g/l. Au avec un écart-type de ±12% pour Hg et ±23% pour Au.

Ce résultat pour le mercure est en accord avec les résultats qu'on trouve dans la littérature.[36] Malheureusement il n'y a pas d'autres études sur la teneur en or de l'eau de la Mer Noire, auxquelles nous pourrions comparer nos résultats.

Nous avons obtenu les mêmes résultats après un traitement préalable d'un échantillon d'eau de la Mer Noire par le Cl_2 à température elevée, d'un autre avec $H_2SO_4 + HNO_3$, et d'un troisième par ultra-sons.

La limite de détection absolue de dosage par la méthode présentée atteint $1\cdot 10^{-7}$ g pour le mercure et $1\cdot 10^{-10}$ g pour l'or, calculée sur la base du critérium 3σ. Pour atteindre une limite de détection plus faible, le dosage pourrait s'effectuer par irradiation pendant une periode plus longue.

En ce qui concerne le mécanisme de fixation du mercure et de l'or, on peut supposer qu'il s'agit d'une réaction du type suivant:

$$PbS + Hg^{2+} \rightarrow HgS + Pb^{2+}$$

$$3PbS + 2Au^{3+} \rightarrow Au_2S_3 + 3Pb^{2+}$$

Il est cependant impossible, à cause de la concentration très faible du mercure et de l'or, de constater la formation d'une phase de HgS ou de Au_2S_3. Les ions du mercure et de l'or sont fixés sur la surface du sulfure de plomb en déplaçant les ions du plomb.

La méthode présentée ci-dessus, comparée aux autres méthodes décrites dans la littérature, offre les avantages suivants: simplicité du procédé de rétention du mercure et de l'or de l'eau de mer sur le PbS, suppression de la nécessité de séparation radiochimique après l'irradiation des échantillons, simplicité de la mesure par spectrométrie gamma non destructive.

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Résumé—On décrit une méthode pour le dosage du mercure et de l'or dans l'eau de mer, basée sur la préconcentration de ces éléments par rétention sur le sulfure du plomb en colonne à pH 1 ($HNO_3 + H_2SO_4$). L'analyse est effectúee par spectrométrie gamma non destructive. On a détermíné $0{,}8 \pm 0{,}2$ µg/l. de mercure et 6 ± 3 ng/l. d'or dans un échantillon d'eau de la Mer Noire aux environs de Varna.

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A l'heure actuelle, le dosage du mercure dans l'eau est un problème étroitement lié au problème de la pollution de l'environnement. Par exemple, le mercure s'accumule dans le corps des poissons et peut mener à des empoisonnements graves. Dans une revue récente, Chilov[1] discute les méthodes de détermination de petites quantités de mercure. Quelques recherches importantes ont été consacrées au dosage du mercure dans l'eau.[2–6]

L'intérêt du dosage de l'or dans l'eau de mer provient des nombreuses tentatives d'extraction industrielle. Différentes méthodes de dosage de petites quantités d'or dans l'eau de mer sont connues.[7–26]

L'application des sorbants inorganiques dans la radiochimie analytique, en particulier dans l'analyse par activation, devient de plus en plus fréquente. Nous présentons ci-dessous nos résultats sur la rétention du mercure et de l'or de l'eau de mer par le sulfure de plomb en colonne, ainsi qu'une nouvelle méthode de dosage de ces éléments par analyse par activation sans séparation radiochimique.

PARTIE EXPERIMENTALE

Colonne

La colonne consiste en un tube de verre, dont la partie inférieure est rétrécie (0,3 cm de diamètre et 3 cm de hauteur). On y introduit 0,5 g de PbS sur un tampon de laine de verre. Le PbS est d'abord dégazé dans 25 ml de HNO_3 0,1 *N* à la température de 20 ± 2° pendant 15 mn, puis versé dans la colonne qu'on relie à un récipient contenant l'eau de mer (Fig. 1).

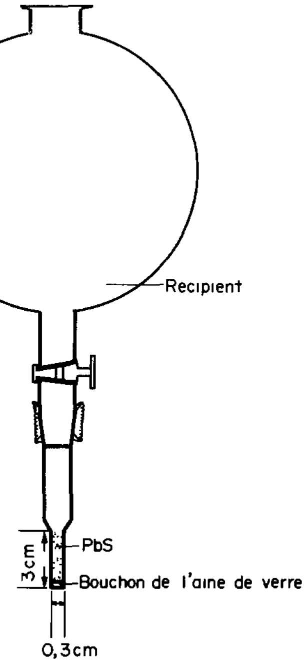

Fig. 1. Appareil utilisé pour la rétention du mercure et de l'or de l'eau de mer sur le PbS.

Reactifs et solutions

Le sulfure de plomb utilisé a été préparé à partir de plomb 99,9999% (Lead-Zinc Plant, Kirdzali, Bulgaria) ne contenant pas de mercure, d'argent et d'or en quantités détectables par radioactivation par neutrons thermiques. Le plomb a été dissous à l'aide de HNO_3 *p.a.* (2 + 1), puis PbS a été précipité par chauffage lent en présence de thioacétamide. Après 24 h de repos et centrifugation, le PbS a été seché a 50°. Le spectre de diffraction X a montré que le produit a la même structure que la galène. Il présente une granulométrie de l'ordre de 0,1 à 0,4 mm, permettant l'emploi facile en colonne. L'analyse par radioactivation par neutrons thermiques a indiqué que, dans le spectre gamma du PbS irradié pendant 6 h et mesuré 6 jours après la fin de l'irradiation, il n'y a pas de pics photoélectriques du mercure et de l'or (Fig. 2*a*).

La solution étalon de mercure a été preparée à partir de $Hg(NO_3)_2$, *p.a.* La concentration précise a été déterminée par la méthode gravimétrique après précipitation du HgS[27]

La solution étalon d'or a été préparée par dissolution d'or métallique, *p.a.*

Les deux solutions étalons contenaient 10^{-3} g/ml de mercure et d'or. Les solutions diluées—$1 \cdot 10^{-6}$–$1 \cdot 10^{-8}$ g/ml de mercure et $1 \cdot 10^{-8}$–$1 \cdot 10^{-10}$ g/ml d'or—ont été préparées le jour de l'utilisation. Les solutions des traceurs ^{203}Hg et ^{198}Au ont été obtenues par radioactivation d'or en poudre et de $HgCl_2$ au réacteur suivie de la dissolution de l'or dans l'eau régale et du $HgCl_2$ dans l'eau. La concentration des solutions utilisées était de $1 \cdot 10^{-8}$–$1 \cdot 10^{-9}$ g/ml pour Au et de $1 \cdot 10^{-6}$–$1 \cdot 10^{-8}$ g/ml pour Hg.

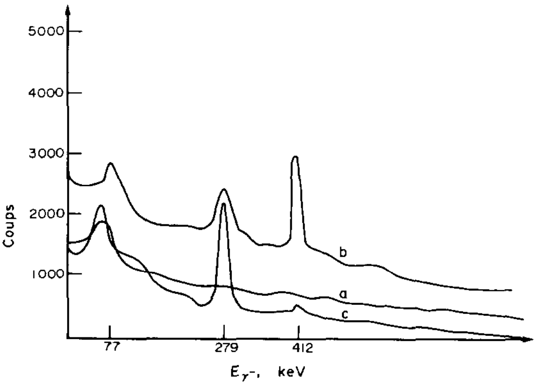

Fig. 2. Spectres gamma: (*a*) de 0,5 g du précipité de PbS irradié pendant 6 h dans un flux de $1{,}2 \cdot 10^{12}$ $n.cm^{-2}.sec^{-1}$, mesuré 6 jours après la fin de l'irradiation; (*b*) de l'étalon (0,5 g PbS + $1 \cdot 10^{-6}$ g Hg + $1 \cdot 10^{-8}$ g Au) irradié pendant 6 h, mesuré 6 jours après la fin de l'irradiation; (*c*) du même étalon, mesuré 15 jours après la fin de l'irradiation. Temps de comptage 15 mn

Irradiation des echantillons

Les échantillons ont été irradiés au réacteur IRT-2000 de FI ANEB, Sofia (Bulgarie) dans un flux de l'ordre de 10^{12} n.cm^{-2}.sec^{-1}. On a mis les échantillons dans de petits cachets de polyéthylène et ceux-ci dans de petites boites de polyéthylène. L'irradiation de PbS, contenant Hg et Au, donne ^{197}Hg, ^{203}Hg et ^{198}Au selon les réactions ^{196}Hg (n,γ) ^{197}Hg, ^{202}Hg (n,γ) ^{203}Hg, ^{197}Au (n,γ) ^{198}Au. Les pics photoélectriques ont des énergies de 77, 288, et 412 keV respectivement et des périodes de 2,7, 47 et 2,7 jours.

Moyens de mesure

Les activités gamma tant en phase solide (PbS) qu'en phase liquide ont été mesurées au moyen d'un analyseur à 100 canaux équipé d'une sonde NaI (Tl) 4,5 × 4,5 cm. Les activités mises en jeu assurent une précision statistique des comptages de ^{203}Hg et ^{198}Au de l'ordre de $\pm 2\%$ (temps de comptage 15 mn).

Mode opératoire

Pour étudier la rétention du mercure et de l'or contenus dans l'eau de mer sur PbS en colonne, on a utilisé les traceurs ^{203}Hg et ^{198}Au. On a fait d'abord des essais pour déterminer le rendement (R) de fixation sur PbS du mercure et de l'or. A un litre d'eau de mer, on ajoute $HNO_3 + H_2SO_4$ (1:1) pour obtenir le pH désiré et 1 ml de la solution contenant les traceurs Après une semaine, on fait passer cet échantillon d'eau de mer sur la colonne. La vitesse d'écoulement (0,2–0,5 ml/mn) dépend des dimensions des grains On lave le PbS sur la colonne avec 100 ml de la solution $HNO_3 + H_2SO_4$, ayant la même valeur de pH que la solution étudiée. On sèche doucement le PbS dans la colonne, puis on le récupère. On mesure la radioactivité gamma du PbS. On mesure aussi la radioactivité des étalons qui représentent 0,5 g PbS sur lequel on a séché 1 ml de la solution des traceurs. On calcule $R\%$.

$$R\% = (A_e/A_0)\cdot 100$$

ou A_e = l'activité (cpm) de PbS en colonne, A_0 = l'activité de l'étalon.

Aux échantillons d'eau de mer qu'on utilise pour le dosage de l'or et du mercure, on ajoute $HNO_3 + H_2SO_4$ (1:1) au moment même où l'on prélève les échantillons de la mer, jusqu'a ce qu'on obtienne pH = 1. Après passage de la solution à travers la colonne, le PbS est lavé avec 100 ml de la solution $HNO_3 + H_2SO_4$ à pH = 1, séché à 50° et transféré dans un cachet de polyéthylène. On prépare deux étalons en séchant à 50° 1 ml de la solution étalon de mercure et d'or sur 0,5 g de PbS. L'un des étalons contient $1\cdot10^{-6}$ g Hg et $1\cdot10^{-8}$ g Au et l'autre $1\cdot10^{-8}$ g Hg et $1\cdot10^{-10}$ g Au.

Trois des échantillons et les deux étalons sont irradiés simultanément pendant 6 h au réacteur dans une boîte de polyéthylène. Après 6 jours, le pic photoélectrique du ^{198}Au est mesuré. On procède de même avec de ^{203}Hg, mais après 15 jours. On mesure des étalons dans les mêmes conditions.

RESULTATS ET DISCUSSION

A l'aide des traceurs ^{203}Hg et ^{198}Au, on a constaté que la quantité de PbS dans la colonne doit être d'environ 0,5 g. Cette quantité assure la rétention complète du mercure et de l'or contenus en petites quantités dans les solutions. Si la quantité du PbS est inférieure à 0,4 g, la vitesse d'écoulement est élevée et le temps de contact n'est pas suffisant pour la rétention complète du mercure et de l'or. Si la quantité est supérieure à 0,5 g la vitesse d'écoulement est très lente. A l'aide de ^{203}Hg et ^{198}Au, on a constaté aussi que le séchage à 50° n'entraine pas de pertes notables de Hg et Au par suite de l'évaporation.

Tableau 1.

	R, %	
pH	Hg	Au
0	87	86
0,5	91	94
1	98	97
1,5	98	96
2	91	88

Les résultats, présentés dans le Tableau 1, indiquent que dans l'intervalle de pH 0,5–1,5 et à la température de 20 ± 2°, le rendement de la fixation du mercure et de l'or sur le PbS dépasse 90% (les chiffres donnés sont des valeurs moyennes pour trois essais).

On peut supposer que, après une semaine, les traceurs ^{203}Hg et ^{198}Au ajoutés à l'échantillon d'eau de mer sont dans le même état que le mercure et l'or contenus dans l'eau des mers et des océans. (A pH 1, la fixation du mercure et de l'or sur le verre est insignifiante.)[28–30] Des études antérieures[31–34] ont permis de constater que l'or est fixé au mieux sur le PbS en milieu acide sulfurique à pH 0,5–1,5 et le mercure en acide nitrique a pH = 1. Dans le mélange $H_2SO_4 + HNO_3$ a pH 1, les rendements de fixation sont de 98 et 97% pour le mercure et l'or respectivement (Tableau 1).

La Fig. 2*a* présente le spectre gamma de 0,5 g de PbS irradié pendant 6 h et mesuré 6 jours après la fin de l'irradiation. On n'y voit pas de pics photoélectriques gênants. La Fig. 2 présente aussi le spectre gamma de l'étalon, mesuré 6 jours (2*b*) et 15 jours (2*c*) après la fin de l'irradiation. La Fig. 3 montre le spectre gamma de 0,5 g de PbS utilisé en colonne pour retenir le mercure et l'or d'un échantillon d'un litre d'eau de la Mer Noire. Le PbS est irradié dans les conditions mentionnées ci-dessus; ^{198}Au est mesuré 6 jours après la fin de l'irradiation (3*a*) et ^{203}Hg 15 jours après la fin de l'irradiation (3*b*).

Après 6 jours, le bruit de fond provenant du PbS et la radioactivité-gamma des éléments à courte durée de vie qui se trouvent sur le PbS diminuent. Les éléments les plus gênants sont ^{24}Na et ^{64}Cu. Leurs quantités dans le PbS sont telles que les pics photoélectriques de ^{203}Hg et de ^{198}Au sont à peine visibles dans leur "compton". Après 15 jours, le pic de ^{198}Au n'empêche plus la mesure de ^{203}Hg. Le pic photoélectrique de ^{197}Hg ne convient pas pour le dosage, car le bruit de fond provenant du PbS est très élevé. Les spectres gamma ont été traités par la méthode de Covell.[35]

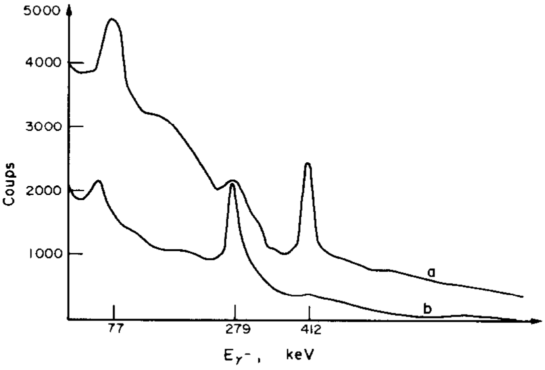

Fig. 3. Spectres gamma de 0,5 g de PbS utilisé en colonne pour retenir Hg et Au dans l'eau de la Mer Noire, irradié pendant 6 h et mesuré (*a*) 6 jours après la fin de l'irradiation; (*b*) 15 jours après la fin de l'irradiation. Temps de comptage 15 mn.

La Fig. 3 indique aussi qu'il suffit d'irradier les échantillons pendant 6 h pour déterminer avec une précision suffisante le mercure et l'or contenus dans 1 litre d'eau de la Mer Noire. Une série de mesures effectuées sur 10 échantillons de 1 litre de la même region de la Mer Noire a donné les résultats suivants: $(8 \pm 2) \cdot 10^{-7}$ g/l. Hg et $(6 \pm 3) \cdot 10^{-9}$ g/l. Au avec un écart-type de ±12% pour Hg et ±23% pour Au.

Ce résultat pour le mercure est en accord avec les résultats qu'on trouve dans la littérature.[36] Malheureusement il n'y a pas d'autres études sur la teneur en or de l'eau de la Mer Noire, auxquelles nous pourrions comparer nos résultats.

Nous avons obtenu les mêmes résultats après un traitement préalable d'un échantillon d'eau de la Mer Noire par le Cl_2 à température elevée, d'un autre avec $H_2SO_4 + HNO_3$, et d'un troisième par ultra-sons.

La limite de détection absolue de dosage par la méthode présentée atteint $1 \cdot 10^{-7}$ g pour le mercure et $1 \cdot 10^{-10}$ g pour l'or, calculée sur la base du critérium 3σ. Pour atteindre une limite de détection plus faible, le dosage pourrait s'effectuer par irradiation pendant une periode plus longue.

En ce qui concerne le mécanisme de fixation du mercure et de l'or, on peut supposer qu'il s'agit d'une réaction du type suivant:

$$PbS + Hg^{2+} \rightarrow HgS + Pb^{2+}$$

$$3PbS + 2Au^{3+} \rightarrow Au_2S_3 + 3Pb^{2+}$$

Il est cependant impossible, à cause de la concentration très faible du mercure et de l'or, de constater la formation d'une phase de HgS ou de Au_2S_3. Les ions du mercure et de l'or sont fixés sur la surface du sulfure de plomb en déplaçant les ions du plomb.

La méthode présentée ci-dessus, comparée aux autres méthodes décrites dans la littérature, offre les avantages suivants: simplicité du procédé de rétention du mercure et de l'or de l'eau de mer sur le PbS, suppression de la nécessité de séparation radiochimique après l'irradiation des échantillons, simplicité de la mesure par spectrométrie gamma non destructive.

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Résumé—On décrit une méthode pour le dosage du mercure et de l'or dans l'eau de mer, basée sur la préconcentration de ces éléments par rétention sur le sulfure du plomb en colonne à pH 1 ($HNO_3 + H_2SO_4$). L'analyse est effectúee par spectrométrie gamma non destructive. On a déterminé 0,8 ± 0,2 μg/l. de mercure et 6 ± 3 ng/l. d'or dans un échantillon d'eau de la Mer Noire aux environs de Varna.

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NON-AQUEOUS QUANTITATIVE DETERMINATION OF THE CARBONYL FUNCTIONAL GROUP BY CONSTANT-CURRENT POTENTIOMETRIC TITRATION

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There is a significant lack of rapid and accurate methods for determination of carbonyl groups. Most of those available involve a back-titration. A direct titration method would be a useful innovation. This paper reports such a procedure.[1] The titrant, sodium fluorenyl, is a strong base[2] as well as a very potent reducing agent, especially towards oxygen and oxygen-containing compounds. In this work its reduction properties were utilized. The titrant and titrands exhibit irreversible electrochemical behaviour; therefore, in the potentiometric titrations two platinum-wire electrodes are used at a small constant current of ~0.5 μA.

EXPERIMENTAL

Reagents

Sodium fluorenyl titrant is prepared by letting an excess of sodium metal shavings (5 g) react with 11 g of recrystallized fluorene in 100 ml of distilled 1,2-dimethoxyethane,[3] which is a 3:1 molar ratio, over a period of 24 hr in a sealed 250-ml round-bottomed flask in an inert atmosphere. It is then filtered through glass wool and diluted with 350 ml of distilled tetrahydrofuran (THF) to yield a final sodium fluorenyl concentration of approximately 0 1*M* The titrant is standardized against freshly distilled 2,4-pentanedione by the procedure described below. The titrant is stored under dry pure argon, the inlet to the titrant reservoir being connected to an argon bubbler which allows the inert gas over the titrant to be kept at atmospheric pressure. A balloon system fails to work properly because of diffusion of oxygen through the walls of the balloon. The THF is stored over sodium metal and under argon to inhibit diffusion of oxygen and water vapour into the system. The titrant is stable for at least a day and it should be noted that the method is not very practical unless a large number of samples is available for analysis on the same day.

The tetrahydrofuran and 1,2-dimethoxyethane are distilled twice under nitrogen, first from lithium aluminium hydride and then from sodium metal. All other compounds were purified by normal laboratory procedures.

Apparatus

A Metrohm potentiograph Model E436, Series 14, was used together with a Model E436D automatic titrator. The potentiograph also supplies the constant current for the electrodes. A simplified circuit diagram is shown in Fig. 1.

Electrode pretreatment

The pretreatment involves the procedures developed by Ashworth and Walisch[4] and by van Name and Fenwick.[5] The platinum electrodes are cleaned by submersion for 5 min in potassium dichromate–sulphuric acid solution, then thoroughly rinsed with distilled, deoxygenated water, and allowed to stand for 12 hr in 2*M* sulphuric acid–0.15*M* ferrous ammonium sulphate solution. Immediately before use the electrodes are heated to a dull red in a burner flame, then plunged into a crystal of sodium bisulphite, care being taken not to amass any bisulphite on the glass around the platinum wire. The electrodes are then heated again to a dull red, allowed to cool for 90–120 sec, and used immediately to measure the potential of the solution being titrated.

This pretreatment procedure produces reproducible electrode surfaces, as indicated by reproducibility of the potentiometric titration curves. The pretreatment procedure is not time-consuming, requiring less than 2 min before each titration.

Cell and apparatus pretreatment

Before each titration the pipette and titration vessel are thoroughly rinsed with acetone and then flushed with nitrogen to remove the acetone. They are then flamed-out to remove any traces of moisture, and allowed to cool under nitrogen. If these procedures are not properly applied, the concentration of water and reducible substances, approximately 0.025*M*, interferes The acetone wash is necessary to remove the reaction product, which is insoluble in water.

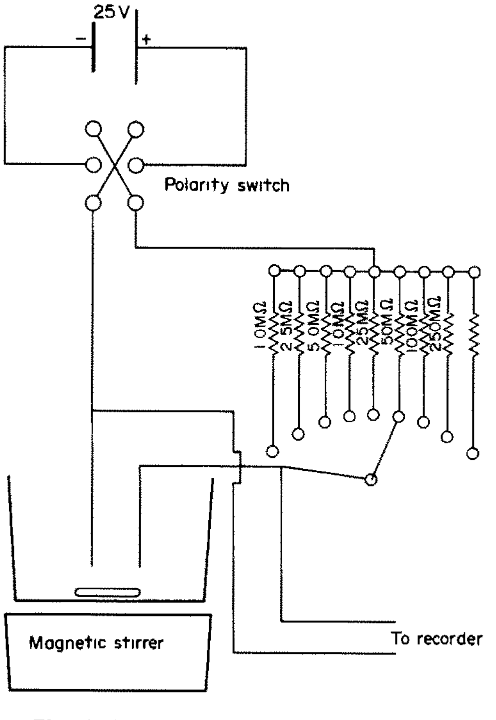

Fig. 1. Electrical circuit employed for use in constant-current titrations. The double-pole, double-throw switch is used to change the polarity of the electrodes.

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Table 1. Results of carbonyl determination

Carbonyl	Average found, %	Coefficient of variance, %	Number of analyses
n-Butyraldehyde	98.0	1.4	6
2-Ethylhexanal	104.9	1.2	5
Cinnamaldehyde	99.3	0.8	5
Benzaldehyde	101.0	1.6	5
3-Hydroxy-4-methoxy-benzaldehyde	105.8	1.3	5
p-Hydroxybenzaldehyde	104.4	0.8	4
p-Methoxybenzaldehyde	102.1	6.8	7
2-Hydroxy-5-nitro-benzaldehyde	105.9	3.3	6
p-Nitrobenzaldehyde	99.4	2.4	6
9-Anthraldehyde	97.3	2.1	4
Acetone	103.8	2.2	5
2-Butanone	106.2	6.1	4
2,4-Pentanedione	100.0	1.8	6
Cyclopentanone	103.6	2.3	9
Cyclohexanone	103.6	2.6	7
Cyclohexanone (6 days old)	129.9	4.2	8
1,4-Benzoquinone	102.8	2.5	7
p-Aminoacetophenone	101.6	4.0	4
Acetophenone	103.3	2.1	6
9-Fluorenone		did not react	
Benzophenone		did not react	
DL-Camphor		did not react	

Titration procedure

Fifteen ml of 0.15*M* sodium perchlorate in tetrahydrofuran, employed as supporting electrolyte, are introduced into the dry titration vessel which has been purged with nitrogen, and deaerated with dry nitrogen for 90–120 sec. The 0.5-μA electrode current is switched on and the titrant added continuously at the optimum flow-rate of 0.85 ml/min. If the flow-rate is faster, slow reaction kinetics cause a false end-point to be obtained for certain carbonyls. Once the titrant flow starts, the nitrogen flow is transferred from the bubbler to an orifice which permits the nitrogen to sweep out the volume above the reaction medium.

The potential of the two indicator electrodes is monitored until a derivative end-point is observed, which corresponds to the reducible impurities originally present in the purified tetrahydrofuran (their concentration is usually 2.5–4.5 × $10^{-3}M$). Immediately afterwards, 2 ml of the carbonyl sample are added, containing approximately 0.2 mmole of carbonyl, and the titration is continued until just after the carbonyl derivative end-point is reached.

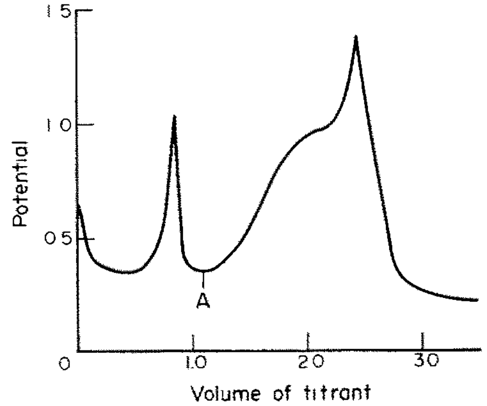

Fig. 2. Typical derivative-type titration curve for a carbonyl with sodium fluorenyl as a titrant. A denotes the point at which the butyraldehyde is injected. The difference between the end-points corresponds to the butyraldehyde and impurities injected.

RESULTS AND DISCUSSION

Aliphatic, aromatic and cyclic ketones, and aliphatic and aromatic aldehydes were investigated in this research and the carbonyls listed in Table 1 were chosen to represent a wide range of steric, configurational, and electronic effects. As can be seen, all types of carbonyl compounds lend themselves to analysis by this procedure.

Steric hindrance, as might be expected from the large size of the fluorenyl anion, plays a major role in the reactivity of certain carbonyls. Three carbonyl compounds investigated were found not to react: 9-fluorenone, benzophenone, and DL-camphor. This inertness most likely results from the bulkiness of the attacking fluorenyl anion and of the compound being attacked. However, 9-anthraldehyde, which was expected to be inert, was found to react rapidly. It is believed that the carbonyl carbon in 9-anthraldehyde, being positioned one carbon atom away from the bulky anthracene moiety, allows the fluorenyl anion the spatial orientation required to make attack possible, whereas in benzophenone and 9-fluorenone the carbonyl carbon is positioned in the 2- and 3-ring moiety, respectively. The carbonyl solution in THF must be freshly prepared so as to avoid build-up of peroxide contaminants. Table 1 shows that when a cyclohexanone solution was examined 6 days after it was prepared, the amount of reducible species corresponded to 129% of the amount originally introduced.

The minimum concentration of carbonyl that can be determined with acceptable accuracy and precision depends on the concentration of the titrant. We used 0.1*M* titrant and the minimum concentration of carbonyl determinable was 7.5 × $10^{-3}M$. Storrs[6] found sodium fluorenyl to be stable at a concentration as low as 0.02*M*. With this titrant concentration, the determination limit might be lowered to 1.2 × $10^{-3}M$.

The accuracy is reasonable, the error being mainly positive, which may be explained by the introduction of impurities during injection of the carbonyl sample. The 2 ml of added tetrahydrofuran solution contains 3–15 × 10^{-3} mmole of reducible impurities. These impurities govern the minimum amount of carbonyl that can be determined. Naturally, the smaller the carbonyl concentration and the larger the concentration of impurities, the larger will be the error in this method.

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A wide variety of compounds was investigated for their ability to react with the titrant. Aliphatic and aromatic alcohols and nitro-compounds, acid chlorides, peroxides, acids and water interfered (Table 2). Acetonitrile, aniline, n-butylamine, diethylamine, dimethylformamide, ethyl acetate and triethylamine did not interfere. Ethers were not tested, but the tetrahydrofuran and 1,2-dimethoxyethane used as solvents did not react with the sodium fluorenyl.

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Hydrogen peroxide	101.0
Nitrobenzene	96.0
Nitromethane	104.0
Phenol	99.9
1,3-Propanediol	119.0
Propanol	78.0
Water	100.0

The interferences occur by an oxidation–reduction or an acid–base mechanism, depending on the particular functional group. All the interferents react quantitatively save for the aliphatic alcohols. The instability of the alcohol carbonium ion is believed to cause the slow reaction of the nucleophilic attack on the alcohol by the sodium fluorenyl. All these interferents react in a 1:1 ratio with sodium fluorenyl except for nitro-groups, which require two equivalents of sodium fluorenyl per mole.

The method could obviously be extended to determination of other reducible functional groups. Indeed, preliminary investigations into other functional groups, namely nitro-groups and acid chlorides, have been performed in the study of interferences in this work. Further investigation could lead to a direct, non-aqueous, analytical titration procedure for other reducible functional groups.

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(*Received* 20 *August* 1975. *Revised* 7 *October* 1975. *Accepted* 31 *January* 1976)

Besides the classical gravimetric methods[1,2] for the determination of iodine, there are a few that use organic reagents.[3,4,5] One of these[5] is based on precipitation of ICl_2^- with the tetraphenylarsonium cation (Ph_4As^+). In view of the properties of Ph_4As^+, the tri-iodide ion would be expected to form an ion-association compound with it. Our investigations confirm this, and we have used the compound for the gravimetric determination of iodine.

EXPERIMENTAL

Composition and properties of tetraphenylarsonium tri-iodide

Tetraphenylarsonium tri-iodide (Ph_4AsI_3) was prepared by mixing solutions of Ph_4AsCl and I_3^-. It is a stable yellowish brown crystalline precipitate, m.p. 165°. It is practically insoluble in water: $K_{sp} = 2.0 \times 10^{-11}$. It is more soluble in polar solvents (CH_3COCH_3, $3 \times 10^{-2}M$; $C_2H_4Cl_2$, $6.6 \times 10^{-2}M$; $CHCl_3$, $7.6 \times 10^{-3}M$; C_2H_5OH, $5.7 \times 10^{-3}M$), giving yellow solutions. In non-polar solvents Ph_4AsI_3 is sparingly soluble (C_6H_6, $1.8 \times 10^{-4}M$; $C_6H_5CH_3$, $6 \times 10^{-5}M$).

Conditions for quantitative precipitation

Iodide is readily converted into iodate.[4] The iodate can then be changed into the equivalent amount of I_3^- if about

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NON-AQUEOUS QUANTITATIVE DETERMINATION OF THE CARBONYL FUNCTIONAL GROUP BY CONSTANT-CURRENT POTENTIOMETRIC TITRATION

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(*Received* 29 *September* 1975. *Accepted* 13 *January* 1976)

There is a significant lack of rapid and accurate methods for determination of carbonyl groups. Most of those available involve a back-titration. A direct titration method would be a useful innovation. This paper reports such a procedure.[1] The titrant, sodium fluorenyl, is a strong base[2] as well as a very potent reducing agent, especially towards oxygen and oxygen-containing compounds. In this work its reduction properties were utilized. The titrant and titrands exhibit irreversible electrochemical behaviour; therefore, in the potentiometric titrations two platinum-wire electrodes are used at a small constant current of ~0.5 μA.

EXPERIMENTAL

Reagents

Sodium fluorenyl titrant is prepared by letting an excess of sodium metal shavings (5 g) react with 11 g of recrystallized fluorene in 100 ml of distilled 1,2-dimethoxyethane,[3] which is a 3:1 molar ratio, over a period of 24 hr in a sealed 250-ml round-bottomed flask in an inert atmosphere. It is then filtered through glass wool and diluted with 350 ml of distilled tetrahydrofuran (THF) to yield a final sodium fluorenyl concentration of approximately 0 1*M* The titrant is standardized against freshly distilled 2,4-pentanedione by the procedure described below. The titrant is stored under dry pure argon, the inlet to the titrant reservoir being connected to an argon bubbler which allows the inert gas over the titrant to be kept at atmospheric pressure. A balloon system fails to work properly because of diffusion of oxygen through the walls of the balloon. The THF is stored over sodium metal and under argon to inhibit diffusion of oxygen and water vapour into the system. The titrant is stable for at least a day and it should be noted that the method is not very practical unless a large number of samples is available for analysis on the same day.

The tetrahydrofuran and 1,2-dimethoxyethane are distilled twice under nitrogen, first from lithium aluminium hydride and then from sodium metal. All other compounds were purified by normal laboratory procedures.

Apparatus

A Metrohm potentiograph Model E436, Series 14, was used together with a Model E436D automatic titrator. The potentiograph also supplies the constant current for the electrodes. A simplified circuit diagram is shown in Fig. 1.

Electrode pretreatment

The pretreatment involves the procedures developed by Ashworth and Walisch[4] and by van Name and Fenwick.[5] The platinum electrodes are cleaned by submersion for 5 min in potassium dichromate–sulphuric acid solution, then thoroughly rinsed with distilled, deoxygenated water, and allowed to stand for 12 hr in 2*M* sulphuric acid–0.15*M* ferrous ammonium sulphate solution. Immediately before use the electrodes are heated to a dull red in a burner flame, then plunged into a crystal of sodium bisulphite, care being taken not to amass any bisulphite on the glass around the platinum wire. The electrodes are then heated again to a dull red, allowed to cool for 90–120 sec, and used immediately to measure the potential of the solution being titrated.

This pretreatment procedure produces reproducible electrode surfaces, as indicated by reproducibility of the potentiometric titration curves. The pretreatment procedure is not time-consuming, requiring less than 2 min before each titration.

Cell and apparatus pretreatment

Before each titration the pipette and titration vessel are thoroughly rinsed with acetone and then flushed with nitrogen to remove the acetone. They are then flamed-out to remove any traces of moisture, and allowed to cool under nitrogen. If these procedures are not properly applied, the concentration of water and reducible substances, approximately 0.025*M*, interferes The acetone wash is necessary to remove the reaction product, which is insoluble in water.

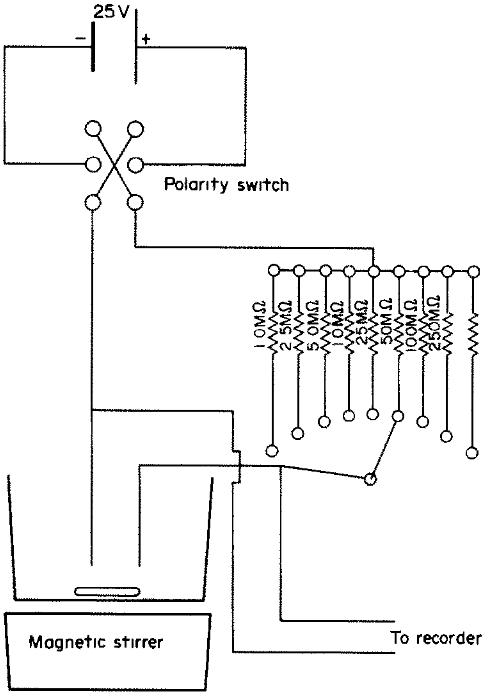

Fig. 1. Electrical circuit employed for use in constant-current titrations. The double-pole, double-throw switch is used to change the polarity of the electrodes.

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Table 1. Results of carbonyl determination

Carbonyl	Average found, %	Coefficient of variance, %	Number of analyses
n-Butyraldehyde	98.0	1.4	6
2-Ethylhexanal	104.9	1.2	5
Cinnamaldehyde	99.3	0.8	5
Benzaldehyde	101.0	1.6	5
3-Hydroxy-4-methoxy-benzaldehyde	105.8	1.3	5
p-Hydroxybenzaldehyde	104.4	0.8	4
p-Methoxybenzaldehyde	102.1	6.8	7
2-Hydroxy-5-nitro-benzaldehyde	105.9	3.3	6
p-Nitrobenzaldehyde	99.4	2.4	6
9-Anthraldehyde	97.3	2.1	4
Acetone	103.8	2.2	5
2-Butanone	106.2	6.1	4
2,4-Pentanedione	100.0	1.8	6
Cyclopentanone	103.6	2.3	9
Cyclohexanone	103.6	2.6	7
Cyclohexanone (6 days old)	129.9	4.2	8
1,4-Benzoquinone	102.8	2.5	7
p-Aminoacetophenone	101.6	4.0	4
Acetophenone	103.3	2.1	6
9-Fluorenone		did not react	
Benzophenone		did not react	
DL-Camphor		did not react	

Titration procedure

Fifteen ml of 0.15*M* sodium perchlorate in tetrahydrofuran, employed as supporting electrolyte, are introduced into the dry titration vessel which has been purged with nitrogen, and deaerated with dry nitrogen for 90–120 sec. The 0.5-μA electrode current is switched on and the titrant added continuously at the optimum flow-rate of 0.85 ml/min. If the flow-rate is faster, slow reaction kinetics cause a false end-point to be obtained for certain carbonyls. Once the titrant flow starts, the nitrogen flow is transferred from the bubbler to an orifice which permits the nitrogen to sweep out the volume above the reaction medium.

The potential of the two indicator electrodes is monitored until a derivative end-point is observed, which corresponds to the reducible impurities originally present in the purified tetrahydrofuran (their concentration is usually 2.5–4.5 × $10^{-3}M$). Immediately afterwards, 2 ml of the carbonyl sample are added, containing approximately 0.2 mmole of carbonyl, and the titration is continued until just after the carbonyl derivative end-point is reached.

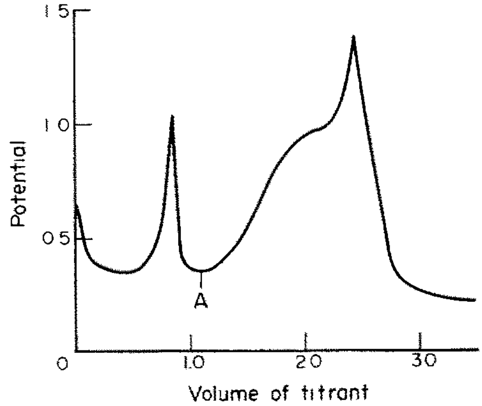

Fig. 2. Typical derivative-type titration curve for a carbonyl with sodium fluorenyl as a titrant. A denotes the point at which the butyraldehyde is injected. The difference between the end-points corresponds to the butyraldehyde and impurities injected.

RESULTS AND DISCUSSION

Aliphatic, aromatic and cyclic ketones, and aliphatic and aromatic aldehydes were investigated in this research and the carbonyls listed in Table 1 were chosen to represent a wide range of steric, configurational, and electronic effects. As can be seen, all types of carbonyl compounds lend themselves to analysis by this procedure.

Steric hindrance, as might be expected from the large size of the fluorenyl anion, plays a major role in the reactivity of certain carbonyls. Three carbonyl compounds investigated were found not to react: 9-fluorenone, benzophenone, and DL-camphor. This inertness most likely results from the bulkiness of the attacking fluorenyl anion and of the compound being attacked. However, 9-anthraldehyde, which was expected to be inert, was found to react rapidly. It is believed that the carbonyl carbon in 9-anthraldehyde, being positioned one carbon atom away from the bulky anthracene moiety, allows the fluorenyl anion the spatial orientation required to make attack possible, whereas in benzophenone and 9-fluorenone the carbonyl carbon is positioned in the 2- and 3-ring moiety, respectively. The carbonyl solution in THF must be freshly prepared so as to avoid build-up of peroxide contaminants. Table 1 shows that when a cyclohexanone solution was examined 6 days after it was prepared, the amount of reducible species corresponded to 129% of the amount originally introduced.

The minimum concentration of carbonyl that can be determined with acceptable accuracy and precision depends on the concentration of the titrant. We used 0.1*M* titrant and the minimum concentration of carbonyl determinable was 7.5 × $10^{-3}M$. Storrs[6] found sodium fluorenyl to be stable at a concentration as low as 0.02*M*. With this titrant concentration, the determination limit might be lowered to 1.2 × $10^{-3}M$.

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Table 2

Taken, μg	Found, μg	Relative error, %	Taken, μg	Found, μg	Relative error, %
1000	1005	+0.5	6000	6027	+0.5
1000	994	−0.6	6000	6000	±0.0
1000	1000	±0.0	6000	6050	+0.8
1000	1011	+1.1	6000	5961	−0.7
1000	1011	+1.1	6000	6016	+0.3
1000	994	−0.6	6000	6038	+0.6
1000	989	−1.1	6000	6022	+0.4
1000	1005	+0.5	6000	5995	−0.1
1000	1038	+3.8	6000	6004	+0.1
1000	1000	±0.0	6000	5994	+0.1

10% more than the theoretical amount of iodide is added. Experiment shows that 50% excess of iodide is needed to precipitate Ph_4AsI_3 quantitatively. This excess of I^-, however, could also be precipitated as Ph_4AsI. To avoid this, the difference between the solubilities of tetraphenylarsonium tri-iodide and tetraphenylarsonium iodide at higher temperatures can be utilized. Table 1 shows that when, after the precipitation, the mixture is heated to 100° and filtered at >60°, correct results are obtained.

The precipitation cannot be done at high temperatures because low values are obtained owing to the volatilization of elementary iodine. However, in the preparation of the I_3^- there may also be loss of iodine. For this reason, a special precipitation procedure is used. To a solution containing Ph_4AsCl and I^-, the acid solution of IO_3^- to be determined is added drop by drop. Under these conditions, Ph_4AsI_3 forms immediately as the I_3^- is produced.

EXPERIMENTAL

Reagents

Hydrochloric acid, 2M.

Chlorine water, saturated and freshly prepared.

Potassium iodide solution. Iodide concentration 5 *mg/ml.*

Ph_4AsCl solution, 0.01M.

Procedure

Place 20–25 ml of a solution containing 1–6 mg of iodide in a flat-bottomed flask marked at a volume of 10 ml. Add 5 ml of chlorine water, 2.5 ml of 2*M* hydrochloric acid and water to 45–50 ml, and evaporate the mixture to a volume of 10 ml. Cool, and add this solution dropwise to a mixture of the 0.01*M* Ph_4AsCl (15 ml) and potassium iodide solution (10 ml) previously placed in a 150-ml beaker, rinsing the flask with three 10 ml portions of water. After the precipitation, stir the mixture for about 2 min, dilute with water to 100 ml, heat to 100°, and filter off the precipitate when the temperature has fallen to 50°. Use the filtrate to transfer the precipitate, wash it twice with 4 ml of warm water and dry it for 1 hr at 120°. Table 2 shows results for the determination of 1 and 6 mg of iodide.

The relative standard deviation for 6 mg of iodide (reliability coefficient 95%) is 0.9% (10 results) and that for 1 mg is 2.5%. NO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^- and Br^- do not interfere. If the sample contains cations with a higher oxidation potential than that of iodine (*e.g.*, Fe^{3+}), these should be removed first in the form of the hydroxides or other insoluble compounds.

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Summary—Tetraphenylarsonium tri-iodide has been prepared and its properties studied. On the basis of its stability and very low solubility a gravimetric method for the determination of mg amounts of iodine has been developed. The mean relative error for amounts of 1–6 mg is about +0.3%. CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^- and Br^- do not interfere.

Table 2. Compounds that react with the titrant

Compound	Average found, %
Acetyl chloride	110.0
Benzoic acid	99.5
Hydrogen peroxide	101.0
Nitrobenzene	96.0
Nitromethane	104.0
Phenol	99.9
1,3-Propanediol	119.0
Propanol	78.0
Water	100.0

The interferences occur by an oxidation–reduction or an acid–base mechanism, depending on the particular functional group. All the interferents react quantitatively save for the aliphatic alcohols. The instability of the alcohol carbonium ion is believed to cause the slow reaction of the nucleophilic attack on the alcohol by the sodium fluorenyl. All these interferents react in a 1:1 ratio with sodium fluorenyl except for nitro-groups, which require two equivalents of sodium fluorenyl per mole.

The method could obviously be extended to determination of other reducible functional groups. Indeed, preliminary investigations into other functional groups, namely nitro-groups and acid chlorides, have been performed in the study of interferences in this work. Further investigation could lead to a direct, non-aqueous, analytical titration procedure for other reducible functional groups.

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Summary—A non-aqueous direct titration procedure has been developed for the determination of aldehydes and ketones. It uses two platinum-wire indicating electrodes with a constant current of ~0.5 μA. The solvent medium is 0.15*M* sodium perchlorate in tetrahydrofuran The titrant is sodium fluorenyl in a mixture of 1,2-dimethoxyethane and tetrahydrofuran. All types of carbonyl compounds react with the sodium fluorenyl, but steric hindrance prevents complete reaction with certain ketones containing bulky groups. The lowest concentration of carbonyl that can be determined with acceptable accuracy and precision is $7.5 \times 10^{-3}M$, the error being <3% and the precision better than ±2.5%. Most reducible compounds interfere, *e.g.*, peroxides, acid halides, nitro-compounds, acids, and water, and cannot be differentiated potentiometrically. The method can be extended to other reducible functional groups, *e.g.*, nitro groups and acid chlorides.

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GRAVIMETRIC DETERMINATION OF IODINE AS TETRAPHENYLARSONIUM TRI-IODIDE

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Besides the classical gravimetric methods[1,2] for the determination of iodine, there are a few that use organic reagents.[3,4,5] One of these[5] is based on precipitation of ICl_2^- with the tetraphenylarsonium cation (Ph_4As^+). In view of the properties of Ph_4As^+, the tri-iodide ion would be expected to form an ion-association compound with it. Our investigations confirm this, and we have used the compound for the gravimetric determination of iodine.

EXPERIMENTAL

Composition and properties of tetraphenylarsonium tri-iodide

Tetraphenylarsonium tri-iodide (Ph_4AsI_3) was prepared by mixing solutions of Ph_4AsCl and I_3^-. It is a stable yellowish brown crystalline precipitate, m.p. 165°. It is practically insoluble in water: $K_{sp} = 2.0 \times 10^{-11}$. It is more soluble in polar solvents (CH_3COCH_3, $3 \times 10^{-2}M$; $C_2H_4Cl_2$, $6.6 \times 10^{-2}M$; $CHCl_3$, $7.6 \times 10^{-3}M$; C_2H_5OH, $5.7 \times 10^{-3}M$), giving yellow solutions. In non-polar solvents Ph_4AsI_3 is sparingly soluble (C_6H_6, $1.8 \times 10^{-4}M$; $C_6H_5CH_3$, $6 \times 10^{-5}M$).

Conditions for quantitative precipitation

Iodide is readily converted into iodate.[4] The iodate can then be changed into the equivalent amount of I_3^- if about

Table 1. Weight of Ph_4AsI_3, obtained, *g*, at various temperatures of filtration

80–90°	70°	60°	50°	40°	Theoretical
0.0532	0.0534	0.0544	0.0543	0.0544	0.0542
0.0536	0.0541	0.0540	0.0541	0.0544	0.0542

Table 2

Taken, μg	Found, μg	Relative error, %	Taken, μg	Found, μg	Relative error, %
1000	1005	+0.5	6000	6027	+0.5
1000	994	−0.6	6000	6000	±0.0
1000	1000	±0.0	6000	6050	+0.8
1000	1011	+1.1	6000	5961	−0.7
1000	1011	+1.1	6000	6016	+0.3
1000	994	−0.6	6000	6038	+0.6
1000	989	−1.1	6000	6022	+0.4
1000	1005	+0.5	6000	5995	−0.1
1000	1038	+3.8	6000	6004	+0.1
1000	1000	±0.0	6000	5994	+0.1

10% more than the theoretical amount of iodide is added. Experiment shows that 50% excess of iodide is needed to precipitate Ph_4AsI_3 quantitatively. This excess of I^-, however, could also be precipitated as Ph_4AsI. To avoid this, the difference between the solubilities of tetraphenylarsonium tri-iodide and tetraphenylarsonium iodide at higher temperatures can be utilized. Table 1 shows that when, after the precipitation, the mixture is heated to 100° and filtered at >60°, correct results are obtained.

The precipitation cannot be done at high temperatures because low values are obtained owing to the volatilization of elementary iodine. However, in the preparation of the I_3^- there may also be loss of iodine. For this reason, a special precipitation procedure is used. To a solution containing Ph_4AsCl and I^-, the acid solution of IO_3^- to be determined is added drop by drop. Under these conditions, Ph_4AsI_3 forms immediately as the I_3^- is produced.

EXPERIMENTAL

Reagents

Hydrochloric acid, 2M.

Chlorine water, saturated and freshly prepared.

Potassium iodide solution. Iodide concentration 5 *mg/ml.*

Ph_4AsCl solution, 0.01M.

Procedure

Place 20–25 ml of a solution containing 1–6 mg of iodide in a flat-bottomed flask marked at a volume of 10 ml. Add 5 ml of chlorine water, 2.5 ml of 2*M* hydrochloric acid and water to 45–50 ml, and evaporate the mixture to a volume of 10 ml. Cool, and add this solution dropwise to a mixture of the 0.01*M* Ph_4AsCl (15 ml) and potassium iodide solution (10 ml) previously placed in a 150-ml beaker, rinsing the flask with three 10 ml portions of water. After the precipitation, stir the mixture for about 2 min, dilute with water to 100 ml, heat to 100°, and filter off the precipitate when the temperature has fallen to 50°. Use the filtrate to transfer the precipitate, wash it twice with 4 ml of warm water and dry it for 1 hr at 120°. Table 2 shows results for the determination of 1 and 6 mg of iodide.

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ANNOTATION

THE EFFECT OF LOW-TEMPERATURE ASHING ON THE STRUCTURE AND COMPOSITION OF MINERAL COMPONENTS

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(*Received* 20 *February* 1976. *Accepted* 16 *March* 1976)

Low-temperature ashing (LTA) is used in analytical chemistry as one of the methods of decomposing samples containing carbon or organic material. LTA has several advantages. The most cited are as follows:

(*a*) There is less chance of losing trace elements by volatilization than with the classical dry ashing technique. Most published work on the use of LTA is concerned with trace element analysis and therefore there is a not inconsiderable body of data available concerning losses of trace elements by LTA.

(*b*) The structure of the mineral component is left unaltered. By structure is meant the microscopic as well as the crystalline structure, and the composition of the mineral residue. Although this has been said by several authors, this statement has not been systematically checked.

Apart from work by Gluskoter[1] and Estep *et al.*,[2] who investigated the changes of a few minerals present in coal, there appears to be no study available on the effect of LTA on the structure of minerals. During an investigation on the composition and structure of small brain calcifications,[3] we developed a procedure in which, after LTA, the inorganic composition (matrix elements and trace elements) was determined, usually by atomic absorption, the mineralogical identity by infrared spectrophotometry and X-ray diffraction, and the microscopic morphology by microscan electron microscopy. Excellent results were obtained. A study on the validity of the results obtained led us to investigate, in a more systematic way than seems to have been done until now, whether LTA indeed leaves the crystalline structure and composition of the inorganic residue unaltered. We wish to report these results here, because we think that they can be valuable for several applications such as the analysis of the minerals present in coal, calcifications in animal and plant tissue, the identification or determination of minerals collected on filters in air pollution studies, the identification of inorganic fibres in lung tissue, *etc.*

EXPERIMENTAL

Apparatus

LTA-505 (Tracerlab). Unicam SP-1000 I.R. spectrophotometer (Pye Unicam). Philips Norelco X-ray diffractometer (with goniometer and Geiger-Müller counter).

Samples

All salts were *p.a.* products. Mineral samples were obtained from Prof. P. Pasteels (Vrije Universiteit Brussel, Belgium).

Procedures

LTA. Samples of about 10–20 mg were ashed during 24 hr at 250 W.

Infrared. A 1–2 mg portion of sample was mixed with 150 mg of KBr and pressed into a pellet.

X-Ray diffraction. Diffractograms were taken, using the Cu $K_{\alpha 1}$-line.

RESULTS AND DISCUSSION

Two kinds of sample were investigated, namely a number of minerals (Table 1) and salts (Table 2). Before

Table 1. Minerals investigated

1. Aragonite ($CaCO_3$)	11. Apatite [$Ca_5(PO_4)_3(OH)$]
2. Calcite ($CaCO_3$)	12. Brucite [$Mg(OH)_2$]
3. Kaolinite [$Al_4Si_4O_{10}(OH)_8$]	13. Dolomite [$CaMg(CO_3)_2$]
4. α-Quartz (SiO_2)	14. Diopside ($CaMgSi_2O_6$)
5. Anhydrite ($CaSO_4$)	15. Orthoclase ($KAlSi_3O_8$)
6. Epsomite ($MgSO_4 \cdot 7H_2O$)	16. Chalcantite ($CuSO_4 \cdot 5H_2O$)
7. Leucite ($KAlSi_2O_6$)	17. Chalcopyrite ($CuFeS_2$)
8 Olivine (Mg_2SiO_4)	18. Pyrite (FeS_2)
9. Talcum [$Mg_6Si_8O_2(OH)_4$]	19. Gypsum ($CaSO_4 \cdot 7H_2O$)
10. Malachite [$Cu_2CO_3(OH)_2$]	20. Fluorite (CaF_2)

Table 2. Salts investigated

1. $FeSO_4\ 7H_2O$
2. $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
3. $CaSO_4 \cdot 2H_2O$
4. K_2SO_4
5. Na_2SO_4
6. $(NH_4)_2SO_4$
7. $Fe_2(SO_4)_3 \cdot H_2O$
8. $KHSO_4$
9. $CaCO_3$
10. Li_2CO_3
11. K_2CO_3
12. $MgCO_3$
13. Na_2CO_3
14. $(NH_4)_2CO_3$
15. $NaHCO_3$
16. K_2HPO_4
17. $Ca(H_2PO_4)_2 \cdot H_2O$
18. $CaHPO_4 \cdot 2H_2O$
19. $MgHPO_4 \cdot 3H_2O$
20. Na_2HPO_4
21. $(NH_4)_2HPO_4$
22. $NaH_2PO_4 \cdot 2H_2O$
23. $Na_3PO_4 \cdot 12H_2O$
24. $Ca_3(PO_4)_2$
25. $Na_2SiO_3\ 9H_2O$

and after LTA, the infrared spectra and the X-ray diffractograms of the minerals were obtained. For the salts only the infrared spectra were measured.

The LTA treatment has no effect on most of the minerals investigated. Changes were detected in only one X-ray diffractogram. It was found that gypsum is converted into the monohydrate $CaSO_4 \cdot H_2O$, so that the effect of the LTA treatment was to remove one of the two molecules of water of crystallization. Changes were also detected in the infrared spectra of pyrite, chalcopyrite, gypsum and chalcanthite. These are due to oxidation and/or dehydration. It is evident that oxidation must have a marked effect on the infrared spectrum since new chemical groups are formed. This is also true for dehydration. This is due[4] either to the formation of another crystalline species (as in the case of gypsum) or because water molecules forming hydrogen bonds with anions and thereby changing their vibration frequency, are eliminated.

Results from classical thermogravimetry, such as those summarized by Duval[5] can help to explain the changes. However, it should be kept in mind that classical thermogravimetry is carried out at normal pressure (while LTA is carried out at very low pressures) and in a much less oxidizing atmosphere.

Pyrite and chalcopyrite are oxidized in part with the formation of SO_4^{2-}, since a sulphate peak was detected in the infrared spectra after LTA It is interesting that no change is found in the X-ray diffractograms of these minerals. This can be explained by assuming that only a rather small part of the sulphide is oxidized, with the formation of an amorphous sulphate. In the chalcanthite infrared spectrum no new bands are formed after LTA, but their relative importance changes drastically. A possible explanation is that some of the water of crystallization has been lost. Classical thermogravimetry[5] shows that chalcanthite loses four molecules of water between 67° and 153°.

For the salts, more changes were observed. We will not try to discuss and explain these systematically, since our principal intention is to see whether LTA causes changes or not. No effects were observed for most sulphates (Nos. 4–8 in Table 2), carbonates (Nos. 10–14), the silicate (No. 25) and some phosphates (Nos. 16–18). The most drastic change is found for $NaHCO_3$ which is entirely converted into Na_2CO_3. The ferrous sulphate (No. 1) is converted into a basic ferric sulphate. This is in agreement with the findings of classical thermogravimetry, since Duval[5] states that partial oxidation and dehydration occur for this salt between 23° and 96° and that complete dehydration with the formation of a basic sulphate occurs at 140°. The spectrum of Mohr's salt (No. 2) still contains sulphate and ammonium bands after LTA This could be interpreted as due to the formation of $NH_4Fe(SO_4)_2$ (*i.e.*, an oxidation of Fe^{2+}). Most phosphates show changes. These are, no doubt, due to dehydration, formation of polymeric phosphates and pyrophosphates. The effect of such changes on the infrared spectra has been discussed by Corbridge[6] and by Bellamy and Beecher[7].

In general, we conclude that in many cases, LTA can be used without changing the composition and the crystalline structure of the inorganic residues. In particular, X-ray diffraction identification of the mineral originally present is possible in almost all cases investigated, even if some change is detected by infrared spectrometry. This is also true for the application which is of the greatest interest to us, namely the study of brain microcalcifications However, it is clear that changes do occur quite often and that, therefore, the often-made statement that LTA leaves the mineral component unaltered, is misleading.

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Summary—To investigate the often-made statement that low-temperature ashing leaves the structure and composition of the mineral residue unaltered, 25 salts and 20 minerals were studied by X-ray diffractometry and infrared spectrophotometry It is concluded that many substances remain unaltered, but some do not, so the statement is misleading.

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For the salts, more changes were observed. We will not try to discuss and explain these systematically, since our principal intention is to see whether LTA causes changes or not. No effects were observed for most sulphates (Nos. 4–8 in Table 2), carbonates (Nos. 10–14), the silicate (No. 25) and some phosphates (Nos. 16–18). The most drastic change is found for $NaHCO_3$ which is entirely converted into Na_2CO_3. The ferrous sulphate (No. 1) is converted into a basic ferric sulphate. This is in agreement with the findings of classical thermogravimetry, since Duval[5] states that partial oxidation and dehydration occur for this salt between 23° and 96° and that complete dehydration with the formation of a basic sulphate occurs at 140°. The spectrum of Mohr's salt (No. 2) still contains sulphate and ammonium bands after LTA This could be interpreted as due to the formation of $NH_4Fe(SO_4)_2$ (*i.e.*, an oxidation of Fe^{2+}). Most phosphates show changes. These are, no doubt, due to dehydration, formation of polymeric phosphates and pyrophosphates. The effect of such changes on the infrared spectra has been discussed by Corbridge[6] and by Bellamy and Beecher[7].

In general, we conclude that in many cases, LTA can be used without changing the composition and the crystalline structure of the inorganic residues. In particular, X-ray diffraction identification of the mineral originally present is possible in almost all cases investigated, even if some change is detected by infrared spectrometry. This is also true for the application which is of the greatest interest to us, namely the study of brain microcalcifications However, it is clear that changes do occur quite often and that, therefore, the often-made statement that LTA leaves the mineral component unaltered, is misleading.

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Summary—To investigate the often-made statement that low-temperature ashing leaves the structure and composition of the mineral residue unaltered, 25 salts and 20 minerals were studied by X-ray diffractometry and infrared spectrophotometry It is concluded that many substances remain unaltered, but some do not, so the statement is misleading.

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EINFLUSS VON VERSCHIEDENEN PARAMETERN UND MESSBEDINGUNGEN AUF DIE ANFÄNGLICHE NEIGUNG VON ATOMABSORPTIOMETRISCHEN EICHKURVEN

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Zusammenfassung—Die anfängliche Neigung a_0 von atomabsorptiometrischen Eichkurven wird durch die gewählten Meßbedingungen und spektroskopischen Kenngrößen des zu bestimmenden Elementes A beeinflußt. In dieser Arbeit wurde eine Beziehung abgeleitet, mit deren Hilfe die Größenordnung von a_0 für verschiedene Meßbedingungen vorausgesagt werden kann. Insbesondere werden die Beeinflussungen von a_0 durch spektroskopische Daten der betreffenden Linie, Erniedrigung der Konzentration von A infolge seiner Ionisation und Verbindung, Konstruktion und Temperatur des Atomreservoirs und durch die spektrale Bandbreite des Monochromators diskutiert. Der Einfluß der Stromstärke von Spektrallampen auf die anfängliche Neigung der Eichkurven wurde ebenfalls untersucht. Ein sog. "Lampenstromeffekt" wurde bei Elementen gefunden, deren Dampfdruck bei 400 K größer als 10^{-14} mmHg ist. Schließlich wurden die Elektronenkonzentrationen bzw. Elektronenpartialdrücke p_e in der Flamme unter Anwendung der Saha-Gleichung aus den atomabsorptiometrisch ermittelten Ionisationsgraden vom Barium berechnet. Man erhielt einen p_e-Wert von $1{,}21 \cdot 10^{-7}$ bzw. $1{,}3 \cdot 10^{-7}$ atm für die metallfreie N_2O/C_2H_2- bzw. Luft/C_2H_2-Flamme.

Bei der atomabsorptiometrischen Bestimmung eines Elementes wird bekanntlich die optische Dichte D gemessen, welche gewöhnlich nur in einem engen optischen Dichtebereich von der Konzentration w_A [Gewichtsbruch, ppm] des zu bestimmenden Elementes A in der untersuchten Lösung linear abhängt. Die anfängliche Neigung a_0 der Funktion (D, w_A) hängt von vielen Faktoren ab:

(1) von spektralen Größen

(2) von der Konstruktion und der Temperatur T des Atomreservoirs (Flamme, Graphitrohrküvette)

(3) von der Elektronik der Signalpräsentation.

Die Elektronik eines Atomabsorptions Spektrophotometers soll hier nicht diskutiert werden. Wir nehmen eine ideale elektronische Signalverarbeitung an, so daß die optische Dichte D immer exakt angezeigt wird:

$$D = \log I_0/I = 0{,}434\, k_\lambda L = a_0 w_A \qquad (1)$$

Hier bedeuten I_0 bzw. I die Intensität [W/cm^2] einer schmalen Resonanzlinie vor bzw. nach dem Atomreservoir der Länge L und k_λ den linearen natürlichen Absorptionskoeffizienten.

k_λ hat einen maximalen Wert k_{λ_0} in der Mitte (bei λ_0) des Absorptionsprofils k_λ,λ. Hat k_λ,λ die Form einer Gauss'schen Normalverteilung, so beträgt[1] k_{λ_0}:

$$k_{\lambda_0} = f_G \cdot \frac{\pi \cdot e^2}{m \cdot c^2} \cdot \frac{\lambda_0^2}{\Delta\lambda_{ab}} \cdot N_j f_{ji} \qquad (2)$$

Hier bedeuten f_G das Verhältnis des Produktes aus der Peakhöhe und der Halbwertsbreite zu der Peakfläche einer Gauss'schen Glockenkurve ($f_G = 2[(\ln 2)/\pi]^{1/2}$), e die Ladung und m die Ruhemasse des Elektrons, c die Lichtgeschwindigkeit, $\Delta\lambda_{ab}$ die Halbwertsbreite der Absorptionslinie, N_j die Anzahl der absorbierenden Atome pro cm^3 und f_{ji} die Oszillatorenstärke, d.h. die effektive Anzahl der Oszillatoren pro Atom. Walsh hat gezeigt,[2] daß k_{λ_0} aus der Gleichung (1) erhalten wird, falls zur Messung der optischen Dichte eine Strahlungsquelle benutzt wird, deren emittierte Resonanzlinie viel schmäler als das Absorptionsprofil ist. In diesem Fall sollte D in einem großen Bereich zu der Konzentration N_j direkt proportional sein, wie man durch Einsetzen von k_{λ_0} anstelle von k_λ in der Gleichung (1) zeigen kann. In der analytischen Praxis findet man gewöhnlich eine Proportionalität zwischen D und w_A bis zu D-Werten von *ca.* 0,2. In dieser Arbeit soll die Beeinflussung der Proportionalitätskonstante durch experimentelle Meßbedingungen diskutiert werden. Insbesondere sollen dabei die Selbstabsorptionsverbreiterung der Emissionslinie (Linien-Selbstumkehr), die Ionisation gewisser Metalle und nicht absorbierbare Störstrahlungen berücksichtigt werden.

EXPERIMENTELLER TEIL

Geräte und Aufnahme der Eichkurven

Man verwendete die Perkin-Elmer Atomabsorptions-Spektrophotometer Modell 303 bzw. 300 für die Flammentechnik bzw. Graphitrohr-Küvettentechnik (HGA 72). Alle Stammlösungen wurden aus analysenreinen Präparaten hergestellt und mit chemischen Analysenmethoden kontrolliert. Durch Verdünnen mit verdünnten Mineralsäuren (s. Tabelle 1) wurden die Eichlösungen erhalten, welche je zweimal in die Flamme bzw. Küvette eingespritzt wurden. Um kleine systematische Fehler zu kompensieren, welche infolge langzeitiger Instabilität des Meßsystems manchmal auftraten, wurden die Lösungen in umgekehrter Reihenfolge ein zweites Mal gemessen. Man verwendete den Mittelwert beider D-Werte. Im allgemeinen wurde bei der Aufnahme der Eichkurven nach der entsprechenden Vorschrift des Geräteherstellers vorgegangen. Wesentliche Abweichungen sind an der entsprechenden Stelle vermerkt.

Bestimmung und Rolle der spektralen Bandbreite

Zur Abschätzung der Störintensität einer nicht absorbierten Strahlung muß die spektrale Bandbreite $\Delta\lambda_M$ bekannt sein. Ihre experimentelle Bestimmung soll nun kurz beschrieben werden.

Jeder Spektrallinie λ_0 entspricht eine Stelle λ_0^* an der Wellenlängenskala, wo das Detektor-Signal S_D seinen Maximalwert $S_{D,max}$ hat. Ein Monochromator ist dann richtig justiert, wenn λ_0 und λ_0^* zahlenmäßig übereinstimmen. Wird nun der Monochromator in Richtung von kleineren oder größeren λ^*-Werten verstellt, so nimmt S_D im Bereich von $\lambda^* \pm \Delta\lambda_M$ linear ab, da sich der Lichtleitwert[3] des Monochromators ändert. Bei den meisten Spektrophotometern sind Eintritts- und Austrittsspalt gekoppelt und haben die gleiche Breite B und Höhe H. Mit dem optischen System wird der Eintrittsspalt auf den Austrittspalt scharf abgebildet.[4,5] Ist zudem das Signal S_D zur der empfangenen Strahlungsleistung proportional, so kann für eine scharfe Spektrallinie die folgende Beziehung abgeleitet werden:

$$S_D = k_D f_{SV} I \frac{BHF}{f^2}\left(1 - \frac{|\lambda_0^* - \lambda^*|}{BR}\right) \qquad (3)$$

Hier bedeuten k_D die Detektorkonstante (Größe des unverstärkten Signals pro Watt Strahlungsleistung), f_{SV} den Signalverstärkungsfaktor, F die Oberfläche des optischen Gitters, R die Lineardispersion am Ort des Austrittsspaltes und f die Brennweite des optischen Abbildungssystems.

Das Produkt BR entspricht bei vollständiger Abbildung der instrumentellen Verbreiterung der durchgelassenen schmalen Spektrallinie λ_0 d.h. der spektralen Bandbreite $\Delta\lambda_M$. Das Verhältnis von S_D bei falscher Einstellung λ^* zu $S_{D,max}$ bei richtiger Einstellung λ_0^* des Monochromators auf die Spektrallinie λ_0 beträgt, nach Gleichung (3):

$$S_D^{rel} = S_D/S_{D,max} = f_S = \left(1 - \frac{|\lambda_0^* - \lambda^*|}{\Delta\lambda_M}\right) \qquad (4)$$

f_S wird als Spaltfunktion bezeichnet, und kann entweder durch Messung von $S_D/S_{D,max}$ für eine scharfe Emissionslinie (s. Kreise in Abb. 1) oder durch Messung der relativen Absorption (% ABS)/(% ABS)$_{max}$ einer polychromatischen Strahlung in einem atomaren Absorber (s. Dreiecke in Abb. 1) in Abhängigkeit von λ^* erhalten werden. Emissions- und Absorptions-Messungen müssen für die gleiche mechanische Spaltbreite B die gleiche Spaltfunktion ergeben, falls $\Delta\lambda_M$ viel größer als $\Delta\lambda_{em}$ bzw. $\Delta\lambda_{ab}$ ist ($\Delta\lambda_{em}$ ist die Halbwertsbreite der Emissionslinie).

Die $\Delta\lambda_M$-Werte wurden als Kehrwerte der Neigungen von f_S, λ^* im Bereich (λ_0^*-$\Delta\lambda_M$) bzw. als absolute Kehrwerte der Neigungen von f_S, λ^* im Bereich (λ_0^* + $\Delta\lambda_M$) und durch Abmessen des Abstandes zwischen beiden Schenkeln der dreieckförmigen Spaltfunktionen bei der halben Höhe der Dreiecke ermittelt [s. Gleichung (4) und Abb.1]. Aus Messungen der Emissions-Intensität der Resonanzlinie des Cadmiums ($\lambda_0 = 228{,}80$ nm) erhielt man daher je 3 Werte für eine bestimmte Spaltbreite des Monochromators. In zwei Fällen wurde zusätzlich auch noch die Absorption einer polychromatischen Strahlung durch Cadmiumatome in der Graphitrohrküvette gemessen, so daß 6 $\Delta\lambda_M$-Werte erhalten wurden. Die Mittelwerte betragen $0{,}17 \pm 0{,}02_6$, $0{,}59 \pm 0{,}08_6$ und $1{,}60 \pm 0{,}13_3$ nm, bei den Spaltpositionen 2, 7 und 20 des Gerätes PE 300. Hierbei ist die Anzahl der Einzelwerte der einfachen Standardabweichung als ein Index zugefügt. Bei den Spaltpositionen 3, 4 und 5 des Gerätes 303 wurden die $\Delta\lambda_M$-Werte von $0{,}29 \pm 0{,}02_3$, $0{,}97 \pm 0{,}12_3$ und $3{,}41 \pm 0{,}53_3$ nm gefunden. Die für das Gerät 300 geltenden Nominalwerte sind im Durchschnitt 1,2-mal größer als die gemessenen Werte. Demgegenüber wurden beim Gerät 303—allerdings nach 7-jährigem Gebrauch—1,4-mal größere Bandbreiten als die Nominalwerte gefunden. Der Justierungsfehler ($\lambda_0^* - \lambda_0$) und die instrumentelle Unsicherheit der Position λ_0^* der Resonanzlinie können aus der Abb. 1 ebenfalls entnommen werden.

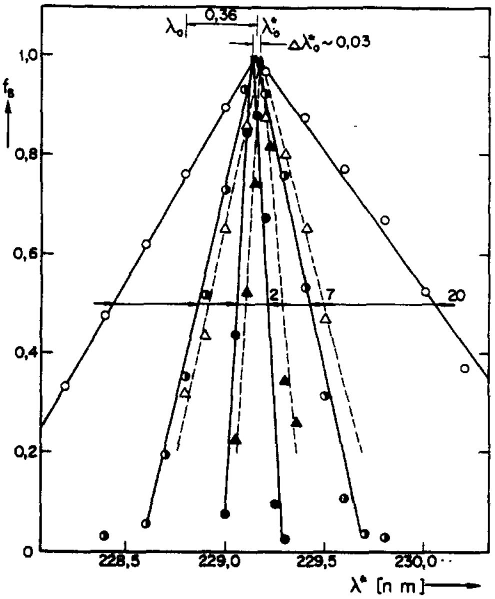

Abb. 1. Mit der Cd-Resonanzlinie (228,8 nm) aufgenommen Spaltfunktionen f_S eines Atomabsorptions-Spektrophotometers (Perkin Elmer 300) bei den Spaltpositionen 2, 7 und 20. Kreise: S_D^{rel}-Werte. Dreiecke: (% ABS)/(% ABS)$_{max}$-Werte, welche mit einer Wasserstofflampe als Strahlungsquelle und 2,2 μg Cd als atomarer Absorber in der Graphitrohrküvette erhalten wurden.

Die wichtigste Konsequenz einer dreieckförmigen Spaltfunktion besteht für die analytische Praxis darin, daß alle Störlinien λ^S im Bereich von $\lambda_0^* \pm \Delta\lambda_M$ einen Einfluß auf meßbare optische Dichte haben. Allerdings beträgt die an der Stelle λ_0^* registrierte Störintensität $I^s_{\lambda^*_0}$ nicht $I^s_{\lambda^*_s}$ sondern nur $f^s_S I^s_{\lambda^*_s}$. Eine polychromatische Störstrahlung mit der Intensitätsdichte

J_λ [$W \cdot cm^{-2} \cdot nm^{-1}$] liefert dagegen den Beitrag von $J_{\lambda_S^*}\Delta\lambda_M$ da J_λ im engen Bereich von $\Delta\lambda_M$ praktisch konstant ist. Lässt nun der Monochromator außer der Hauptresonanzlinie λ_0 mit der Intensität I_0 die schwächer absorbierten Linien $\lambda_1^a \ldots \lambda_m^a$ und die nicht absorbierten Störlinien $\lambda_1^s \ldots \lambda_m^s$ mit den relativen Intensitäten $I_1^a/I_0 \ldots I_m^a/I_0$, und $I_1^s/I_0 \ldots I_m^s/I_0$ durch, so wird die folgende optische Dichte gemessen:

$$D = \log \frac{1 + \Sigma f_{Sm}^a(I_m^a/I_0) + \Sigma f_{Sm}^s(I_m^s/I_0) + J_{\lambda_0^*}^q \Delta\lambda_M/I_0}{\exp[-a_0 w_A] + \Sigma f_{Sm}^a(I_m^a/I_0)] \exp[-a_m w_A + \Sigma f_{Sm}^s(I_m^s/I_0) + (J_{\lambda_0^*}^q + J_{\lambda_0^*}^r)\Delta\lambda_M/I_0} \tag{5}$$

Die Intensität von polychromatischen Störstrahlungen der Quelle q und des Atomreservoirs r können gewöhnlich vernachläßigt werden. Ihr Beitrag ist aber bei großen Spaltbreiten und schwachen Intensitäten der Resonanzlinien zu berücksichtigen. Die anfänglichen Neigungen der Eichkurven für die Linien λ_0, $\lambda_1, \ldots \lambda_m$ wurden in dieser Gleichung mit a_0, $a_1, \ldots a_m$ bezeichnet. Sie müssen mit einer derart engen Bandbreite bestimmt werden, daß keine Störlinien und nur unwesentliche polychromatische Strahlung in den Detektor gelangen.

Ermittlung des Ionisationsgrades von Ba, Na und Li und der freien Elektronenkonzentration in der Flamme

Bariumeichlösungen mit je $5 \cdot 10^{-4}M$ Bariumchlorid bzw. Bariumnitrat und 0,1*M* Perchlorsaüre bzw. Salpetersaüre sowie mit verschiedenen Kaliumchlorid- bzw. Kaliumnitrat-Konzentrationen wurden in die N_2O/C_2H_2- bzw. Luft/C_2H_2-Flamme eingespritzt. Aus den gemessenen optischen Dichten D_I (bei der Resonanzlinie von Ba, 553,6 nm) und D_{II} (bei der Resonanzlinie von Ba^+, 455,4 nm) wurden der Ionisationsgrad f_I^0 von Barium und die Konzentration N_e^0 der freien Elektronen in der Flamme ohne Kaliumzusatz (Index "o" oben rechts) nach den folgenden Beziehungen berechnet:

$$\frac{1 - D_I/D_I^0}{D_{II}/D_{II}^0 - D_I/D_I^0} = f_I^0 = \frac{1}{1 + N_e^0/K_{I_{Ba}}} \tag{6}$$

Man erhielt f_I^0-Werte für Barium von 0,916 ± 0,009 in der N_2O/C_2H_2-Flamme bzw. 0,10 ± 0,02 in der Luft/C_2H_2-Flamme. Diese entsprechen einer Elektronenkonzentration von $2{,}97 \cdot 10^{11}$ bzw. $3{,}9 \cdot 10^{11}$ cm^{-3} oder einem Elektronpartialdruck von $1{,}21 \cdot 10^{-7}$ bzw. $1{,}3 \cdot 10^{-7}$ atm. Die zur Berechnung von N_e^0 benötigte Ionisationskonstante $K_{I_{Ba}}$ von Barium wurde aus der Saha-Gleichung[6] berechnet. Sie beträgt $10^{12{,}51}\,cm^{-3}$ bei 3000 K bzw. $10^{10{,}64}\,cm^{-3}$ bei 2500 K.

Mit den f_I^0-Werten wurde nun der chemischen Ionisationsgrad f_I^K von Barium und die Elektronenkonzentration N_e^K in Gegenwart von Kalium aus der folgenden Beziehung berechnet:

$$f_I^0 \frac{D_{II}}{D_{II}^0} = f_I^K = \frac{1}{1 + N_e^K/K_{I_{Ba}}} \tag{7}$$

In Abb. 2 sind f_I^K und N_e^K gegen die Molarität [K] des Kaliums in der eingespritzten Lösung graphisch aufgetragen. Zur Berechnung der N_e^K-Werte wurden die Mittelwerte der beiden f_I^K-Werte eingesetzt.

Die Elektronenkonzentration N_e^K nimmt mit zunehmender [K] langsamer zu als die berechnete Elektronenkonzentration N_e^*. Letztere kann unter der Annahme erhalten werden, daß die Flammengase das Ionisationsgleichgewicht

$$K \rightleftharpoons K^+ + e^-; K_{I_K} = N_{K^+} \cdot N_e^*/N_K \tag{8}$$

nicht stören. N_e^* bedeutet also die Elektronenkonzentration in einem hypothetischen Atomreservoir, welches nur K, K^+ und e^- enthält, sonst aber die gleichen Kenngrößen wie die Flamme aufweist. In diesem Reservoir sind N_{K^+} und N_e^* immer gleich groß, so daß die Auflösung von Gleichung (8) nach N_e^* bei gleichzeitiger Elimination der unbekannten Konzentration N_K ergibt:

$$N_e^* = \tfrac{1}{2}[-K_{I_K} + (K_{I_K}^2 + 4\,K_{I_K}[K] \cdot 6{,}02 \cdot 10^{20}/f_{VF})^{1/2}] \tag{9}$$

Bei der Herleitung dieser Beziehung wurde angenommen, daß die Verdünnung f_{VF} des Kaliums beim überführen aus der Lösung in die Flamme bzw. in das hypothetische Atomreservoir dieselbe ist, so daß N_K durch Subtraktion von N_e^* ($= N_{K^+}$) von der Totalkonzentration $[K] \cdot 6{,}02 \cdot 10^{20}/f_{VF}$ erhalten wird. Die Verdünnung f_{VF} beim Uberführen des Kaliums aus der Lösung in die N_2O/C_2H_2-Flamme betrug $6{,}23 \cdot 10^5$ [s. auch Gleichung (12)]. Die N_e^*-Werte ergeben eine leicht gekrümmte Kurve (s. Abb. 2), welche *ca.* 2-mal steiler ist als die experimentelle N_e^K-Gerade. Offensichtlich geben die K-Atome ihre Elektronen zum Teil an die Komponenten des Flammengases ab.

Das Barium erwies sich als ein guter Indikator für die freie Elektronenkonzentration N_e^K bei verschiedenen Kalium-konzentrationen in der N_2O/C_2H_2-Flamme. In der kälteren Luft/C_2H_2-Flamme liegt alles Barium in Form von Ba und BaO vor, falls [K] größer als *ca.* 0,002 *M* ist. Das Verhältnis D_{II}/D_{II}^0 kann daher nicht genügend genau bestimmt werden und kann nicht als Maß für N_e^K dienen. Ein geeignetes Indikatorelement wäre das Cäsium, welches in der Luft/C_2H_2-Flamme in Abwesenheit leicht ionisierbarer Elemente eine Ionisation von 92% erleidet. Cs^+ hat leider keine Resonanzlinie im Spektralbereich von 200 bis 900 nm. Aus der Messung von D_I in Abhängigkeit von [K] kann f_I^{Cs} nur mit gewissen Annahmen berechnet werden, worauf hier verzichtet wird.

Unter den untersuchten Metallen haben außer Barium und Cäsium noch Lithium und Natrium

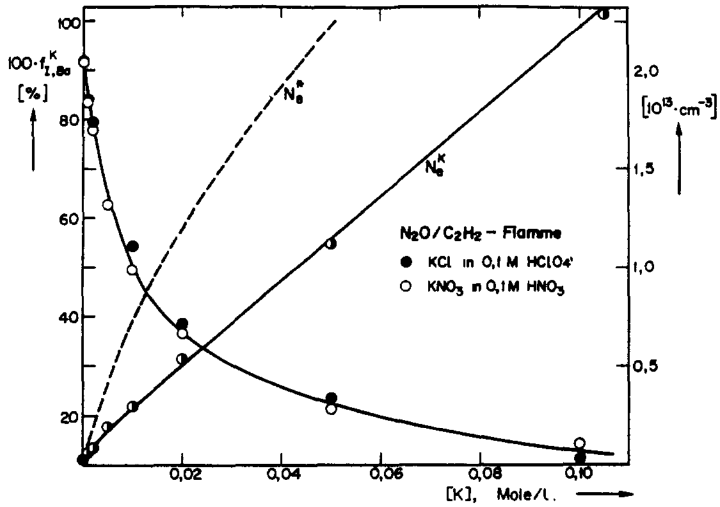

Abb. 2. Ionisationsgrad $f^{K}_{I,Ba}$ von Barium und Konzentration N_e^K der freien Elektronen in der C_2H_2/N_2O-Flamme bei verschiedenen Kaliumkonzentrationen in der eingespritzten Lösung. ($Q_{bg} = 8{,}4$, $Q_{ox} = 17{,}1$ l./min $T = 3000$ K, Beobachtung *ca.* 10 mm über der Austrittsöffnung).

kleine Ionisationsenergien und somit große Ionisationskonstanten K_I von $10^{9,61}$ und $10^{10,12}\,cm^{-3}$ bei 2500 K. Setzt man diese Werte und die mit Barium als Indikator ermittelte Elektronenkonzentration N_e^0 von $3{,}9 \cdot 10^{11}$ in die Gleichung (6) ein, so erhält man einen Ionisationsgrad von 1,0% bzw. 3,3% für Lithium bzw. Natrium.

RESULTATE UND DISKUSSION

Zur Diskussion der Empfindlichkeit von atomabsorptiometrischen Bestimmungen muß N_j in der Gleichung (2) mit der experimentell zugänglichen Konzentration w_A der Lösung in Zusammenhang gebracht werden. Dabei muß berücksichtigt werden, daß ein Teil der Atome eventuell chemisch gebunden (N_C) oder ionisiert (N_I) ist. Die freien Atome befinden sich in verschiedenen energetischen Zuständen, 0, 1,...*j*,...*i*,...*m*, wobei 0 den Grundzustand, *j* das untere Niveau (meistens $j = 0$) und *i* das obere Niveau des Überganges *ij* und *m* die Termlaufzahl bezeichnen.

$$N_t = N_C + N_I + N_0 + N_1 + \dots + N_j + \dots + N_i + \dots + N_m = N_A/f_C(1 - f_I) \quad (10)$$

Hier bedeuten $f_C = (N_A + N_I)/N_t$ den Dissoziationsgrad, $f_I = N_I/(N_A + N_I)$ den Ionisationsgrad und N_A die Summe von N_0 bis N_m.

Die totale Konzentration N_t aller A-Spezies kann aus der Konzentration w_A [μg A/g der Lösung] der in das Atomreservoir (r, d.h. die Flamme bzw. Küvette) eingespritzten Lösung berechnet werden:

$$N_t = 6{,}022 \cdot 10^{17} \cdot d\, w_A/f_V\, M \quad (11)$$

In dieser Gleichung bedeuten *d* die Dichte der eingespritzten Lösung, *M* die relative Molmasse und f_V die Verdünnung ($= N_{t,L_g}/N_{t,r}$). Wenn das Atomreservoir eine Flamme (F) ist, kann f_{VF} der eingestellten Strömungsgeschwindigkeit [ml/min] des Brenngases Q_{bg} und des Oxidants Q_{ox} berechnet werden. Nimmt man an, daß sich sowohl die Flamme mit der Temperatur T_F als auch die Brennmischung bei der Raumtemperatur T_R ideal verhalten, erhält man für f_{VF}:

$$f_{VF} = \frac{(Q_{bg} + Q_{ox})(T_F/T_R)(n_F/n_R)}{Q_{L_g} f_Z} \quad (12)$$

Das Verhältnis n_F/n_R der Molzahlen nach und vor Ablauf der Verbrennungsreaktion[7] berücksichtigt die durch die Teilchenzahlerhöhung bedingte Ausdehnung der Flamme. Q_{L_g} bezeichnet die Geschwindigkeit der Lösungszufuhr [ml/min], von welcher nur der Anteil $f_Z Q_{L_g}$ in die Flamme gelangt.

Die Verdünnung in der Küvette kann nur näherungsweise berechnet werden, da im Gegensatz zur Flamme keine stationäre Zu- und Abfuhr der Atome erfolgt. Man atomisiert den A-Gehalt einer Lösungsmenge *V* von 5 bis 50 μl während einer kurzen Zeit[8] (z.B. 0,5 bzw. 2 s im Falle von Cadmium bzw. Kupfer). Wenn wir annehmen, daß die Atomwolke die Küvette mit dem Radius *r* und der Länge L_K beim Erscheinen des Absorptionsmaximums gleichmäßig ausfüllt, erhalten wir:

$$f_{V_K} \simeq r^2 \pi L_K/V \quad (13)$$

In Kenntnis von N_A kann nun der Anteil N_j der absorbierenden Atome berechnet werden. In einer laminaren Flamme und in einer Graphitrohrküvette herrscht zwischen den verschiedenen Zuständen 0, 1,...*j*...*i*...*m* mit den Energien E_0, E_1,...E_j...E_i...E_m ein thermodynamisches Gleichgewicht, so daß diese Zustände nach der Boltzmann-Verteilung populiert sind:

$$N_j = (2\,J_j + 1)\frac{\exp[-(E_j - E_0)/kT]}{F_A(T)} \cdot N_A = g_j f_A N_A \quad (14)$$

Hierbei bedeuten J_j die Gesamtdrehimpulsquantenzahl, k die Boltzmann-Konstante und $F_A(T)$ die atomare, innere Zustandsumme:

$$F_A(T) \equiv \sum_{0}^{m^*} g_m \exp\left[-(E_m - E_0)/kT\right] = g_0 \sum_{0}^{m^*} N_m/N_0 \tag{15}$$

Die Summierung kann bei demjenigen Grenzterm m^* abgebrochen werden, dessen Beitrag kleiner als die gewünschte Genauigkeit (z.B. 0,002 in dieser Arbeit) ist.

Schließlich muß man noch berücksichtigen, daß die Halbwertsbreite $\Delta\lambda_{em}$ der Emissionslinie in Wirklichkeit nicht vernachlässigbar klein ist. Wenn das Profil der Emmisionslinie ebenfalls der Form einer Gauss'schen Glockenkurve entspricht, kann[9] dieses dadurch geschehen, daß man $\Delta\lambda_{ab}$ in der Gleichung (2) einfach durch $(\Delta\lambda_{ab}^2 + \Delta\lambda_{em}^2)^{1/2}$ ersetzt. Berechnet man gleichzeitig das Produkt der Konstanten, so ergibt die Kombination der Gleichungen (1), (2), (10), (11) und (14) die folgende Beziehung zwischen D und w_A:

$$D = (2{,}175 \cdot 10^5\ \mathrm{cm \cdot mole^{-1}}) \frac{f_C(1 - f_I)dL}{M f_V} \times \frac{\lambda_0^2 (gf) f_A}{(\Delta\lambda_{ab}^2 + \Delta\lambda_{em}^2)^{1/2}} \cdot w_A = a_0 w_A \tag{16}$$

a_0 kann als die anfängliche Neigung der Eichkurven D, w_A experimentell bestimmt werden. Bei g und f wurden die Indizies weggelassen, da $g_j f_{ji} = g_i f_{ij}$.

Von den zur Berechnung der a_0-Werte benötigten Daten sind d, L, M, und f_V leicht zu ermitteln. f_A kann gemäß der Definitionsgleichung (14) aus dem Termschema[10] des betreffenden Atoms beliebig genau berechnet werden. Der Ionisationsgrad f_I hängt bei einer bestimmten Temperatur des Atomreservoirs nur von der Konzentration der freien Elektronen ab [s. auch Gleichungen (6) und (7)]. Gewöhnlich ist die totale Konzentration N_t des zu bestimmenden Elementes viel kleiner als die Elektronenkonzentration N_e^0 der Flamme selbst, so daß f_I im ganzen Meßbereich von w_A konstant ist und nur die anfängliche Neigung von D, w_A beeinflußt sonst aber keine Krümmung der Eichkurven verursacht.

Die emissionspektroskopisch ermittelten (gf)-Werte[11] sind nicht besonders präzise. Die in der Tabelle 1 angegebenen Halbwertsbreiten $\Delta\lambda_{ab}$ der Absorptionslinien sind Mittelwerte von berechneten Grenzwerten[12] und weisen daher eine recht große Unsicherheit auf. Ebenfalls sind die chemischen Dissoziationsgrade sehr schwierig zu ermitteln. Für die Halbwertsbreiten $\Delta\lambda_{em}$ der Emissionslinien stehen nur vereinzelt Daten zur Verfügung. Daher wurden alle Abschätzungen mit der Annahme von $f_C = 1$ und $\Delta\lambda_{em} = 0$ berechnet (a_0^*-Werte in der Tabelle 2). Für das Cäsium wurde kein a_0^*-Wert abgeschätzt, da der Ionisationsgrad f_I in Gegenwart von 0,01M Kaliumchlorid in der eingespritzten Lösung (s. Tabelle 1) nicht bestimmt wurde. Bei der Berechnung der a_0^*-Werte wurde bei allen Messungen mit der Luft/C_2H_2-Flamme die gleiche Verdünnung f_{VF} angenommen, was ebenfalls nur näherungsweise zutrifft.

Aus den erwähnten Gründen erwartet man, daß die abgeschätzten Neigungen a_0^* nur näherungsweise mit den anfänglichen Neigungen a_0 der Eichkruven D, w_A übereinstimmen. Dabei muß ein Verhältnis $a_0/a_0^* \geq 0{,}2$ bereits als eine gute Voraussage für die Größenordnung der meßbaren optischen Dichte betrachtet werden. Im Falle von $Cd_{a,b,c}$, Zn, Pd, Ni, Fe und Na trifft dies zu. Barium und Indium bzw. Lithium liegen zum Teil als Oxide bzw. als Hydroxid in der Flamme vor und ergeben daher eine kleinere Empfindlichkeit als man unter der Annahme von $f_C = 1$ erwartet. Das Platin atomisiert vermutlich un-

Tabelle 1. Zusammenstellung der für die untersuchten Metallionen gebrauchten Lösungsmittel, spektroskopischen Daten und der oberen Grenzen w_A^{lin} der linearen Meßbereiche

A	Lösungsmittel	λ_0^*, nm	gf[11]	f_A	$\Delta\lambda_{ab}$,[12] pm	w_A^{lin}, ppm
Ba†	0,1M $HClO_4$ 0,01M KCl	553.6	0,90	0,826	3,4	10
Cd	0,1M HNO_3	228,8	0,92	1,000	0,95	6
Cd	H_2O	326,1	0,0014	1,000	1,5	1200
Cs	0,1M H_2SO_4 0,01M KCl	852,1	1,40	0,498	7,0	40
Fe	0,1M HNO_3	248,3	3,10	0,0483	1,4	20
In	0,1M HNO_3 0,001M $LaCl_3$	304,0	0,99	0,321	1,4	40
Li	0,1M HNO_3	670,8	0,80	0,500	13	7
Na	0,1M HNO_3	589,0	0,95	0,500	6,3	5
Ni	0,1M HNO_3	232,0	0,86	0,0405	1.2	15
Pd	0,5M HCl	247,6	0,10	0,806	1,1	40
Pt	0,5M HCl	265,9	0,87	0.0625	1,0	300
Zn	0,1M HNO_3	213,8	1,30	1,000	1,1	5

* Bei allen diesen Linien ($\lambda_0 = hc/(E_i - E_j)$) ist das zugehörige untere Niveau j mit dem Grundzustand 0 identisch so daß $f_A = 1/F_A(T)$ ist (wegen T s. folgende Bemerkung.)

† Ba wurde in der Acetylen/Lachgas-Flamme (T = 3000 K) und die übrigen Elemente wurden in der Acetylen/Luft-Flamme (T = 2500 K) bestimmt.

vollständig, was die Unempfindlichkeit der Platinbestimmung erklärt.

Die Gleichung (16) erklärt die Befunde bei Änderungen wichtiger experimenteller Parameter in befriedigendem Maße.

1. Eine empfindliche Bestimmung ist nur bei Wellenlängen des betreffenden Elementes möglich, welche dem Übergang des Atoms aus dem Grundzustand oder aus einem dem Grundzustand 0 energetisch nahe liegenden Zustand j in den angeregten Zustand i angehören. Der Faktor f_{A} nimmt nämlich mit $(E_j - E_0)$ exponentiell ab.

2. Die Ionisation von Metallen mit niedrigen Ionisationsenergien muß durch Erhöhung der Konzentration der freien Elektronen in der Flamme zurückgedrängt werden. Die maximale Empfindlichkeit wird natürlich bei $f_{\mathrm{I}} = 0$ erreicht. Bei der Bestimmung des Bariums in der N_2O/C_2H_2-Flamme wird dieses nur erreicht, wenn die Konzentration vom Kaliumchlorid in der eingespritzten Lösung mehr als $0.1M$ beträgt. Solche Lösungen sind jedoch für die analytische Praxis nicht gut geeignet, da sich Störungen infolge Kaliumchlorid-Abscheidung an der Austrittsöffnung des Brenners einstellen. Eine Kaliumchlorid-Konzentration von $0{,}01M$ stellt eine gute Kompromißlösung betreffend Empfindlichkeit und Präzision dar. In Abwesenheit leicht ionisierbarer Begleitstoffe kann natürlich auch die Resonanzlinie von Ba^+ benutzt werden.

3. Damit keine systematischen Eichfehler entstehen, muß f_{VF} beim Einspritzen von Eichlösungen und der zu analysierenden Lösungen dieselbe sein. Gemäß der Definitionsgleichung (12) müssen daher alle Lösungen dieselbe Temperatur haben, und müssen alle drei Flüsse Q_{bg}, Q_{ox} und Q_{Lg} konstant bleiben. Damit alle Lösungen gleich schnell angesaugt und mit dem gleichen Wirkungsgrad f_{Z} zerstäubt werden, müssen alle Lösungen ungefähr die gleiche Viskosität haben. Das wird praktisch der Fall sein, wenn die Konzentrationen der Begleitstoffe in allen Lösungen auf mindestens 10% übereinstimmen.

Die Größenordnung der Erhöhung der Empfindlichkeit beim Übergang von der Flammen- zu der Küvettentechnik kann mit der kleineren Verdünnung in der Küvette in befriedigender Weise erklärt werden. Während die gemessene Empfindlichkeitszunahme $a_{0,\mathrm{K}}/a_{0,\mathrm{F}}$ für die Resonanzlinie (228,8 nm) des Cadmiums 1620 betrug, ergibt Gleichung (16) für $a^{\bullet}_{0,\mathrm{K}}/a^{\bullet}_{0,\mathrm{F}}$ einen Wert von 4400, wenn f_{VK} 40 beträgt, d.h. wenn in der Küvette je 100 μl von Cadmiumlösungen verschiedener Konzentration atomisiert werden. Bei der Küvettentechnik ist die in die Küvette eingebrachte Menge q_{A} des zu bestimmenden Elementes A maßgebend, so daß die Eichkurven meistens in der Form D, q_{A} dargestellt werden. Aus der anfänglichen Neigung $b_{0,\mathrm{K}}$ dieser Eichkurve kann $a_{0,\mathrm{K}}$ leicht berechnet werden: $a_{0,\mathrm{K}} = b_{0,\mathrm{K}} V d$. Nach unserer Erfahrung sind die Eichkurven D, w_{A} bei konstantem Einspritz-Volumen V der Eichlösungen verschiedener Konzentration w_{A} besser reproduzierbar als die Eichkurven D, q_{A} bei variablen Mengen einer einzigen Eichlösung. Im letzten Fall beeinflussen nämlich die Benetzung der Graphitoberfläche durch die Lösung und die Verteilung der Atomwolke in der Küvette die meßbare optische Dichte, wobei aber diese Beeinflussung vom V in schlecht kontrollierbarer Weise abhängt.

4. Gemäß Gleichung (16) beträgt das Verhältnis $a^{\bullet}_0/a^{\bullet}_1$ der Neigung der Hauptresonanzlinie λ_0 zu der Neigung der Negenresonanzlinie λ_1, $(\lambda^2 gf/\Delta\lambda_{\mathrm{ab}})_0/(\lambda^2\, gf/\Delta\lambda_{\mathrm{ab}})_1$. Dieses entspricht bei den Linien des Cadmiums einem theoretischen Verhältnis von 510. Die Messungen ergaben den beinahe gleichen Wert von 475.

5. Verwendet man eine polychromatische Strahlungsquelle PQ anstelle einer Spektrallampe SL, so muß $\Delta\lambda_{\mathrm{em}}$ in der Gleichung (16) durch $\Delta\lambda_{\mathrm{M}}$ ($\gg \Delta\lambda_{\mathrm{ab}}$) ersetzt werden. Unter Vernachlässigung des kleinen Formfaktors f_{G} erhält man für dieselbe Linie des betreffenden Elementes: $a_0^{\mathrm{SL}}/a_0^{\mathrm{PQ}} = \Delta\lambda_{\mathrm{M}}/\Delta\lambda_{\mathrm{ab}}$. Nach dieser Beziehung liegen die Verhältnisse der anfänglichen Neigungen beider Eichkurven $(D, w_{\mathrm{A}})_{\mathrm{SL}}$ und $(D, w_{\mathrm{A}})_{\mathrm{PQ}}$ in der Größenordnung von 10 bis 100 falls eine spektrale Bandbreite von 0,1 nm benutzt wird. Die $\Delta\lambda_{\mathrm{ab}}$-Werte liegen nämlich im Bereich von 10^{-2} bis 10^{-3} nm (s. Tabelle 1).

6. Irgendwelche Voraussagen der Gleichung (16) treffen nur dann zu, wenn der Monochromator nur die gewünschte Linie durchläßt. Bei der Erhöhung der spektralen Bandbreite fallen eventuell mehrere Linien in den Detektor, was die meßbare optische Dichte beeinflußt. Dieses kann experimentell am einfachsten durch Aufnahme der Kurve D, $\Delta\lambda_{\mathrm{M}}$ beim Konstanthalten der Konzentration w_{A} in der eingespritzten Lösung geprüft werden (s. Kurven für Li, K und Fe in Abb. 3).

Die beiden Komponenten des Resonanzdoubletts von Lithium sind auch bei der kleinsten spektralen Bandbreite nicht aufgelöst. In dem Spektralbereich von 670,8 ± 20 nm befinden sich keine Störlinien. Zudem ist hier auch die polychromatische Störstrah-

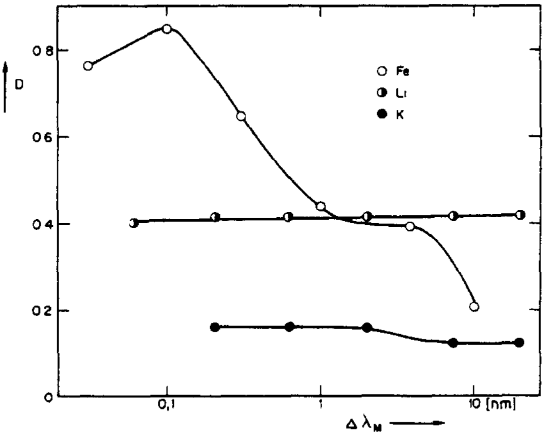

Abb. 3. Einfluß der spektralen Bandbreite $\Delta\lambda_{\mathrm{M}}$ auf die meßbare optische Dichte D bei konstanter Konzentration von Fe, Li bzw. K in der eingespritzten Lösung.

Tabelle 2. Abhängigkeit des Einflußes der Stromstärke (mA) auf die anfängliche Neigung a_0 der Eichkurven D, w_A vom Dampfdruck des betreffenden Hohlkathodenelementes A bei 400 K

A	log p_A, (p_A = mmHg)	LS (60%) *mA*	Füllgas	$\Delta\lambda_M$, *nm*	a_0 (60%) ± VB* g Lg/μg A	a_0^*	$\frac{a_0(60\%)}{a_0(100\%)}$
Cd_a	−5,7	6	Ar	0.97	$(9{,}69 \pm 0{,}14_6)\cdot 10^{-2}$	0,27	3.60 ± 0,10
Cd_b	−5,7	24	Ar	0.97	$(7{,}24 \pm 0{,}27_6)\cdot 10^{-2}$	0,27	1,07 ± 0,05
Cd_c	−5,7	6	Ar	0.97	$(2{,}04 \pm 0{,}01_6)\cdot 10^{-4}$	$5{,}4\cdot 10^{-4}$	0,94 ± 0,02
Cd_d	−5,7	6	Ar	0.59	$(1{,}57 \pm 0{,}18_5)\cdot 10^{+2}$	$1{,}2\cdot 10^{+3}$	—
Zn	−8,0	12	Ne	0.97	$(1{,}13 \pm 0{,}02_5)\cdot 10^{-1}$	0,49	1,41 ± 0,04
Li	−12,4	15	Ar	1.90	$(9{,}03 \pm 0{,}36_6)\cdot 10^{-2}$	1,2	1,12 ± 0,05
Ba	−14,4	18	Ar	0.66	$(5{,}65 \pm 0{,}09_8)\cdot 10^{-3}$	$4{,}7\cdot 10^{-2}$	1,12 ± 0,02
In	−22,0	12	Ne	0.97	$(3{,}12 \pm 0{,}08_6)\cdot 10^{-3}$	0,11	0,95 ± 0,03
Ni	−33,1	21	Ne	0.29	$(1{,}28 \pm 0{,}04_6)\cdot 10^{-2}$	$1{,}6\cdot 10^{-2}$	0,98 ± 0,06
Pd	−38,5	9	Ne	0.29	$(9{,}80 \pm 0{,}38_5)\cdot 10^{-3}$	$2{,}5\cdot 10^{-2}$	1,04 ± 0,06
Fe	−41,9	24	Ne	0.29	$(2{,}07 \pm 0{,}13_5)\cdot 10^{-2}$	$7{,}1\cdot 10^{-2}$	1,19 ± 0,09
Pt	−61,9	21	Ne	0.97	$(8{,}49 \pm 0{,}41_7)\cdot 10^{-4}$	$1{,}2\cdot 10^{-2}$	0,94 ± 0,06
Cs	−2,6	500	—	6,6	$(6{,}27 \pm 0{,}13_4)\cdot 10^{-3}$	—	1,69 ± 0,06
Na	−5,9	700	—	0,66	$(1{,}86 \pm 0{,}03_5)\cdot 10^{-1}$	0,32	1,20 ± 0,02

Bemerkungen Cd_a: 228,8 nm, Flammentechnik (F), nicht thermostatisierte (nt) Hohlkathode
Cd_b: Wie Cd_a, Hohlkathode bei 20°C thermostatisiert
Cd_c: 326,1 nm, (F)
Cd_d: 228,8 nm, Graphitrohr-Küvettentechnik, nt
* VB = Vertrauensbereich für 95%-ige stat. Sicherheit (Index rechts unten = Anzahl der Meßpunkte)
Konstante: $f_{V_K} = 40$ ($V = 100$ μl), f_{V_F} (N_2O) $= 6{,}23\cdot 10^5$, f_{V_F} (Luft) $= 4\cdot 10^5$, $L_K = 5$ cm, L_F (N_2O) $= 5{,}5$ cm, L_F (Luft) = 11.

lung sehr schwach. In diesem Idealfall ist D gemäß Gleichung (5) von $\Delta\lambda_M$ unabhängig (s. Gerade "Li" in Abb. 3). Im Falle von Kalium beträgt die Resonanzaufspaltung 3,4 nm. Dementsprechend sinkt die optische Dichte bei $\Delta\lambda_M > 3$ nm entsprechend der Voraussage von Gleichung (5). Nach dieser muß nämlich bei größeren Bandbreiten neben der Hauptresonanzlinie λ_0 (= 766,5 nm) auch noch die schwächer absorbierte Komponente λ_1^a (= 769,9 nm) des Resonanzdubletts berücksichtigt werden. Das Eisenatom hat mehrere Linien in der Umgebung der Hautresonanzlinie. Bei Öffnen des Spaltes müssen sukzessive immer mehr Linien λ^a und λ^a berücksichtigt werden, so daß sich D mit zunehmender $\Delta\lambda_M$ auf einen Viertel reduziert. Merkwürdigerweise wird eine maximale optische Dichte nicht bei dem engsten Spalt erhalten. Das kann nur mit starker polychromatischer Störstrahlung erklärt werden. Diese konnte quantitativ nicht ermittelt werden, so daß auf die Berechnung der Kurve D, $\Delta\lambda_M$ mit Hilfe der Gleichung (5) verzichtet wird. Mit Hilfe der Kurven D,$\Delta\lambda_M$ kann die optimale Spaltbreite leicht ermittelt werden. Da das elektronische Rauschen des Detektorsignals mit zunehmender Strahlungsintensität abnimmt, muß die größte spektrale Bandbreite, bei welcher noch keine wesentliche Abnahme der meßbaren optischen Dichte auftrifft, als optimal angesehen werden.

7. Schließlich soll noch der Einfluß des Lampenstromes LS der Spektrallampe auf die meßbare Intensität kurz diskutiert werden. Dieser Effekt wurde im Falle von Cadmium bei Messungen sowohl mit der Flamme[13] als auch mit der Graphitrohrküvette[14] als Atomreservoir beobachtet. Wir haben diesen Effekt systematisch untersucht, wobei Eichkurven für mehrere Metalle mit unterschiedlichem Dampfdruck bei zwei möglichst verschiedenen Stromstärken aufgenommen wurden. Diese Metalle sind in der ersten Kolonne der Tabelle 2 in der Reihenfolge ihres abnehmenden Dampfdruckes[15] bei 400 K angeführt. Log p_A wurde für diese Temperatur berechnet, da in der Hohlkathode ungefähr diese Temperatur[16] herrschen soll. Als maximale Stromstärke (max. LS) wählte man den vom Hersteller empfohlene Maximalwert (100%). Als möglichst kleine Stromstärke wurde 60% des Maximalwertes gewählt, da eine weitere Stromreduktion Schwankungen der Linienintensitäten zur Folge hatte. Das Verhältnis $a_0(60\%)/a_0(100\%)$ der anfänglichen Neigungen beider Eichkurven erwies sich als eine geeignete Kenngröße für den "Lampenstromeffekt". Die Fehlerangaben für diese Kenngröße bedeuten den Vertrauensbereich für 95%-ige statistische Sicherheit und wurde durch Fehlerfortpflanzung aus den Fehlern beider a_0-Werte ermittelt. Wenn der Dampfdruck p_A des Hohlkathodenelementes größer als 10^{-15} mmHg bei der betreffenden Hohlkathodentemperatur beträgt, wird die anfängliche Neigung und auch die Form der Eichkurven D, w_A eine Stromabhängigkeit zeigen. Den größten Lampenstromeffekt zeigt das Cadmium mit besonders hohem Dampfdruck. Cadmium hat zugleich einen tiefen Schmelzpunkt, welcher zur Erklärung des Lampenstromeffektes herangezogen wurde.[13] Indium schmilzt jedoch viel tiefer als Cadmium und zeigt einen kleinen, eher umgekehrten Lampenstromeffekt, was eine Korrelation zwischen dem Schmelzpunkt und Stromabhängigkeit der Neigung nicht zuläßt. Bei der Bestimmung von Cäsium und Natrium wurden Gasentladungsröhren verwendet. Bei diesen kann eine Entladungsstromeffekt ebenfalls beobachtet werden. Der Effekt ist jedoch viel

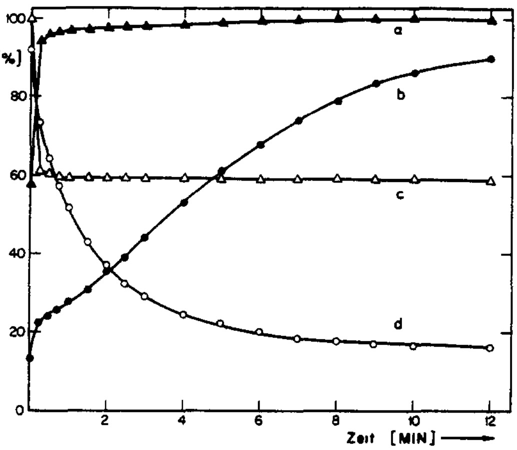

Abb. 4. Zeitlicher Verlauf der relativen Intensität der Resonanzlinie (228,8 nm) einer handelsüblichen Cd-Hohlkathodenlampe (HLK) und einer Cd-HKL mit thermostatisierter Hohlkathode nach plötzlicher Änderung des Lampenstromes um 25%. Dreiecke: thermostatisierte Cd-HKL, 1,2 mmHg Ar, 28°C. *a*: Erhöhung der Stromstärke von 28 auf 32 mA *c*: Verminderung der Stromstärke von 32 auf 24 mA Kreise: käufliche HKL, Ar *b*: Erhöhung der Stromstärke von 6 auf 8 mA *d*: Verminderung der Stromstärke von 8 auf 6 mA

weniger ausgeprägt da sich der Dampfdruck in diesen Lampen bei Erhöhung des Entladungsstromes nur wenig erhöht.

Um einen direkteren Beweis für den Zusammenhang zwischen dem Dampfdruck p_{Cd} und dem großen Lampenstromeffekt von 3,6 zu erbringen, wurde eine Hohlkathodenlampe mit thermostatisierter Kathode gebaut. Der Lampenstrom-Effekt für diese Lampe ist kaum nachweisbar (s. Tabelle 2). Für die analytische Praxis bringt die Thermostatierung der Hohlkathode einen bemerkenswerten Vorteil: nach einer Veränderung des Lampenstromes stellt sich die relative Emissionsintensität sehr rasch auf einen neuen Wert ein (s. Kurven *a* und *c* in Abb. 4). Die relative Intensität I_{rel} einer käuflichen Lampe mit nicht thermostatierter Hohlkathode nimmt dagegen erst nach 15 Minuten einen einigermassen konstanten Wert an. Der Verlauf der Kurven *b* bzw. *d* entspricht einer typischen Aufheiz- bzw. Abkühlkurve. Dieses unterschiedliche Verhalten beider Cadmium-Lampen und die Tatsache, daß die Hohlkathodenlampen mit schwerflüchtigen Elementen keinen Lampenstromeffekt zeigen, beweisen eindeutig, daß es sich bei der Verbreiterung der Emissionslinie um Linienumkehr handelt. Bei dieser Art Linienverbreiterung besitzt die Emissionslinie der Hohlkathodenlampe kein glockenförmiges Profil. Aus diesem Grunde würde die Auflösung von Gleichung (16) nach $\Delta\lambda_{em}$ nur eine hypothetische Halbwertsbreite ergeben.

Die Bedeutung der analytischen Form der Funktion D, w_A (Gleichungen (5) und (16)), besteht ganz allgemein nicht in zahlenmäßigen Voraussagen, sondern in komprimierter Darstellung aller atomabsorptiometrisch wichtigen Faktoren.

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APPLICATION OF SECONDARY-ELECTRON CAPTURE NEGATIVE-ION (SECNI) MASS SPECTROMETRY TO THE ANALYSIS OF METAL-ORGANIC COMPOUNDS[*][†]

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Summary—The application of secondary-electron capture negative-ion (SECNI) mass spectrometry to the analysis of metal-organic compounds is described and typical examples are discussed. Negative-ion mass spectra are simple, molecular anions and ligand ions being the predominant species. Metallic or ligand impurities are readily identified by this technique, which makes it extremely useful for the determination of purity and formulation of metal-organic compounds. Because of its sensitivity, the technique is also valuable for trace metal analysis.

Positive-ion electron-impact mass spectrometry is a useful analytical tool for both inorganic and organic compounds and the applications of this technique have been reviewed comprehensively.[1,2] The possibility of using chemical ionization mass spectrometry for the analysis and study of metal-organic compounds has been proposed, but this application has so far been restricted.[3–5]

For the analysis of metal-organic compounds, and particularly metal chelates, both of these techniques have limitations. The disadvantages of conventional mass spectrometry as an analytical tool for metal-organic compounds are twofold. Interaction of a 70-eV electron beam with a metal-organic molecule frequently produces excessive fragmentation, yielding a complex mass spectrum (especially for mixtures of species containing different polyisotopic metal atoms). Further, the absence of intense peaks due to metal cations in the spectra of many metal-organic compounds can lead to erroneous analytical conclusions. The chemical ionization technique is limited for general use because of the need for high-pressure source and reagent-gas facilities.

The application of secondary-electron capture negative-ion (SECNI) mass spectrometry to the analysis of metal-organic compounds overcomes many of these difficulties. Although this technique is also, in principle, applicable to the analysis of organic compounds it would have less versatility in this field. The number of organic compounds amenable to the capture of secondary or thermal electrons with the formation of molecular anions is very limited unless appropriate derivatives are first synthesized.[6–9] The main value of the SECNI technique is in the analysis of metal-organic compounds, since either the metal or the ligand may act as a site for electron capture. With polyisotopic metals, ready identification of both molecular and fragment anions can be achieved.[10–12] The present paper gives examples of the application of this new technique to the analysis of metal-organic compounds.

EXPERIMENTAL

The instrument used was a modified Hitachi Perkin-Elmer RMU-6L single focusing mass spectrometer, capable of operating in both the positive and negative ion modes. Instrumental parameters used for SECNI spectra were as follows: electron energy 70 eV, filament current 3.2 A, target voltage 100 V, target current 40 μA, total emission 50 μA, ion accelerating voltage 3.2 kV, repeller voltage zero and ion-source pressures $<5 \times 10^{-6}$ mmHg. Total negative-ion currents, measured with a retractable probe placed after the ion-exit of the source, were commonly 1–10% of those obtained for positive ions for the same samples, although with some samples this value may reach approximately 50%. Thus, with an electron-multiplier detector with a gain of $>10^6$, ample sensitivity for the detection of negative ions was available. Spectra were obtained at the lowest possible sample and ionization-chamber temperatures. Additional characterization of each compound was obtained by recording its positive-ion mass spectrum within minutes of its negative-ion spectrum, the same temperature and ion-source conditions being maintained. Care was taken to show that pyrolysis, followed by electron impact, was not the route to the production of the significant ions in the spectra. All spectra were checked for reproducibility. Mass-marking was accomplished by running a duplicate spectrum in the presence of perfluorokerosene. Ion identification was assisted by comparing the spectrum with a computer simulation based on known isotopic abundances.[11] All compounds were prepared by standard published methods and were recrystallized or sublimed before use.

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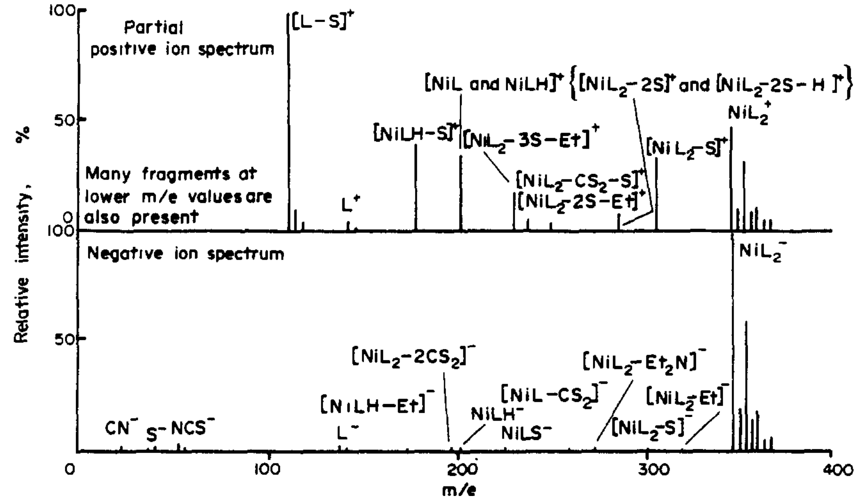

Fig. 1. 70-eV positive- and negative-ion mass spectra of bis(diethyldithiocarbamato)nickel(II) (NiL_2), where $L = (S_2CNEt_2)^-$. For clarity only complete clusters are shown for the molecular ions (with the *m/e* scale expanded); other fragment ions are shown in terms of ^{58}Ni (or ^{32}S for species containing no metal ion).

RESULTS AND DISCUSSION

The following examples have been chosen to illustrate the advantages of secondary-electron capture negative-ion mass spectrometry as an analytical tool for metal-organic compounds. The most important features of negative-ion mass spectra of metal-organic compounds are their extreme simplicity and absence of instrumental background. These features are demonstrated in Fig. 1 where the complete negative-ion and partial positive-ion mass spectra of bis(diethyldithiocarbamato)nickel(II) are compared. Significantly, 97% of the total negative-ion current is carried by the molecular anion. Virtually all bivalent metal dialkyldithiocarbamate compounds of this type give similar simple negative-ion mass spectra[13] and these ligands are useful chelating reagents for quantitative trace metal analysis[14] by this technique. Inclusion of an aromatic ring in the dithiocarbamate ligand leads to a greater degree of fragmentation of the complex as shown by the SECNI spectrum of bis(ethylphenyldithiocarbamato)nickel(II).[13] Even so, this fragmentation is not extensive enough to preclude the use of this ligand for analytical purposes.

The advantages of such simple spectra for analytical work are obvious since both identification of complexes and determination of particular metals in mixtures may be readily achieved. An additional example is provided by the metal hexafluoroacetylacetonates;[15] in Fig. 2 the positive- and negative-ion mass spectra of the aluminium complex are illustrated. Again, the negative-ion spectrum is much the simpler and the dominant negative ions are the molecular ion and the ligand fragment ion formed from it in the process $[Al(CF_3COCHCOCF_3)_3]^- \xrightarrow{*} (CF_3COCHCOCF_3)^-$. Similar negative-ion mass

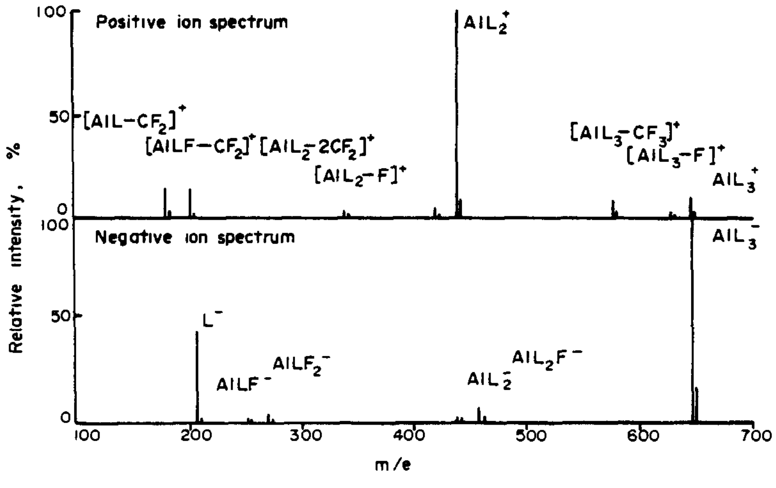

Fig. 2. 70-eV positive- and negative-ion mass spectra of tris(hexafluoroacetylacetonato)aluminium(III) (AlL_3), where $L = (CF_3COCHCOCF_3)^-$.

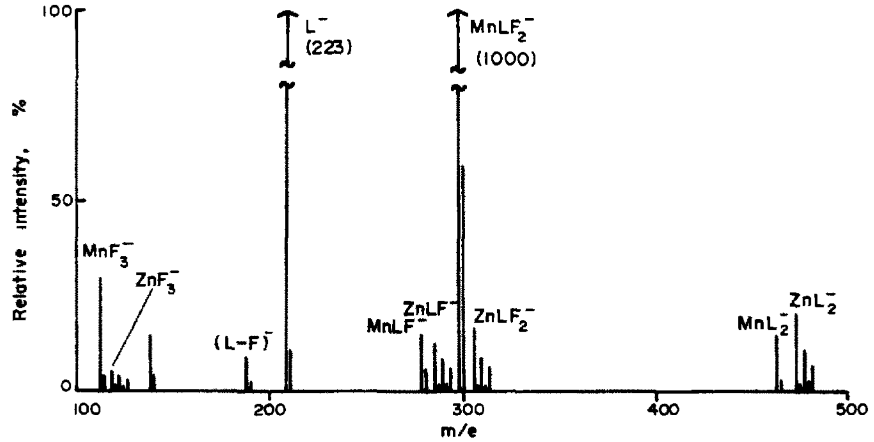

Fig. 3. 70-eV negative-ion mass spectrum of a sample of bis(hexafluoroacetylacetonato)manganese(II), (MnL$_2$), which contained the analogous zinc(II) complex as an impurity, (ZnL$_2$), where L = (CF$_3$COCHCOCF$_3$)$^-$.

spectra are obtained for metal complexes of other fluorinated β-diketones.[16]

The SECNI technique is also useful for the detection of trace metal impurities in complexes because of the ease of assignment[11,12] of peaks. In particular, the presence of characteristic clusters of peaks due to polyisotopic metals facilitates the identification of these impurities.[11] In Fig. 3, a sample of bis(hexafluoroacetylacetonato)manganese(II) is shown to contain the analogous zinc(II) complex as an impurity even though the manganese complex was prepared from "pure" reagents. The use of positive-ion mass spectrometry is not satisfactory for this purpose because neither metal complex gives a relatively intense molecular cation peak and the spectra are further complicated by extensive fragmentation peaks.

An additional advantage is in the detection of ligand impurities in a metal complex. A sample of bis-(1,1,1-trifluoro-7-methyl-2,4-octanedionato)copper(II), prepared from copper(II) acetate and the ligand, sublimed and having a satisfactory elemental analysis, was analysed by its SECNI spectrum, illustrated in Fig. 4. This spectrum revealed the presence of the complex bis(1,1,1-trifluoro-5-methyl-2,4-hexanedionato)copper(II) as an impurity. SECNI mass spectral analysis of the ligand used for the original synthesis confirmed the presence of 1,1,1-trifluoro-5-methyl-2,4-hexanedione as an impurity.

The technique can also be used for detection of mixed-ligand complexes, *e.g.*, thio-β-diketone complexes. Dimerization usually prevents isolation of pure thio-β-diketones and hence the metal complexes must be prepared *in situ*[17] in the presence of the appropriate metal salt.

Figure 5 shows the negative-ion mass spectrum of a sample of the mixed-ligand nickel(II) complex which gave elemental analyses consistent with the formula Ni(CH$_3$CSCHCSCH$_3$)(CH$_3$CSCHCOCH$_3$). It is obvious from this spectrum that the method of synthesis we have used[17] has led to a sample

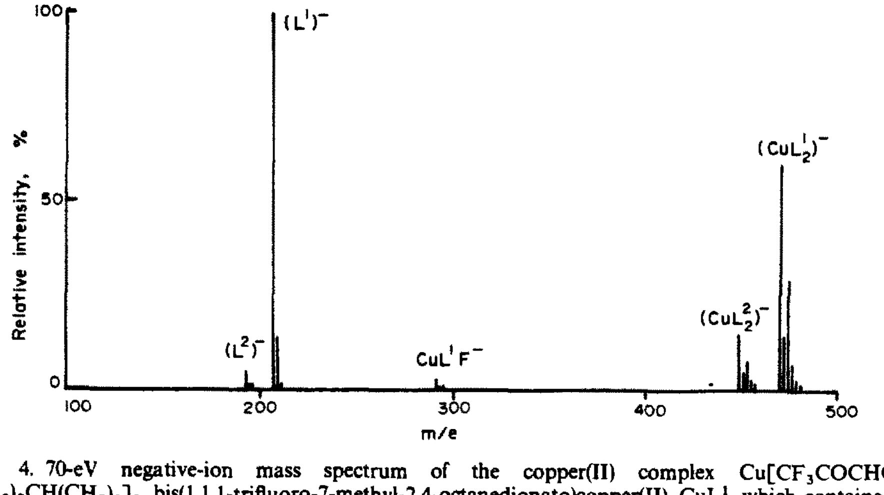

Fig. 4. 70-eV negative-ion mass spectrum of the copper(II) complex Cu[CF$_3$COCHCO(CH$_2$)$_2$CH(CH$_3$)$_2$]$_2$, bis(1,1,1-trifluoro-7-methyl-2,4-octanedionato)copper(II), CuL$^1_2$, which contained as an impurity the complex Cu[CF$_3$COCHCOCH$_2$CH(CH$_3$)$_2$]$_2$, bis(1,1,1-trifluoro-5-methyl-2,4-hexanedionato)copper(II), CuL$^2_2$.

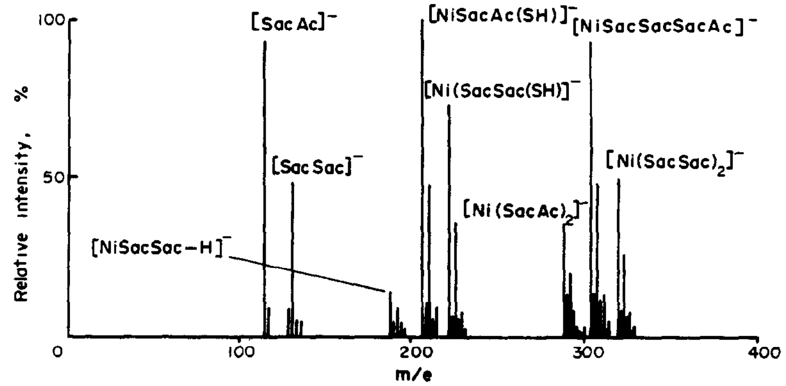

Fig. 5. 70-eV negative-ion mass spectrum of a sample of Ni(SacSac) (SacAc), 4-thiolopent-3-ene-2-thione-4-thiolopent-3-en-2-one nickel(II), which also contained $Ni(SacSac)_2$ and $Ni(SacAc)_2$, where SacSac = $(CH_3CSCHCSCH_3)^-$ and SacAc = $(CH_3CSCHCOCH_3)^-$.

Table 1. Temperature, pressure, and relative ion abundance for bis(hexafluoroacetylacetonato)copper(II)

Pressure, 10^{-6} *mmHg*	2.2	2.2	2.3
Temperature, °C	100	150	200
$Cu(CF_3COCHCOCF_3)_2^-$, %	100	45	17
$(CF_3COCHCOCF_3)^-$, %	56	100	100

containing virtually all combinations of the dithio- and monothio-β-diketone ligands, a conclusion substantiated by the presence in high abundance of the $(CH_3CSCHCSCH_3)^-$ and $(CH_3CSCHCOCH_3)^-$ species.

A final example concerns the thermal stabilities of metal complexes, which can be established from the simple negative ion spectra. In Table 1 are listed relative abundances for the predominant negative ions given by bis(hexafluoroacetylacetonato)copper(II) at similar source pressures but at different temperatures. Even though the process $Cu(CF_3COCHCOCF_3)_2^- \xrightarrow{*} (CF_3COCHCOCF_3)^-$ occurs in the field-free region, it is apparent that thermolysis contributes to the increased abundance of ligand ions observed as the ion-source temperature is increased. The complexity of positive-ion spectra makes the presence of any thermolysis process difficult to detect. However, because of the greater simplicity of negative-ion mass spectra, thermal processes leading to the rupture of metal–ligand bonds are readily detected by means of the resultant increase in intensity of the ligand-ion peaks at higher temperatures. In this respect the facility to use the mass spectrometer in both the positive- and negative-ion modes within minutes under the same ion-source conditions is of great value. SECNI mass spectra have been obtained for other types of metal-organic compounds[18,19] and the results are similar to those described here.

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POLAROGRAPHIC REDUCTION OF SOME POTENTIAL ANTIDIABETIC COMPOUNDS WITH MORE THAN ONE REDUCTION SITE

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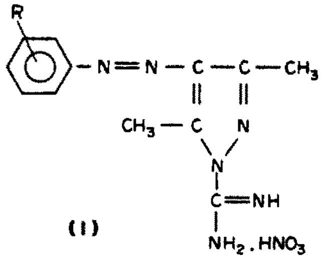
Summary—The polarographic reduction of a number of *N*′-guanylarylazopyrazole nitrates has been studied over a range of concentration and pH values. The effect of substituent groups on the value of the half wave potential has been determined.

In recent years, interest in the electrochemical behaviour of biologically important compounds[1–3] has increased. However, as few organic redox systems behave reversibly, valid potentiometric data have been obtained for only a few compounds. As most organic compounds behave in an irreversible manner, studies of their redox behaviour have been based on polarography.

The present paper summarizes the results of polarographic examination of 4-arylazo-*N*′-guanyl-3,5-dimethylpyrazole nitrates (I), well known for their antidiabetic activity.[4]



(I)

In these compounds the possible reduction sites are the C=C and C=N groups of the pyrazole ring and the –N=N– and –C=N– extra-nuclear groups. As extranuclear sites are more susceptible to reduction,[5] it can be assumed that the reduction takes place at the extranuclear –N=N– and –C=N– sites. This view is supported by the fact that simple pyrazoles are not electroactive, while guanine is electroreducible.

EXPERIMENTAL

Reagents and solutions

Substituted phenylazo-*N*′-guanyl-3,5-dimethylpyrazole nitrates having as substituents hydrogen, 2-nitro, 3-nitro, 4-nitro, 3-chloro, 4-chloro, 2-bromo, 4-bromo, 3-methyl and 4-methyl groups were synthesized.[6] In order to study the effect of substituents at positions 3 and 5, two more compounds, 4-phenylazo-*N*′-guanyl-3-methyl-5-phenylpyrazole nitrate and 4-phenylazo-*N*′-guanyl-3,5-diphenylpyrazole nitrate were synthesized. All the compounds were purified by recrystallization from ethanol and their purity was checked by nitrogen estimation. Britton–Robinson buffers[7] in the pH range 2.0–11.0 were prepared. Solutions ($1 \times 10^{-3}M$) of all the pyrazoles were prepared in pure methanol.

Apparatus

A Cambridge pen-recording polarograph was used. The capillary characteristics were 3.75 $mg^{2/3}\,s^{-1/2}$ at $h = 50$ cm. Triply distilled mercury was used and the temperature of the solution was maintained at 30 ± 0.1°.

Procedure

Working solutions were prepared by taking the appropriate buffer (8 ml) and a fixed amount of pyrazole solution (1 ml). The ionic strength was kept constant by adding 1.0 ml of 1*M* potassium chloride. An inert atmosphere was maintained by passing purified nitrogen for about 15 min. Corrections for residual current were made in all cases. The value of *n*, the number of electrons involved in the reduction, was determined by controlled potential electrolysis as recommended by DeVries and Kroon,[8] with a platinum wire as the anode and the mercury pool as the cathode. Values of *n* are given in Table 1.

RESULTS AND DISCUSSION

All the arylazopyrazoles are reduced in two 2-electron reduction waves. The nitro-substituted pyrazoles exhibit a further reduction wave at a less negative potential. Some typical polarograms are shown in Fig. 1.

Reduction of the azo group

As the –N=N– group is more susceptible to reduction than the –C=N– group, the former is reduced at a less negative potential than the latter. The first

Table 1. Millicoulometric measurements at pH 2.3 for *N*′-guanyl-3,5-dimethyl-4-phenylazopyrazole nitrate (V_1 and $V_2 = 0.3$ ml; C_1 and $C_2 = 1 \times 10^{-4}M$)

	i_d μA		Drop time, *sec*		
Substance	Initial	Final	Initial	Final	*n*
Time 120 min, potential −1.10 V *vs.* mercury pool					
$CdSO_4$	2.50	1.75	3.58	3.60	2.00
(R=H)	2.13	1.40	3.33	3.41	
Time 120 min, potential −1.50 V *vs.* mercury pool					
$CdSO_4$	2.50	1.75	3.58	3.60	2.00
(R=H)	1.87	1.31	3.29	3.55	

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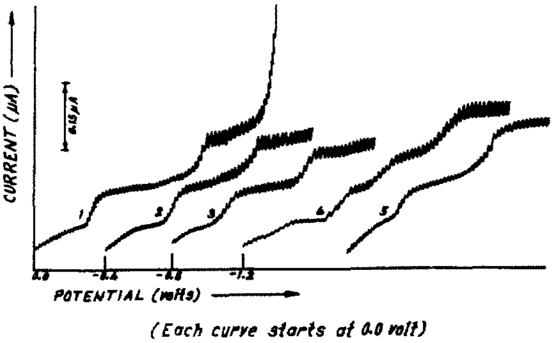


Fig. 1. Typical polarograms of pyrazoles (1) R = 4-Cl, $c = 1.0 \times 10^{-4}M$, pH = 3.8 (2) R = 4-CH_3, $c = 1.0 \times 10^{-4}M$, pH = 3.8. (3) R = 3-Cl, $c = 1.0 \times 10^{-4}M$, pH = 3.8. (4) R = 4-NO_2, $c = 1.5 \times 10^{-4}M$, pH = 8.9. (5) R = 2-Br, $c = 1.0 \times 10^{-4}M$, pH = 3.8.

wave is therefore assigned to the reduction of the –N=N– group. The limiting current was diffusion-controlled, as can be deduced from plots of i against $h^{\frac{1}{2}}$. The wave-heights are independent of pH (2.0–11.0) and the temperature coefficient is in the range 1.5–1.6% per deg. The concentration of the depolarizer influences the electrode process and shifts the $E_{\frac{1}{2}}$ towards a more negative potential. The $E_{\frac{1}{2}}$ of the wave is dependent on pH and shifts towards a more negative value with increase in pH. The plots of $E_{\frac{1}{2}}$ against pH give straight lines with a slope of 0.06.

To obtain an indication of the reversibility, various concentrations of these pyrazoles were polarographed and it was found that the half-wave potential shifts to a more negative potential, revealing the irreversible nature of the waves (Table 2).

Azo compounds are reduced in a two-electron step to hydrazo derivatives,[9–11] the overall process being

$$\text{R–N=N–R}' \xrightarrow{2e+2H^+} \text{R–NH–NH–R}'$$

As the nature of R and R′ will alter the electron density at the –N=N– group, electron-donating groups will facilitate the reduction and electron-withdrawing groups will make reduction more difficult.[12] This behaviour is observed with the present compounds (Table 3).

Reduction of the azomethine group

It may be seen from Fig. 1 that the second wave is well-defined and well-separated from the first wave. This wave may be assigned to the reduction of the extranuclear azomethine (–C=N–) group. It is interesting to note that the half-wave potential of all these waves becomes more negative with increase in pH. However, unlike the case of the azo group, the half-wave potential for the reduction of –C=N– fails to give a linear relationship with pH. A similar nonlinearity has been reported by other workers.[13] The shift of $E_{\frac{1}{2}}$ with increasing pH indicates the involvement of the hydrogen ion in the electrode reaction. Zuman[14] and other workers[15] have reported that plots of $E_{\frac{1}{2}}$ against pH can be represented by extrapolation as sets of linear segments of different slopes (*cf.* Fig. 2). The intersections of the linear segments give the values of pK for the oxidized or reduced species. The pK values calculated from these plots are given in Table 3 and all lie in the same range.

The behaviour of the wave at various concentrations gives an idea of the reversibility or irreversibility of the electrode process. For a reversible process $E_{\frac{1}{2}}$ is independent of concentration, whereas in the case of an irreversible process $E_{\frac{1}{2}}$ shifts to a more negative value.[16] The concentration was varied from

Table 2. Effect of concentration on $(E_{\frac{1}{2}})_1$, $(E_{\frac{1}{2}})_2$ and $(E_{\frac{1}{2}})_3$ for guanylarylazopyrazole nitrates

			$-E_{\frac{1}{2}}$ at various concentrations					
No.	R		$1 \times 10^{-4}M$	$1.5 \times 10^{-4}M$	$2.0 \times 10^{-4}M$	$2.5 \times 10^{-4}M$	$3.0 \times 10^{-4}M$	pH
1.	H	$(E_{\frac{1}{2}})_1$	0.58	0.61	0.63	0.66	0.70	7.60
		$(E_{\frac{1}{2}})_2$	1.02	1.04	1.04	1.06	1.08	
2.	2-NO_2	$(E_{\frac{1}{2}})_1$	0.60	0.64	0.66	0.69	0.74	7.60
		$(E_{\frac{1}{2}})_2$	1.15	1.18	1.22	1.24	1.26	
		$(E_{\frac{1}{2}})_3$	0.40	0.44	0.46	0.50	0.52	
3.	3-NO_2	$(E_{\frac{1}{2}})_1$	0.70	0.72	0.74	0.75	0.77	7.60
		$(E_{\frac{1}{2}})_2$	1.06	1.07	1.09	1.11	1.14	
		$(E_{\frac{1}{2}})_3$	0.46	0.49	0.51	0.53	0.56	
4.	4-NO_2	$(E_{\frac{1}{2}})_1$	0.74	0.78	0.84	0.88	0.92	8.90
		$(E_{\frac{1}{2}})_2$	1.12	1.18	1.22	1.38	1.42	
		$(E_{\frac{1}{2}})_3$	0.52	0.55	0.57	0.60	0.62	
5.	3-Cl	$(E_{\frac{1}{2}})_1$	0.58	0.62	0.64	0.66	0.70	8.90
		$(E_{\frac{1}{2}})_2$	1.00	1.02	1.02	1.04	1.05	
6.	4-Cl	$(E_{\frac{1}{2}})_1$	0.58	0.63	0.66	0.68	0.70	7.60
		$(E_{\frac{1}{2}})_2$	1.12	1.15	1.18	1.20	1.24	
7.	2-Br	$(E_{\frac{1}{2}})_1$	0.50	0.53	0.54	0.58	0.60	7.60
		$(E_{\frac{1}{2}})_2$	1.000	1.02	1.06	1.10	1.14	
8.	4-Br	$(E_{\frac{1}{2}})_1$	0.52	0.56	0.57	0.60	0.62	7.60
		$(E_{\frac{1}{2}})_2$	1.10	1.14	1.18	1.18	1.20	
9.	3-CH_3	$(E_{\frac{1}{2}})_1$	0.54	0.56	0.59	0.61	0.63	7.60
		$(E_{\frac{1}{2}})_2$	1.04	1.08	1.10	1.16	1.20	
10.	4-CH_3	$(E_{\frac{1}{2}})_1$	0.70	0.72	0.74	0.75	0.80	7.60
		$(E_{\frac{1}{2}})_2$	1.32	1.34	1.34	1.38	1.40	

Table 3. Comparison of half-wave potentials and wave-heights of substituted guanylpyrazole nitrates [$1 \times 10^{-4}M$, pH 3.8, a and b from the relation $-E_{\frac{1}{2}} = a(\text{pH}) + b$]

No.	R	$-E_{\frac{1}{2}}$, V $(-E_{\frac{1}{2}})_1$	$(-E_{\frac{1}{2}})_2$	$(-E_{\frac{1}{2}})_3$	i_d, μA $(i_d)_1$	$(i_d)_2$	$(i_d)_3$	pK	a*	b
1.	H	0.36	0.82	—	0.075	0.082	—	5.5	0.060	0.150
2.	2-NO_2	0.42	0.84	0.20	0.067	0.082	0.127	5.5	0.056	0.230
3.	3-NO_2	0.50	0.82	0.34	0.089	0.082	0.135	5.6	0.056	0.300
4.	4-NO_2	0.44	0.78	0.36	0.082	0.075†		6.2	0.056	0.240
5.	3-Cl	0.31	0.80	—	0.075	0.067	—	5.6	0.054	0.110
6.	4-Cl	0.32	0.84	—	0.067	0.082	—	5.6	0.058	0.120
7.	2-Br	0.30	0.82	—	0.067	0.089	—	5.2	0.058	0.100
8.	4-Br	0.32	0.88	—	0.075	0.075	—	5.4	0.060	0.100
9.	3-CH_3	0.34	0.88	—	0.075	0.082	—	5.5	0.060	0.120
10.	4-CH_3	0.40	0.86	—	0.067	0.075	—	6.3	0.064	0.160

* For the reduction of the azo group.
† Slight maxima observed.

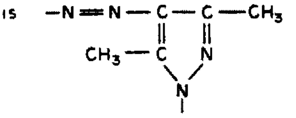
0.5×10^{-4} to $4 \times 10^{-4}M$ and it was found that $E_{\frac{1}{2}}$ varied with concentration (Table 2), revealing the irreversible nature of the electrode process. The diffusion currents increase linearly with concentration and the temperature coefficients are below 1.6% per deg in all cases. The diffusion currents (i_d) for all the waves are constant at different values of pH. The plots of i_d against $h^{\frac{1}{2}}$ are linear, indicating the diffusion-controlled nature of the waves.

The value of n, the number of electrons involved in the reduction of the azomethine group, was determined by the millicoulometric method and found to be 2, suggesting the following mechanism:

$$RR'C{=}NH \xrightarrow{2H^+ + 2e} RR'CH{-}NH_2$$

where

R is



R′ is $-NH_2.HNO_3$

Similar reduction steps have also been proposed by Kastening,[17] Zuman[18] and others.[19]

Reduction of the nitro group

In the case of nitro-substituted arylazopyrazoles, such as N'-guanyl-3,5-dimethyl-4-(2-nitrophenylazo)-pyrazole nitrate, and the 3-nitro and 4-nitro analogues, an additional wave appeared at a less negative potential. Since the nitro group in both aliphatic and aromatic compounds is easily reducible at a dropping mercury electrode, this behaviour is understandable.[20] The reduction takes place by a 4-electron process in the pH range 2.0–11.0. The waves are diffusion-controlled, as shown by the plots of i against $h^{\frac{1}{2}}$ and of i against concentration of depolarizer, which were linear. The half-wave potential shifts to a more negative potential with increase in pH, but the limiting current is almost independent of pH. The plots of $E_{\frac{1}{2}}$ against pH are linear. These waves were found to be irreversible as the plot of $E_{d.e.}$ against $\log i/(i_d - i)$ showed a higher slope and $E_{\frac{1}{2}}$ shifted to a more negative potential with increase in concentration (Table 2).

In the case of m-nitro-substituted arylazopyrazoles and p-nitro-substituted pyrazoles, the reduction waves of the nitro group merge with those of the –N=N– group in the pH range 2.0–6.2. At higher pH, the two waves separate, giving two well-defined waves (Fig. 3).

A mechanism for the reduction of the nitro group, similar to that suggested by Fields[21] and other workers,[22] can be proposed for these compounds.

Effect of substituents on the half-wave potential

Table 3 gives the values of $E_{\frac{1}{2}}$ for substituted arylazopyrazoles. These values become more positive for electron-donating substituent groups, except in the case of 4-methylphenylazopyrazole, where the value shifts to a more negative potential. This behaviour may be due to the *ortho* effect,[5] while the shift to

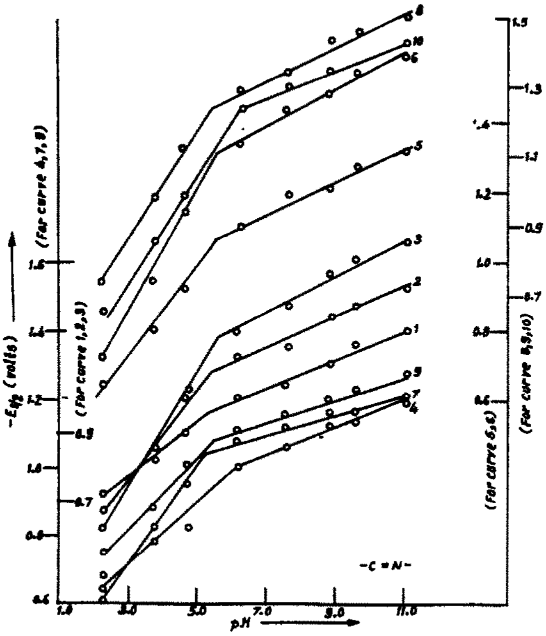
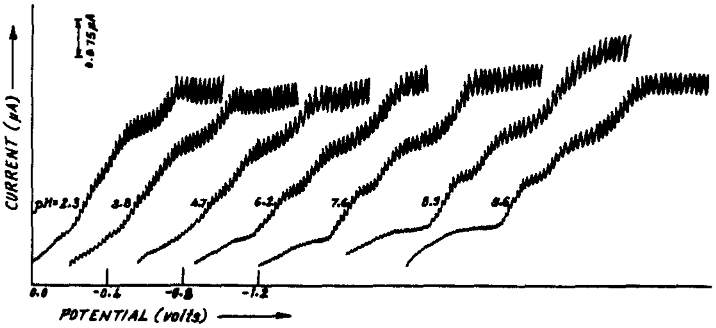


Fig. 2. Variation of $E_{\frac{1}{2}}$ with pH for the reduction of the azomethine group.



(Each curve starts at 0.0 volt)

Fig. 3. Separation of the waves for the reduction of the $-NO_2$ group and the azo group with increase of pH.

Table 4. Comparison of $E_{\frac{1}{2}}$ values for substituents at positions 3 and 5 at pH 3.8

No.	R_1	R_2	$(-E_{\frac{1}{2}})_1, V$	$(-E_{\frac{1}{2}})_2, V$	$(\Delta E_{\frac{1}{2}})_1, V$	$(\Delta E_{\frac{1}{2}})_2, V$
1.	CH_3	CH_3	0.360	0.820	—	—
2.	CH_3	C_6H_5	0.365	0.800	0.005	0.020
3.	C_6H_5	C_6H_5	0.370	0.760	0.010	0.040

$(-E_{\frac{1}{2}})_1$ and $(-E_{\frac{1}{2}})_2$ are for the reduction of the azo group and azomethine group respectively.

a more positive potential is explained by assuming an increase of electron density at the site of reduction (–N=N–). The 3-Cl, 4-Cl, 2-Br, 4-Br and $3\text{-}CH_3$ substituents shift the half-wave potential to a more positive value (with respect to the parent compound). Electron-withdrawing substituents, $2\text{-}NO_2$, $3\text{-}NO_2$ and $4\text{-}NO_2$, give half-wave potentials more negative than that of the unsubstituted pyrazole by decreasing the electron density at the reduction site. Bromo and nitro substituents show positive polarographic *ortho* shifts (Δ_o), indicating that *o*-substituted arylazopyrazoles undergo reduction more easily than the corresponding *p*-substituted analogues.

$$(E_{\frac{1}{2}})_{o\text{-Nitro}} = (E_{\frac{1}{2}})_{p\text{-Nitro}} = -0.02\ \text{V at pH 3.8}$$

$$(E_{\frac{1}{2}})_{o\text{-Bromo}} - (E_{\frac{1}{2}})_{p\text{-Bromo}} = -0.02\ \text{V at pH 3.8}$$

In the case of azomethine group reduction, the substituents are remote from the reaction site and hence no systematic change in $E_{\frac{1}{2}}$ was observed. A change in the $E_{\frac{1}{2}}$ value with various substituents may be attributed to the conjugated double bond in (I). It was also found that substituents at positions 3 and 5 appreciably affect the $E_{\frac{1}{2}}$ value for this reduction site (–C=N–). Thus the introduction of an electron-withdrawing C_6H_5 group at position 3 shifts the $E_{\frac{1}{2}}$ value to a more positive potential (Table 4) and this shift is greater if a second C_6H_5 group is introduced at position 5. Similar behaviour has been reported for the case of substituted benzalanilines.[23]

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A COULOMETRIC METHOD FOR THE ASSAY OF SOME EASILY OXIDIZED ORGANIC SUBSTANCES WITH IODINE AS AN OXIDIZING AGENT

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Summary—A coulometric method for the assay of easily oxidized organic substances, using iodine as an oxidizing agent, has been developed. The principle of the method is to oxidize the substance with an excess of iodine in a water–acetic acid medium and then titrate the iodide formed, with anodically generated silver ion. The titration is followed by dead-stop indication using two platinum electrodes. The method has been applied to the assay of dihydric phenols with hydroxyl groups in the *ortho* or *para* positions and to the determination of ascorbic acid in various pharmaceutical preparations. The absolute relative error varied between 0.2 and 2.8% for the 8 phenols investigated and the relative standard deviation between 0.2 and 1%. For standard solutions of ascorbic acid the absolute relative error was 0.9% and for the 6 pharmaceutical preparations investigated the relative standard deviation lay in the range 0.3–0.9%. The method is easy to apply and has a number of advantages over current iodimetric methods.

Iodine and other halogens are frequently used as oxidizing agents. Iodine is often preferred because it gives rise to fewer side-reactions than do bromine and chlorine. The reaction between iodine and a dihydric phenol with hydroxyl groups in the 1,2- or 1,4-positions furnishes the corresponding quinones and iodide ion, *e.g.*, for hydroquinone

$$\text{Hydroquinone} + I_2 \rightleftharpoons p\text{-Benzoquinone} + 2I^- + 2H^+ \quad (1)$$

Kolthoff[1] titrated hydroquinone with iodine, both directly with potentiometric indication of the end-point and indirectly with back-titration of the excess of iodine with thiosulphate or arsenic trioxide and end-point indication with starch. Kolthoff also studied the influence of the pH on the result. He calculated that for a quantitative reaction the pH must be 6 or higher as the equilibrium in equation (1) lies too far to the left at lower pH. Another fact which may complicate a determination is that some dihydric phenols are easily oxidized by air at higher pH. Thus Preiss[2] got erroneous results when titrating hydroquinone with iodine in sodium hydrogen carbonate solution at pH 8–9 and Ashworth *et al.*[3] had the same experience with hydroquinone in $1M$ sodium acetate solution. There is also a tendency for iodine solutions to produce iodide at higher pH, in a slow reaction which is difficult to control.[4]

Some attempts to apply coulometric methods to the oxidation of dihydric phenols, using anodically generated iodine, have been made. Bajalovic and Nikolic[5] titrated hydroquinone amperometrically in phosphate buffer at pH 8, and Čůta and Kučera[6] titrated hydroquinone at pH 7–8 and pyrocatechol at pH > 7. The amount of hydroquinone titrated was in the range 110–1100 μg and the results were given as 99.00 ± 0.36%. For pyrocatechol no quantitative result was obtained at pH above 7.

As mentioned above, there is a lower pH-limit for the quantitative oxidation of a 1,2- or 1,4-dihydric phenol by iodine. On the other hand too high a pH can cause low results because of interference from aerial oxidation of the phenol. Hence it is desirable to perform the oxidation at the lowest possible pH which is compatible with quantitative oxidation. When performing the titration in the conventional way, *i.e.*, either directly by adding iodine up to the end-point or indirectly with back-titration of the excess of iodine, the assay is based on a determination of the iodine consumed. However, equation (1) suggests that there should be another way of evaluating the result of the oxidation, namely by determining the iodide formed.

This procedure should have a number of advantages over the methods currently in use. Thus the equilibrium in equation (1) will be displaced to the right by the consumption of iodide ion and the displacement can be further enhanced by using a large excess of iodine. Because of this the titration can be performed at a lower pH than when the assay is based on the iodine consumption, with decreased risk of aerial oxidation. Losses of iodine during the titration are also unimportant in this case. In our method the iodide formed is determined by constant-current coulometry using anodically generated silver ion. Accordingly, the method has the general advantage of coulometric methods, *i.e.*, no titrants are necessary. The titration can also be performed with rather simple and inexpensive equipment found in most laboratories. As will be discussed in more detail later in this paper, the appearance of the titration curve gives an indication of the reliability of the assay. Hence there are a number of advantages associated with this method which should make it an attractive competitor to existing iodimetric methods.

Methods used for the assay of ascorbic acid (vitamin C) have been discussed by Hashmi[7] and Hajratwala.[8] They can be divided into two main groups, *viz.* spectrophotometric methods and redox methods. The former, although generally specific, are often time-consuming. The latter are based on the reducing properties of ascorbic acid and are subject to interference from other reducing substances present. One of the most frequently used methods was originally proposed by Tillmans *et al.*[9] and is based on the use of 2,6-dichlorophenolindophenol as an oxidation agent. Its reaction with ascorbic acid is accompanied by a colour change which can be followed visually, photometrically or electrometrically. Although it has been adopted as an official method for the assay of ascorbic acid in pharmaceutical products[10] it is often not usable because of interfering reducing substances present. It is also time-consuming and demands considerable experimental skill for good results to be obtained.[11]

Iodine oxidation of ascorbic acid has also been recommended and exploited a good deal for its determination.[12] It is used as an official method for pharmaceutical preparations.[10] The usual way is to add iodine solution in excess and back-titrate the excess with thiosulphate, using starch as an indicator. This procedure is reported to be time-consuming, owing to slow equilibration near the equivalence point.[13] However, improved indication methods have been developed, utilizing polarized platinum electrodes[14] or platinum–tungsten electrodes[15] to follow the progress of the titration.

An elegant method for the assay of ascorbic acid, based on controlled potential coulometry, has recently been described by Karlsson.[16] Iodine in slight excess is generated at a platinum anode and allowed to react with the ascorbic acid. After the reaction is finished the excess of iodine is reduced, and the result obtained on an electronic integrator can be related to the amount of ascorbic acid. The greatest disadvantage of this method seems to be the need for expensive, specialized apparatus, not available in most laboratories. The advantages of the method developed in this work were previously outlined in connection with the discussion of the iodine oxidation of dihydric phenols. The conclusions then drawn are applicable also to the constant-current coulometric assay of ascorbic acid, using iodine as oxidizing agent.

EXPERIMENTAL

Apparatus

The oxidation was performed in a Metrohm titration vessel EA 875-20 as described below and the amount of iodide ion formed titrated with silver ion, generated from a 0.1-mm thick 20 × 10 mm rectangular silver plate (see Fig. 1). A constant current of 1 mA was taken from a Knick "Präzision Stromgeber". The counter-electrode was a platinum plate placed in 2*M* sulphuric acid. This electrode was made by modifying a Metrohm EA 247 electrode according to Fig. 1. The fritted glass disc was of porosity D3, and 10 mm in diameter. Replacement of the original fritted glass disc was necessary to increase the electrical conductance. The titration was followed by means of an indicating double platinum point electrode (Metrohm EA 235) through which a constant current of 1 μA passed, taken from a Knick constant-current generator. The electrode polarization was measured by registering the potential drop between the electrodes. This method of indication was preferred to the one used in previous work where a constant polarization voltage was applied to the double platinum point electrode and the current registered,[17] which gave rise to currents of 7 μA in the depolarized state, which might adversely affect the titration results in the present case.

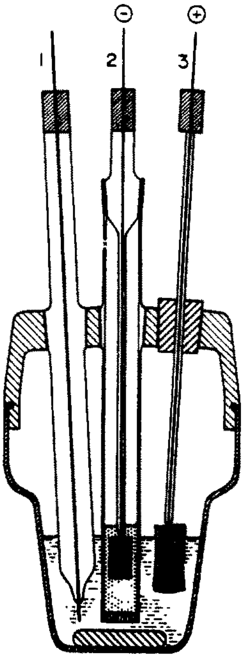

Fig. 1. Cell for coulometric titration. 1—indicating electrode, 2—cathode containing 2*M* sulphuric acid, 3—silver-ion generating electrode (anode).

Reagents

Phenols. The dihydroxybenzenes were of the best grade commercially available and were used without further purification.

Vitamin preparations. The vitamin preparations analysed were obtained from Ferrosan AB, Sweden. For their content of various vitamins see Table 2.

Ascorbic acid. Merck PA.
Acetic acid. Merck 99–100%.
Sodium acetate. Merck PA.
Iodine. Mallinckrodt AR, resublimed.

Oxidation and titration procedure

A standard solution of iodine was prepared by dissolving iodine in glacial acetic acid to give a concentration of 40m*M*. This solution was stable for several months if protected from water. A reaction solution was prepared by adding 2 ml of this solution to the titration vessel, followed by 10 ml of glacial acetic acid and 8 ml of water in that order to prevent precipitation of iodine. In one case the composition of the reaction solution had to be changed

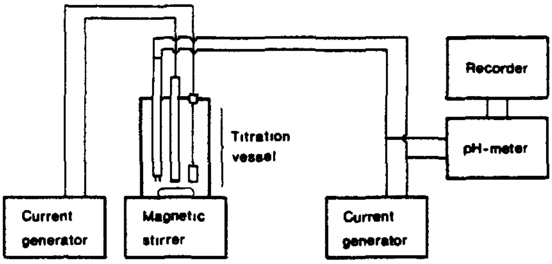

Fig. 2. Schematic diagram showing the connections in the coulometric apparatus.

(see Table 1). The compound to be oxidized was then added to the reaction solution.

The phenols were weighed, and dissolved in glacial acetic acid in a 50-ml volumetric flask to give a concentration of 0.001–0.01*M*. From this solution a volume containing about 4 μmoles of phenol was dispensed into the titration vessel by means of an Agla micrometer syringe.

In the case of ascorbic acid, standard solutions as well as various vitamin preparations were analysed. The standard solutions (0.005–0.01*M*) were prepared by dissolving ascorbic acid in deaerated 8% v/v acetic acid in water. The liquid vitamin preparation ABCDin was dispensed as such into the reaction solution by means of the Agla syringe. The remainder of the vitamin preparations, which were tablets, were treated in the following way. Five vitamin tablets were crushed in an agate mortar and an amount of the powder calculated to give 100 ml of an approximately 0.01*M* solution of ascorbic acid when dissolved, was weighed out. The powder was leached with deaerated 8% v/v acetic acid–water and the solution filtered into a 100-ml volumetric flask and made up to the mark with more of the leaching solution. The vitamin preparation Multiplex Comp N contains Fe^{2+} which was removed by pouring the filtered solution through a tube containing a 2-cm thick layer of Amberlite CG 120, 400–600 mesh, cation-exchanger in acid form. All volumetric flasks containing ascorbic acid were wrapped in aluminium foil in order to prevent decomposition by light during storage. An exact volume, containing about 4 μmoles of ascorbic acid, was transferred from the volumetric flask to the reaction solution in the usual way by an Agla syringe.

The electrodes were inserted and connected to their electric circuits (see Fig. 2). The magnetic stirrer was set at a relatively high speed and the pH-meter set to READ. The silver-ion generator current was adjusted to 1.000 mA, the indicator generator current to 1 μA, the recorder speed to 30 mm/min and the measuring range set to MILLIVOLT. The silver-ion generation and the indication circuit were started simultaneously as the recorder pen crossed a vertical line on the chart after a stable base-line had been achieved. The generation of silver ion was continued until the second polarization of the indicator electrode. The appearance of the titration curve as well as the method for determining the end-point are shown in Fig. 3. A blank containing only the reaction solution was titrated in the same way and the iodide ion formed is equivalent to the distance A–B in Fig. 3. Generally the blank consumption was very small or negligible. Increased blank consumption can result from deterioration of the indicator electrode or be caused by the reaction solution being kept for a long time before addition of the determinand. The indicator electrode should be washed with demineralized water after each titration and if there is any sign of contamination it should also be wiped with wet filter paper. Contamination generally affects the blank titration curve, which assumes a different appearance from the normal one shown in Fig. 3. The amount of oxidized substance (in μmoles) is calculated from

$$m/M = 1000tI/Fn \qquad (2)$$

where m = the amount titrated in μg; t = the time in sec (= twice the distance A–B in mm); I = generating current, in mA; M = molecular weight of oxidized substance; F = Faraday constant = 96487 C/eq; n = number of electrons transferred per mole of oxidized substance.

RESULTS AND DISCUSSION

Appearance of titration curve

A typical titration curve is shown in Fig. 3. It consists of two regions corresponding to depolarization, connected by a section corresponding to polarization. At the beginning of the titration the indicator electrode is depolarized, probably by the I_2/I_3^- couple. As the iodide ion is consumed by the silver ion a polarization takes place and the electrode is polarized to a level dependent on the concentration of acetate ion, since addition of sodium acetate decreases it. This can be explained by the formation of silver acetate complexes, AgOAc and $Ag(OAc)_2^-$, which reduces the concentration of silver ion, controlling the level to which the electrode is polarized. When the production of silver ion is continued the indicator electrode becomes depolarized again. For this depolarization to take place the presence of Ag^+ as well as I_2 seems to be necessary. There is at present no obvious explanation of this behaviour. It might be that the couple I_2/AgI_2^+ is responsible for the depolarization. Arotsky *et al.*[18] have assumed the AgI_2^+ complex to be formed when silver sulphate is added to a solution of iodine in sulphuric acid. In the present investigation it was found that when ultraviolet spectra were run for successive portions taken during a blank titration, a new absorption band appeared as a shoulder at 430 nm. As Arotsky *et al.* have reported that the AgI_2^+ complex absorbs at 520 nm with a weak shoulder at 420 nm, there seems to be some justification for the assumption made above. The main absorption band for AgI_2^+ at 520 nm cannot be observed in the present case as iodine has a strong absorption band in the same region.

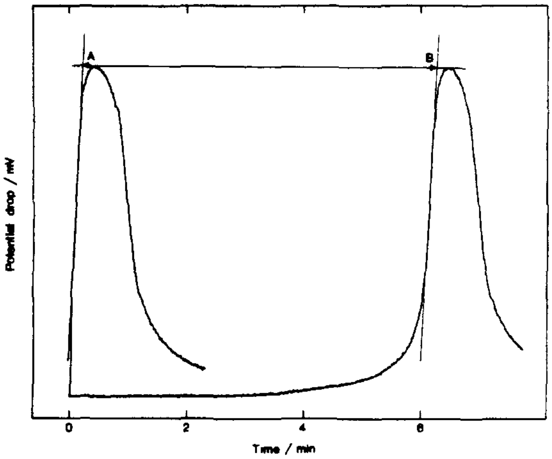

Fig. 3. Titration curve with construction for evaluating the end-point.

The width and height of the polarization part of the curve give some indication of the reliability of the titration. Ideally the width and height should be the same as in the blank titration. Increased width is a sign of disturbing reactions and, if the widening is considerable, the result should be discarded. The Fe^{2+} in Multiplex Comp N reacts with iodine, causing a broadening of the polarization part of the titration curve. This interference can be remedied by removing the iron on a cation-exchanger as described in the experimental part. Turbid solutions can also give rise to a broadening, *e.g.*, when assaying vitamin C in fruit juices. For the vitamin preparation ABCDin a slight broadening is observed, which contributes to the somewhat high results obtained for this preparation.

Reaction and titration medium

It has been shown that no oxidation takes place when ascorbic acid is added to iodine in glacial acetic acid,[19] and that iodide cannot be titrated with silver ion in this medium either. Experiments with aqueous acetic acid indicated that a water content of 40% v/v was suitable and this mixture has been used throughout as reaction and titration medium. The measured pH of this medium is 1.6 when compared with standard buffer solutions. This value is not directly comparable with Kolthoff's pH 6 which refers to aqueous solution, but, in the medium chosen, quantitative results were obtained for all but one of the phenols investigated. The exception was 1,2-dihydroxy-4-methylbenzene in which case the pH had to be raised to 2.9 by making the reaction medium 0.25*M* with respect to sodium acetate. The fact that the titration can be carried out at a relatively low pH diminishes the risk of losses of dihydric phenols by aerial oxidation. Substitution reactions due to iodination are also less likely to interfere at low pH.

Stability of solutions

Glacial acetic acid is a suitable solvent for dihydric phenols, their solutions being stable for several days. For ascorbic acid, aqueous acetic acid containing 8% v/v acetic acid has been recommended as an appropriate extraction medium.[16] Ascorbic acid is not stable in this medium, the decomposition amounting to about 10% after 10 hr. A solution of ascorbic acid in aqueous acetic acid of the prescribed composition should therefore not be kept for more than 1–2 hr before analysis. The presence of B-vitamins in several of the vitamin preparations could, however, contribute to decreased decomposition of ascorbic acid in their solutions.[7]

Interfering substances

The vitamin preparations investigated contain other compounds besides ascorbic acid, *e.g.*, sugars of various kinds, chloride, and iron in the form of Fe^{2+}. Of these, iron in Multiplex Comp N has already been discussed. It might be expected that chloride would interfere with the determination of iodide. However, the presence of chloride up to 5% of the amount of iodide did not influence the results. This can be explained by the difference in solubility between the silver halides. Various kinds of sugars used in tablet formulations were tested, but none of them was found to interfere significantly, nor have we encountered any sign of interference from other kinds of vitamins present in the preparations. It thus appears that the method proposed for the assay of ascorbic acid is comparatively free from interferences by other substances compounded in the vitamin preparations.

Results

The results of the assay of dihydric phenols and ascorbic acid have been collected in Tables 1–3. The mean relative error is ±1.0% for the 8 phenols listed in Table 1 and the relative standard deviation lies in the range 0.2–1%. These results must be considered satisfactory, taking into account that the phenols are not 100% pure but contain impurities of unknown composition.

As the purity of the ascorbic acid used for preparing the standard solution was better than 99.5%, the results given in Table 3 seem to indicate that the method gives somewhat low results. However, as certain losses due to aerial oxidation cannot be avoided,

Table 1. Determination of dihydroxybenzenes

Compound	Added, *µmole*	Found, *µmole*	Error, %	Relative standard deviation,* %
1,4-dihydroxybenzene (hydroquinone)	3.696	3.676	−0.5	0.54
1,4-dihydroxy-2-methylbenzene	3.682	3.622	−1.6	0.50
2-chloro-1,4-dihydroxybenzene	3.764	3.741	−0.6	0.29
1,4-dihydroxy-2,5-di-tert.butylbenzene†	3.728	3.622	−2.8	0.30
1,2-dihydroxybenzene (pyrocatechol)	3.622	3.697	+1.0	0.97
1,2-dihydroxy-3-methylbenzene	3.541	3.507	−1.0	0.43
1,2-dihydroxy-4-methylbenzene§	3.688	3.662	−0.2	0.71
4,4′-dihydroxybiphenyl	3.692	3.686	−0.2	0.22

* Based on 5 analyses.

† Technical grade.

§ 60% v/v acetic acid, 0.25*M* in sodium acetate.

Table 2. Determination of ascorbic acid in some commercially available vitamin preparations (5 analyses of each)

Vitamin preparation	Ascorbic acid found by official methods *mg/tablet*	Ascorbic acid found by present method *mg/tablet*	Difference, %	Relative standard deviation, %
IDO-C$^{(1)}$	508	516	+1.6	0.31
Bascoplex$^{(2)}$	296	297	+0.3	0.29
Minorplex N$^{(3)}$	43.0	41.6	−3.3	0.87
Multiplex N$^{(4)}$	64.2	63.2	−1.6	0.20
Multiplex Comp N$^{(5)}$	62.2	59.4	−4.5	0.62
ABCDin$^{(6)}$	583*	610	+4.6	0.50

(1) Vitamin C; (2) vitamins B (B_1, B_2, B_6), C, Ca-pantothenate and nicotinamide; (3) vitamins A, B (B_1, B_2, B_6), C, D, Ca-pantothenate and nicotinamide; (4) vitamins A, B (B_1, B_2, B_6), C, D, E, Ca-pantothenate and nicotinamide; (5) vitamins A, B (B_1, B_2, B_6), C, D, E, Ca-pantothenate, nicotinamide and iron(II)fumarate; (6) vitamins A, B (B_1, B_2), C, D, and nicotinamide.

* mg/100 ml.

the method should in fact be more exact than is indicated by these figures. In the case of the vitamin preparations two figures are given in Table 2 for the content of ascorbic acid. The first one is the result obtained by a pharmaceutical laboratory using official methods and the second the result given by the present iodimetric method. The agreement is surprisingly good considering the errors inherent in the two methods and the statistical error accompanying the tablet analyses. A more exact comparison could be made if the assays in the two cases were made on a solution prepared from the same five tablets. However, as this could not be realized, the comparison in Table 2 refers only to the same batch of tablets, which causes an additional uncertainty due to the variation in the content of ascorbic acid from tablet to tablet. The relatively large error for Multiplex Comp N might be expected to be caused by the ion-exchange treatment to remove Fe^{2+} from the solution. However, when solutions of ascorbic acid were subjected to the same treatment, no losses of ascorbic acid were observed.

CONCLUSIONS

The iodimetric method proposed in this paper for the assay of easily oxidized organic substances has been shown to function well for dihydric phenols with hydroxyl groups at the *ortho* or *para* positions and for ascorbic acid in various pharmaceutical preparations. The special advantages of the method are the elimination of titrant solutions, easy evaluation of the end-point, and the possibility of performing the oxidation at a relatively low pH, thereby decreasing the risk of aerial oxidation. It is concluded that it should be possible to apply the method to numerous other substances which can be quantitatively oxidized by iodine.

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Table 3. Determination of ascorbic acid in standard solution (6 analyses)

Added, *μmole*	Found, *μmole*	Error, %	Relative standard deviation, %
4.068	4.030	−0.9	0.15

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SHORT COMMUNICATIONS

QUANTITATIVE REFLECTOMETRY—III*. DETERMINATION OF PROTEIN IN AQUEOUS MEDIA

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The first two papers in this series demonstrated the principles of direct reflectance measurements,[1] established the precision that can reasonably be expected, and discussed the nature of interferences.[2] The work described in this paper is concerned with test-strips for the determination of protein in aqueous media and with comparisons between commercially available and laboratory-prepared strips. The commercial protein strips are similar to those available for nickel, consisting of a plastic backing (0.5 × 8.0 cm) to which is attached a 0.5-cm square of reagent-impregnated absorbent paper at one end. The reagent used is Tetrabromophenol Blue, which is yellow under slightly acid conditions and turns green–blue on immersion in protein-containing solutions. Colour charts provided with the commercial product cover the range from 5 to >1000 mg of albumin per 100 ml of solution and the strips are intended for the semi-quantitative determination of protein in urine samples.

EXPERIMENTAL

Reagents and apparatus

Standard protein solution. Bovine serum albumin (30% aqueous solution), Ortho Pharmaceuticals Ltd. Additional standards to cover the range 0.25–10 mg/ml were prepared by dilution with distilled water.

Urine control sample. "UR-Sure Urinalysis Control", Travenol Laboratories, protein level 1.30 ± 0.1 mg/ml.

Protein test-strips. "Albustix", Ames Company.

Tetrabromophenolphthalein, ethyl ester, sodium salt.

Aerosol contact adhesive. "Photomount", 3M Company.

Preparation of protein test-strips

Chromatographic paper (Whatman 3 mm) was cut into strips (10 × 2.5 cm) which were impregnated with reagent by immersing them for 1 min in a 0.1% methanolic solution of tetrabromophenolphthalein ethyl ester buffered to pH 2.8 with 0.05*M* citric acid/sodium citrate. Excess of reagent solution was removed by shaking, and the strips were dried in a horizontal position, with a hot-air blower (5 min). Smaller pieces (3 × 1.5 cm) were cut from the prepared strips and attached to one end of plastic backing material (3 × 10 cm) with an aerosol contact adhesive.

Visible reflectance spectra of the protein test-strips

All reflectance measurements were made on the Unicam SP 8000 spectrophotometer fitted with an SP 890 diffuse-reflectance attachment, with freshly prepared magnesium oxide as reference standard (made by burning magnesium ribbon beneath a brass disc, on which the magnesium oxide vapour condenses to give a uniform layer). Strips prepared in the laboratory or the commercially available "Albustix" were immersed for 3 sec in a series of freshly-diluted and unstirred solutions of bovine serum albumin (0.25–10 mg/ml). Each strip was shaken to remove excess of protein solution and dried horizontally for 4 min with a hot-air blower. As the size of the "Albustix" test area is only 0.5 × 0.5 cm, six strips were immersed in each test solution to provide an adequate area for subsequent measurement. These were mounted on a card as described previously.[1] Reflectance spectra are shown in Fig. 1.

Optimization of conditions for quantitative measurements

All measurements were made on laboratory-prepared test-strips.

Immersion time. Strips were immersed in a 5-mg/ml solution of protein for 2 sec and 10 sec respectively. After shaking to remove excess of protein solution, they were dried in a horizontal position with a hot-air blower for 4 min. Reflectance measurements are given in Table 1.

Drying conditions. Strips were immersed in a 5-mg/ml protein solution for 2 sec, shaken, and dried in either a vertical or a horizontal position for 2–6 min. The position of the hot-air blower was varied so as to alter both the temperature at the surface of the strip and the degree of disturbance of the surface moisture by the air stream. Reflectance measurements are given in Table 1.

Buffer efficiency. Separate portions of a 5-mg/ml protein solution were adjusted to pH 4 and 9 and test-strips immersed in each solution for 2 sec. After shaking and drying in a horizontal position for 4 min, the reflectance of each was measured (Table 1).

Precision of quantitative measurements

Groups of five test-strips were immersed for 2 sec in standard protein solutions covering the range 0–10.0 mg/ml. Each was dried for 4 min in a horizontal position with a hot-air blower. Reflectance measurements and relative precisions are given in Table 2.

Determination of protein in urine

Protein-free urine was spiked with bovine serum albumin to give protein concentrations of up to 10.0 mg/ml. Groups of five test-strips were immersed in each sample solution and dried for 4 min as before. Reflectance measurements were recorded and the precision at several concentration levels calculated (Table 2). Standards were also prepared in the range 0.80–2.00 mg/ml protein and the level of protein in two urine control samples measured from a calibration curve.

RESULTS AND DISCUSSION

Adsorption indicators such as Bromophenol Blue (tetrabromophenolsulphonephthalein) are used extensively for

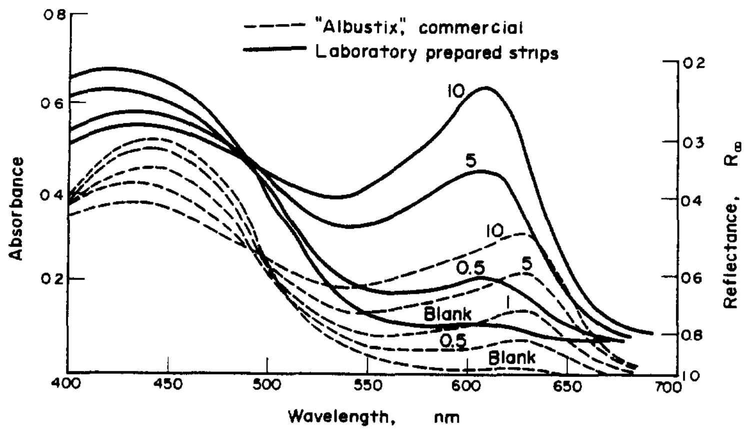

Fig. 1. Reflectance spectra of protein test-strips (reference MgO, numbers by the curves refer to albumin concentration, mg/ml).

the detection of proteins separated by electrophoresis.[3] They are acid–base indicators, the colour transition range of which is modified by the formation of a salt-like adsorption product with the protein molecules. The colour reaction may be observed in solution or at the surface of reagent-impregnated absorbent paper after immersion in a protein-containing solution. Commercially available test-strips for protein in urine ("Albustix") employ Tetrabromophenol Blue as the chromogenic reagent. During preliminary work with laboratory-prepared test-strips impregnated with the same reagent, rapid bleeding of the indicator into the test solution was observed. As this did not occur with "Albustix" it was assumed that they must be specially treated during manufacture to render them resistant to bleeding. A similar indicator, tetrabromophenolphthalein ethyl ester, which has been recommended by Feigl[4] as a spot-test reagent for proteins, bled much more slowly and was used for all subsequent work. The observed colour transition range for this reagent is pH 3.2–6.4, the change being from yellow to blue. Below pH 3.2 and in the presence of protein, a proton is displaced from the indicator molecule, which assumes a blue salt-like form according to the equation:

$$\underset{\text{yellow}}{\mathrm{HIn}} + \text{protein} = \underset{\text{blue}}{\mathrm{In^{-}\text{-}protein}} + \mathrm{H^{+}}$$

Protein hydrolysis products, including amino-acids, di- and tripeptides and peptones do not cause a colour change.[4] As the indicator is normally present in considerable excess, the observed final colour is generally between yellowish-green and greenish-blue, depending on the level of protein present. The laboratory-prepared strips were buffered to pH 2.8 with citric acid ($pK_a = 3.1$) and sodium citrate to provide a stable and reproducible pH at the surface and to allow for some variation in the pH of the sample solutions.

Table 1. Effect of immersion time, drying procedure and pH of sample solution on the reflectance function $F(R_\infty)$ of protein test-strips (5.00 mg/ml protein)

	$F(R_\infty)$*						
	Immersion time, *sec*		Drying time, *min*			Sample solution pH	
	2	10	2	4	6	4	9
	0.235	0.265	0.155	0.250	0.231	0.228	0.258
	0.265	0.228	0.138	0.222	0.250	0.243	0.243
	0.228	0.282	0.178	0.233	0.269	0.258	0.277
Mean	0.243	0.258	0.157	0.235	0.250	0.243	0.259

* $F(R_\infty)$ is the reflectance function for absolute reflectance measurements, with MgO as a standard.

Table 2. Statistical evaluation of reflectance readings for the determination of albumin in water and urine

	$F(R_\infty)$* (mean of 5 replicates)		Standard deviation		Relative precision, %	
Albumin, *mg/ml*	Water	Urine	Water	Urine	Water	Urine
0	0.0320	0.0675	0.0010	0.0024	3.1	3.6
0.50	0.113	0.326	0.0056	0.0057	5.0	1.7
1.25	0.177	0.569	0.0077	0.017	4.4	3.0
2.50	0.299	0.934	0.0089	0.021	3.0	2.2
5.00	0.609	1.61	0.032	0.089	5.3	5.5
10.00	1.25	2.60	0.071	0.118	5.7	4.5

* See Table 1.

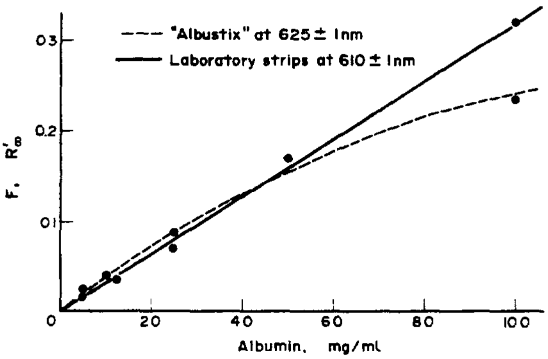

Fig. 2. Kubelka–Munk plot for albumin in water, 2-sec immersion (reference MgO).

Visible reflectance spectra of commercial and laboratory-produced test-strips (Fig. 1) show two fairly broad maxima. The one between 425 and 440 nm corresponds to the yellow acid form of the indicator and that between 610 and 625 nm to the blue indicator–protein adsorption product. The slightly shorter wavelengths of maximum absorbance observed for the laboratory test-strips may arise from the change of indicator. Alternatively, the commercial strips may be manufactured from paper with a somewhat coarser fibrous structure than those prepared in the laboratory. An interesting feature of the spectra is the occurrence of an isosbestic point in the region of 500 nm, confirming that the two maxima are derived from a single species existing in two distinct forms.

Kubelka–Munk plots for the commercial and laboratory-prepared test-strips are shown in Fig. 2. The difference in the range of reflectance function values $F(R_\infty)$ (where R'_∞ is the reflectance measured relative to a blank) for identical concentration ranges is again indicative of the different indicators used in the two types of strip, although differences in paper quality or reagent concentrations may also be contributory factors. The better linearity and wider range of $F(R'_\infty)$ values found for the laboratory-prepared strips would be an advantage where quantitative rather than semi-quantitative information is required. An upper protein concentration limit of 10 mg/ml was selected as levels of clinical interest are largely below this value.

Quantitative measurements

For quantitative measurements an immersion time of 2 sec is considered preferable to 10 sec in the interests of speed and to minimize the risk of the indicator–protein complex dispersing into the sample solution. This was observed in exploratory work for strips immersed for more than 10 sec. Drying conditions must be such as to avoid redistribution of the complex on the surface of the strips while excess of moisture is present. This was achieved by shaking the strips to remove excess of sample solution and by laying them horizontally 3–4 ft beneath a hot-air blower. Reflectance readings were found to be stable and reproducible after a minimum of 4 min drying in this manner. The buffer capacity of the strips was found to be adequate to cope with sample solutions with pH as high as 9. This is considerably above that normally encountered in urine samples, which range in pH between 5.5 and 7.0.

A statistical assessment of the data has established that relative precisions of 1.7–5.7% over the protein concentration range 0.5–10 mg/ml in both water and urine (Table 2) can be expected. This is in agreement with an estimated value of 2.9% derived from Ringbom curves, assuming an instrumental reading error of 0.5%. The individual Ringbom plots did not show the full extent of the normal S-shaped curves as concentrations exceeding 10 mg/ml were not examined. This is particularly noticeable for the commercial strips, where reflectances are generally higher than those of the laboratory-prepared strips for reasons already discussed. Precision is unaffected by storage for at least three months, as evidenced by a comparison of stored strips with those which provided the data in Table 2. The accuracy of the method was assessed by analysing two urine control samples, each containing 1.30 ± 0.10 mg/ml protein, as determined by the biuret method. The results were 1.17, 1.29, 1.22 (mean 1.23) and 1.18, 1.12, 1.28 (mean 1.19) mg/ml, and demonstrate an acceptable accuracy for the proposed method. The slightly lower figures suggest that the urine samples may have contained some protein hydrolysis products which would react with the biuret reagent but not with the test strips.

CONCLUSIONS

A method for the determination of protein in aqueous media has been described and shown to have a relative precision of between 1.7 and 5.7% over the concentration range 0.5–10 mg/ml. Results for the analysis of urine control samples show good agreement with figures obtained by the biuret method. All experimental work was done using bovine serum albumin but the reagent will also react with other native proteins. The method has a potential application in clinical analysis where quantitative rather than semi-quantitative data are required. It would be suitable for the determination of protein in urine, as in cases of proteinurea, and in cerebrospinal fluids. In conjunction with a portable reflectance meter the method could provide data quickly and cheaply.

Acknowledgement—I am grateful to Mr. P. W. Dalton of the New Charing Cross Hospital who was responsible for some of the experimental work described in this paper.

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Summary—The determination of protein in aqueous media by using commercial and laboratory-prepared test-strips has been investigated. Adsorption indicators of the Bromophenol Blue type form the basis of the colour-forming reaction, which is selective for natural protein. The relative precision of reflectance measurements is 1.7–5.7% over the concentration range 0.5–10 mg/ml, for bovine serum albumin. The method would be suitable for the rapid determination of protein in urine and other body fluids.

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ANALYTISCHE ASPEKTE DER KOORDINATIONSREAKTIONEN DES HEXAMETHYLPHOSPHORSÄURETRIAMIDS IN WÄSSRIGEN LÖSUNGEN

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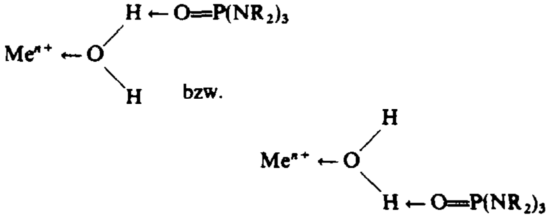
Nach ersten Arbeiten von Donoghue und Drago[1] über die Darstellung von Koordinationsverbindungen des Hexamethylphosphorsäuretriamids (HMPT) mit Kobalt-, Nickel-, Kupfer- und Zinksalzen wurde von den Unterzeichnern über Komplexverbindungen des HMPT sowie des Octamethylpyrophosphorsäuretetramids (OMPA) und des Diisopropylfluorophosphats (DFP) mit Salzen des Eisens-(III), Wismuts, Urans, Thoriums, Vanadiums, Zinns(II) und (IV), des Goldes sowie des Zinks berichtet.[2] Ebenso waren Verbindungen des HMPT mit verschiedenen Übergangsmetall-Cyano- und Rhodanosäuren, sowie mit der Säure $H[B(C_6H_5)_4]$ Gegenstand unserer Untersuchungen. Ferner wurden extraktiv-analytische Methoden erstellt für die selektive Erfassung von Eisen(III),[3] Gold[4] und von Zink.[5] Ab 1967 haben daraufhin zahlreiche Autoren weit über 100 Verbindungen des Typs $(HMPT)_m[MeX_n]$ (I) beschrieben.[6] Über Darstellungsmöglichkeiten von komplexen Säuren $H[MeX_n(HMPT)_m]$ (II) unter Erhöhung der Koordinationszahl, wie in $H[BiX_4(HMPT)_2]$ bzw. $H[AuX_4(HMPT)_2]$ ($\delta^1H = 13{,}67$ ppm für den Chlorokomplex in D_2O; $\Delta\nu = -28\,cm^{-1}$) wie auch über Verbindungen des Typs $(HMPTH)_mH_2[MeX_n]$ (III), wie $(HMPTH)_2H_2[Fe(CN)_6]$, sagt die Literatur nichts Weiteres aus. Diese Verbindungen wurden erstmals von den Autoren dargestellt.

Bei der Darstellung des Verbindungstyps (I), z.B. von $[Fe(SCN)_3(HMPT)_3]$ ist eine geringe Acidität der Probelösung erforderlich, um die Bildung der komplexen Säure $H_3[(Fe(SCN)_6)]$ hintan zu halten. Die quantitativ eintretende Fällung des Eisens erfolgt hier auch aus verdünnten Lösungen des Eisens unter vollständigem Ligandenaustausch des in wässrigen Lösungen am Eisen-ion koordinierten Wassers. Erst durch diese vollständige Ligandenhydrophobierung wird eine Extraktion mit chlorierten Kohlenwasserstoffen möglich. Diese selektive Extrahierbarkeit z.B.[3] des Eisens als $[FeCl_3(HMPT)]$ aus vorzugsweise chloridhaltigen Lösungen ist somit auf die Bildung von nicht extrahierbaren Mischkomplexen von H_2O und HMPT an den anderen vorhandenen Übergangsmetallen zurückführbar. Erkennbar wird dies bei späteren Darstellungsmethoden für Übergangsmetall–HMPT-Komplexe, bei denen auf größtmögliche Wasserfreiheit in den Ansätzen geachtet werden mußte, da die unvollständige Entfernung koordinierten Wassers zu wasserlöslichen Verbindungen führte und Fällungen verhinderte.[6]

Tabelle 1. HMPT-Komplexe von Alkali- und Erdalkalimetallen

Verbindung	ν PO, *cm*$^{-1}$	νPN, *cm*$^{-1}$	Smpt., °*C*.
$Na(HMPT)_4J$	1200	746	94
$Na(HMPT)_2SCN$	1190	750	75
$K(HMPT)_2SCN$	1198	750	58
$MgCl_2(HMPT)_2(H_2O)_3$	1194	756	113/121
$MgBr_2(HMPT)_2(H_2O)_4$	1193	750	162
$MgBr_2(HMPT)_3(H_2O)_3$	1196	750	164
$MgJ_2(HMPT)_2(H_2O)_6$	1192	755	157
$CaBr_2(HMPT)_2H_2O$	1194	753	128/136
$CaBr_2(HMPT)_2(H_2O)_4$	1197	753	130/132
$SrCl_2(HMPT)_2(H_2O)_2$	1191	753	190 Zers.
$SrBr_2(HMPT)_3\ H_2O$	1190	750	200 Zers.
$SrB_2(HMPT)_4\ H_2O$	1193	751	240 Zers.
$SrJ_2(HMPT)_4$	1193	750	271
$BaBr_2(HMPT)_2(H_2O)_2$	1193	751	200 Zers.

Tabelle 1 zeigt 14 neue HMPT-Komplexe mit Alkali- und Erdalkalimetallen. Erstgenannte Verbindungen fallen nur aus wasserfreiem Medium, denn Wasser verhindert durch seine koordinative Bindung die vollständige Koordination des HMPT. An Erdalkalimetallen kann Wasser gleichzeitig koordinieren. Da, wie weiter unten näher beschrieben, das HMPT nicht nur am Metall koordiniert, sondern auch mit den Wasserprotonen reagiert, wird die Koordination überschüssigen HMPT's am Metallkation noch erleichtert:



Es handelt sich also bei den beschriebenen Reaktionen um Ligandenaustauschreaktionen, bei denen die Liganden auch miteinander eine Reaktion eingehen.

EXPERIMENTELLER TEIL

Darstellung der Verbindungen der Tabelle 1

Die Alkalimetall-Verbindungen sind darstellbar durch Lösen der entwässerten Halogenide in HMPT, das auf 70–100° erhitzt ist. Nach dem Auskristallisieren in der Kälte wird zweimal mit je 5 ml Petroläther (Kp 130°) gewaschen und im Vakuum über Kaliumhydroxid getrocknet.

Die Erdalkalimetall-Verbindungen werden dargestellt durch Suspendieren von 3–5 g der Erdalkalihalogenid-hydrate in 15 ml Methylenchlorid, und Auflösen durch Zusatz von 8–10 ml HMPT. Man kristallisiert im Vakuum, wäscht mit Petroläther und trocknet im Vakuum über Kaliumhydroxid.

Geräte

IR-Aufnahmen: Hitachi Perkin-Elmer, Typ 180; ^1H-NMR-Aufnahmen: Hitachi Perkin-Elmer, Typ R 24 A; ^{31}P-NMR-Aufnahmen: Bruker, Typ RM 504.

Die Widerstandsmessungen wurden mit einem Instrument der Firma WTW durchgeführt. Bei der benutzten Elektrode handelte es sich um platinierte Platinbleche. (Gerätekonstante: $K = 0{,}582\,cm^{-1}$).

Physikalische Untersuchungen am System HMPT–H_2O

Est ist seit längerer Zeit bekannt, daß HMPT auf Grund seiner außerordentlich hohen Donor-Eigenschaft mit prak-

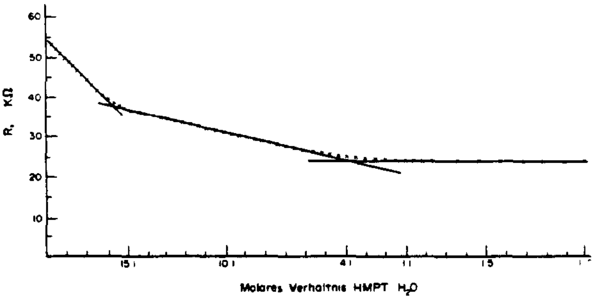
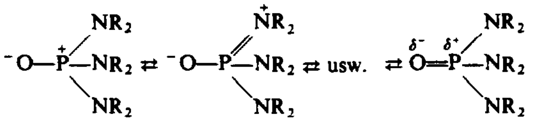


Abb. 1. Widerstand von Mischungen des HMPT mit Wasser.

tisch allen protischen Substanzen über den Phosphorylsauerstoff reagiert.[7] Die große Koordinationsfähigkeit ist auf die hohe Mesomeriemöglichkeit der positiven Partialladung des Phosphors zurückzuführen:[7]



Aus ramanspektroskopischen Untersuchungen ist nachgewiesen worden, daß die P=O-Bindung zu 50% Ionencharakter besitzt.[7] Als Beispiel für eine Reaktion des HMPT mit einer protischen Substanz wurde aus den oben dargelegten Gründen die Reaktion

$$(H_2O)_m + n\mathrm{HMPT} \rightarrow [(\mathrm{HMPT})_n(\mathrm{HOH})_m]$$

untersucht. Diese Reaktion wurde durch Messung der Leitfähigkeit, der ^{1}H-NMR, der ^{31}P-NMR und der IR-Spektroskopie verfolgt.

Leitfähigkeitsmessungen. Durch Zugabe von doppeltdestilliertem Wasser zu reinem HMPT wird eine Zunahme der Leitfähigkeit erreicht. Eine konduktometrische Mikrotitration einer bekannten, vorgegebenen Menge HMPT mit Wasser ist in Abb. 1 dargestellt. Hierbei wurde das Titrationsgefäß auf 53° thermostatiert und die Mischung nach jedem Zutropfen *ca.* eine Minute gerührt. Während der anschließenden Widerstandsmessung wurde der Magnetrührer abgestellt. Die Widerstandsmessung wurde mit Hilfe einer Wheatstoneschen Brücke durchgeführt, die zur Vermeidung störender Polarisationseffekte mit einer Wechselspannung von 3 kHz betrieben wurde. Analoge Titrationen mit anderen Ausgangsmengen an HMPT oder anderen Temperaturen (20–60°) zeigen der Abb. 1 analoge Kurvenverläufe. Aus der Kurve sind zwei Knickpunkte bei den molaren Verhältnissen HMPT: H_2O = 16:1 und 4:1 abzulesen. Ab dem molaren Verhältnis 1:1 bis in das Gebiet großer Verdünnungen bleibt der Widerstand weitgehend konstant.

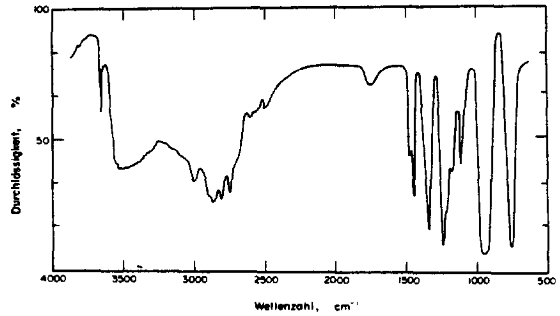


Abb. 2. IR-Spektrum der Mischung HMPT:H_2O = 6:1.

IR-spektroskopische Untersuchungen. Abbildung 2 zeigt ein typisches IR-Spektrum einer HMPT-H_2O-Mischung innerhalb des Bereiches 10:1–4:1 (hier als Beispiel 6:1). Neben den zu erwartenden, auf das HMPT zurückführbaren Banden, tritt bei 3680 cm^{-1} ein scharfer Peak auf, der einem OH^--Ion in festen Hydroxyden entspricht.[8] Weiterhin tritt zum Unterschied zum reinem HMPT eine sehr breite Bande von 3000 cm^{-1} bis 3600 cm^{-1} auf, die einer Wasserstoffbrückenbindung P=O···H···O=P zugeordnet werden muß.

Aus den bisherigen Untersuchungen können folgende Schlüsse gezogen werden: bei dem Molverhältnis HMPT:H_2O = 4:1 liegt eine Koordination von vier Phosphorylsauerstoffen des HMPT an einem Wasserproton vor, gemäß einer Verbindung $[H(HMPT)_4^+]OH^-$. Die Existenz von Hydroxylionen ist durch die IR-Spektren nachgewiesen. Der Knickpunkt der Titrationskurve beim molaren Verhältnis HMPT:H_2O = 4:1 zeigt, daß das Wassermolekül vollständig dissoziiert ist. Dem Molverhältnis 16:1 entspricht eine in zweiter Sphäre noch vorhandene zusätzliche Koordination durch weitere zwölf HMPT-Moleküle.

^{1}H-NMR-Messungen. Bestätigungen der gemachten Angaben über die Koordinationsspezies des HMPT-Sauerstoffs an einem Wasserproton ergeben sich durch die Messung der ^{1}H-NMR des "Wassers" in Abhängigkeit von dessen molarer Konzentration in HMPT. Hierzu wurden Verdünnungsstufen HMPT-H_2O im molaren Bereich 10:1 bis 1:20 hergestellt und von jeder Mischung sowie von reinem Wasser als auch von reinem HMPT ^{1}H-NMR-Aufnahmen gemacht (ext. Standart TMS, 0 ppm). Das ^{1}H-NMR-Spektrum von reinem HMPT zeigt zwei Methylbanden bei 2,55 und 2,37 ppm. Der Grund für die Aufspaltung in zwei Peaks ist die Kopplung der Methylprotonen mit dem ^{31}P-Kern (Abb. 3).

Reines, doppeltdestilliertes Wasser zeigt einen Peak bei 4,80 ppm. Abbildung 4 zeigt die chemische Verschiebung des Wasserprotons in Abhängigkeit vom molaren Verhältnis HMPT:H_2O. Man erkennt, daß im Bereich 10:1–4:1 die chemische Verschiebung und damit gleichbedeutend die Elektronendichte am komplexierten Proton gleichbleibt. Bei dem Verhältnis 4:1 werden δ = 3,45 ppm gemessen. Dies bedeutet einen Unterschied von 1,35 ppm

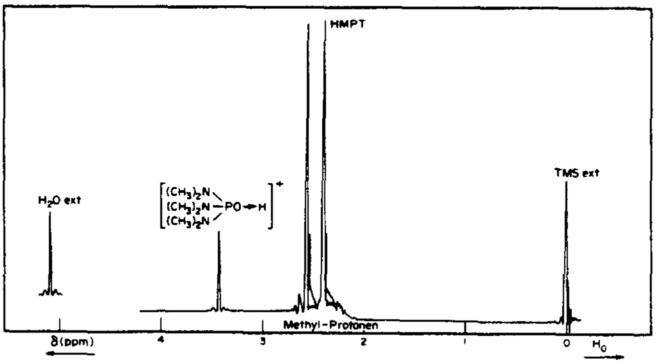


Abb. 3. ^{1}H-NMR-Spektrum der Mischung HMPT:H_2O = 4:1.

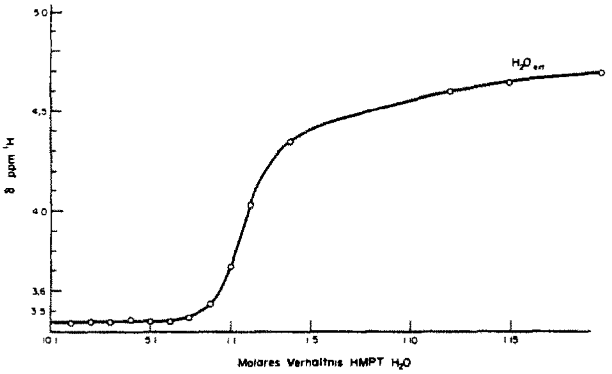


Abb. 4. ^{1}H-NMR-Verschiebungen von HMPT-Wasser-Mischungen.

gegenüber reinem Wasser. Es ist also ersichtlich, daß bei einer Komplexzusammensetzung $[H(HMPT)_4^+]OH^-$ die maximale Elektronendichte am zentralen Proton erreicht ist. Komplexe der Zusammensetzung $[H(HMPT)_x^+]OH^-$ mit $x > 4$ existieren nicht. Weiter zugefügtes HMPT baut, wie die konduktometrische Titration zeigt, eine zweite Koordinationssphäre auf. Im Bereich größerer Verdünnungen (HMPT:H_2O wie 4:1 bis 1:10 usw.) nähert sich der Peak mehr und mehr dem des reinen Wassers bei 4,8 ppm.

^{31}P-NMR-Messungen. Von den bereits unter ^{1}H-NMR erwähnten Verdünnungsstufen sowie von reinem HMPT wurden ^{31}P-NMR-Spektren angefertigt. Als externer Standart diente konz. H_3PO_4 (Abb. 5). Es wurde jeweils der höchste Peak eines HMPT-Signals ausgemessen und die δ^{31}P-Werte gegen das molare Verhältnis wie oben aufgetragen. Die Kurve zeigt den gleichen Sachverhalt wie bei Abb. 4. Auch hier ist ein deutlicher Knickpunkt beim molaren Verhältnis HMPT:H_2O = 4:1 erkennbar. Im Bereich 10:1–4:1 erfolgt keine wesentliche Änderung der Elektronendichte am Phosphor. Erst ab dem Verhältnis 4:1 greift eine zunehmend stärker werdende Entschirmung des ^{31}P-Kerns Platz.

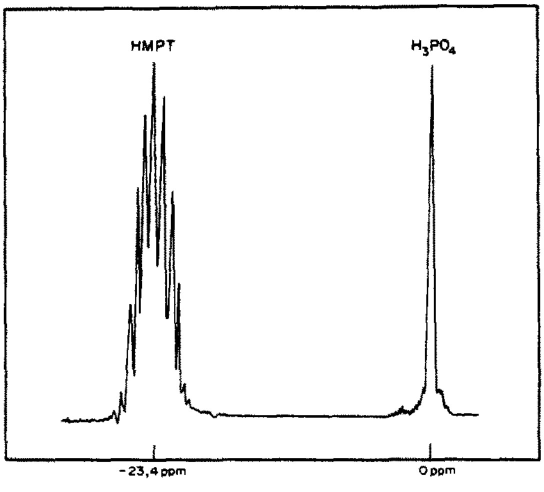


Abb. 5. ^{31}P-NMR-Spektrum des HMPT.

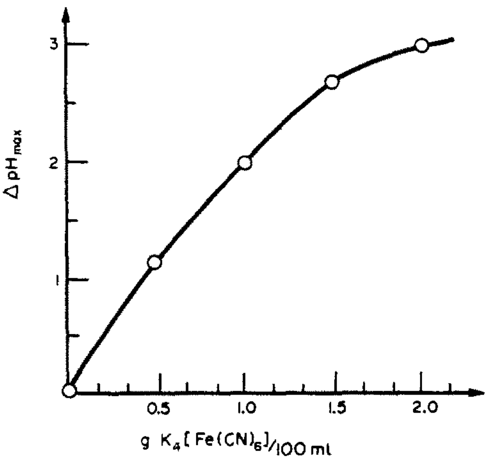


Abb. 6. Maximale pH-Wert-Erhöhungen durch Zusatz von HMPT und $K_4[Fe(CN)_6]$zu Probelösungen.

Als Interpretationsmöglichkeit dieses und des analogen Verhaltens in Abb. 4 ist ein stufenweiser Abbau des Komplexes $[H(HMPT)_4^+]OH^-$ bis zur Verbindung H–O–H···O=$P(NR_2)_3$ denkbar. Weitere Überlegungen sowie experimentelle Untersuchungen, insbesondere über die strukturellen Gegebenheiten bei hohen Wassergehalten in HMPT, sind im Gange. Hierüber wird berichtet werden.

Verbindungstyp $(HMPT)_mH_k[1MeX_n)]$

Die Verbindungen des Typs (III), in denen wie eingangs erwähnt, der Phosphorylsauerstoff des HMPT mit den Protonen schwacher komplexer Metallsäuren (z.B. $H_4[(Fe(CN)_6)]$) reagiert, erweisen sich insbesondere dann als in Wasser schwerlöslich, wenn sich die Protonen bereits in einer intramolekularen Wasserstoffbrücke mit den Liganden des Metalls befinden.[9] Unter diesen (Tabelle 2) ist die Verbindung $(HMPTH)_2H_2[(Fe(CN)_6)]$ auch in organischen Solventien der verschiedensten Art praktisch unlöslich. Hieraus ergeben sich Schwierigkeiten für die Strukturaufklärung mittels ^{1}H-NMR-Spektroskopie. Die zunächst überraschende Tatsache, daß sich die Vertreter dieses Verbindungstyps jedoch in überschüssigem HMPT lösen, ist durch die gewonnenen Erkenntnisse über die Reaktionen des HMPT mit Protonen erklärbar. Beispiel:

$$(HMPT)H[B(C_6H_5)_4] + 3HMPT \rightarrow H(HMPT)_4^+ + [B(C_6H_5)_4]^-$$

Tabelle 2. HMPT-Komplexe des Typs (HMPTH) $n(MeX_m)$

Nr.	Substanz	Smpt., °C	$\Delta\nu_{PO}$* cm^{-1}
1	$[\{(CH_3)_2\ N\}_3PO\ H][(C_6H_5)_4B]$	176	−16
2	$[\{(CH_3)_2N\}_3PO\ H][Cr(SCN)_4(NH_3)]$	150 Zers.	−33
3	$[\langle\{(CH_3)_2N\}_3PO\rangle_2H_2][Fe(CN)_5NO]$	103 Zers.	−32
4	$[\langle\{(CH_3)_2N\}_3PO\rangle_2H_2]H_2[Fe(CN)_6]$	170 Zers.	−33

* Bezogen auf freies HMPT.

Bestimmung der "sauren" Protonen: 1,2,3, direkt und indirekt; 4, indirekt. Löslichkeit: in Wasser, 1,4 sehr schwer löslich; 2,3 schwer löslich; in Alkoholen, 1,23 leicht löslich, 4 sehr schwer löslich.

Das Auftreten des Kations ist durch ^{1}H-NMR-Spektroskopie nachgewiesen.

Trotz der außerordentlichen Schwerlöslichkeit der Verbindung $(HMPTH)_2H_2[Fe(CN)_6]$ in allen gängigen Lösungsmitteln läßt sich die Protonenzahl indirekt durch Messung der Differenz der Aciditäten vor und nach der Ausfällung bestimmen. Sofern die betreffenden Verbindungen in Wasser–Alkohol–Gemischen löslich sind, kann ihr Gehalt an Protonen auch direkt durch Titration mit Natriumhydroxid ermittelt werden.

Durch Zufügen von $K_4[Fe(CN)_6]$ zu verdünnten Mineralsäuren bei Gegenwart von HMPT lassen sich durch "Protonenfällung" auch bestimmte pH-Werte im Bereich 0–4 einstellen. Abbildung 6 zeigt die mögliche pH-Wert-Steigerung von Lösungen, deren Anfangs-pH-Wert zwischen 0,5 und 3 lag.

$$4HCl + K_4[Fe(CN)_6] + 2HMPT \rightarrow (HMPTH)_2H_2[Fe(CN)_6] + 4KCl$$

Aus dieser Gleichung ist ersichtlich, daß die Protonen in der Lösung durch Kalium-Ionen ersetzt werden. Dies hat gegenüber dem Einsatz von Puffern, deren Anionen Metalle komplexieren Vorteile (hierüber wird berichtet werden).

Der Deutschen Forschungsgemeinschaft, Bonn-Bad Godesberg und dem Fond der Chemischen Industrie danken wir für die Unterstützung der vorliegenden Arbeit.

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Zusammenfassung—Es wird die Erklärung für die erreichten Spezifitäten bei der Selektivierung von Übergangsmetallen unter Verwendung von Hexamethylphosphorsäuretriamid gegeben. Sie liegt in der Bildung nicht extrahierbarer Mischkomplexe des HMPT und des Wassers an den Fremdmetallionen. Eine gleichzeitige Reaktion des HMPT mit Wasser unter Bildung der Verbindung $[H(HMPT)_4]^+OH^-$ läuft den ebengenannten Koordinationsreaktionen parallel. Die Bildung diskreter Komplexe des HMPT mit H_2O wurde ausgewiesen durch Konduktometrie, IR-, ^{1}H-NMR- und ^{31}P-NMR-spektroskopische Untersuchungen. Innerhalb des Verbindungstyps $(HMPTH)_mH_k(MeX_n)$ eröffnet die Verbindung $(HMPTH)_2H_2[Fe(CN)_6]$ die Möglichkeit der Protonenfällung an Stelle der Pufferung.

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ANALYTICAL APPLICATIONS OF COMPLEX FORMATION IN NON-AQUEOUS SOLUTIONS—I

COMPLEXES OF BISMUTH(III) WITH POTASSIUM DIPHENYLDISELENOPHOSPHATE IN ORGANIC SOLVENTS

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Reactions in non-aqueous solution are used in analytical chemistry mainly in electrochemical and titrimetric methods,[1,2] but are also promising for development of spectrophotometric methods based on complex formation.[3,4] The stability constants, composition and spectral properties of the complexes are obviously of importance in this connection.

This report is concerned with the complex formed by Bi(III) with potassium diphenyldiselenophosphate in a number of non-aqueous solvents with various physical and chemical properties. The diphenyldiselenophosphate is a new analytical reagent, an analogue of the dialkyldithiophosphoric acids used for extraction–photometric determination of bismuth and other elements.[5,6] Its usefulness as a ligand in complex formation is as yet unknown and awaits special study.

EXPERIMENTAL

Reagents

Anhydrous $BiCl_3$ was purified by distillation in quartz apparatus at 447°. Its solutions were standardized complexometrically, with Xylenol Orange as indicator. Solvents were freed from water according to Weissberger.[7] Potassium diphenyldiselenophosphate was synthesized in the Department of Organic Chemistry of the Lvov State University, by interaction of diphenylchloroselenophosphate with potassium hydroselenide (recrystallized from benzene/acetone, m.p. 172°, decomp.). The PMR spectrum of potassium diphenyldiselenophosphate in D_2O at 90 MHz was a singlet at $\delta = 2.6$ ppm with respect to H_2O and 7.6 ppm with respect to tetramethylsilane. This absorption is due to the protons of the phenyl ring (characterized by a resonance signal in the region $\delta = 6.5$–8.0 ppm.[8]

Apparatus

Absorbances were measured on Hitachi EPS-3 and SP-4A spectrophotometers at 25 ± 0.1°. Infrared spectra were taken on an IR-10 spectrometer, with KBr pellets. PMR spectra were recorded on a WH-90 spectrometer.

RESULTS AND DISCUSSION

Potassium diphenyldiselenophosphate absorbs in the infrared at 610 cm^{-1} (ν_1) and 510 cm^{-1} (ν_2). The two absorption bands can be accounted for by asymmetric (ν_1) and symmetric (ν_2) stretching frequencies of the diphenyldiselenophosphate P(Se)Se group.[9] Complex formation leads to a decrease in both frequencies ν_1 and ν_2 and to ν_1 splitting into a doublet. For Bi(III) diphenyldiselenophosphate isolated from methanol ν_1 is 510 cm^{-1} and ν_2 450 cm^{-1}, showing that the diphenyldiselenophosphate is attached to the Bi(III) through both selenium atoms. Figures 1 and 2 show the absorption spectra of solutions of bismuth(III) chloride, potassium diphenyldiselenophosphate and the bismuth complex, in acetonitrile, ethanol, dimethylformamide, dimethylsulphoxide, acetone, methanol and carbon tetrachloride. The complex can be obtained in carbon tetrachloride medium by extraction from 0.3*M* hydrochloric acid. It is seen from Figs. 1 and 2 that the spectrum is rather similar whatever the solvent, being characterized (just as in carbon tetrachloride with minimum solvation) by a more intense short-wave band at 350–370 nm and a less intense waveband forming a shoulder at 390–450 nm. The two absorption bands can be accounted for by singlet–singlet and singlet–triplet transitions respectively, with charge transfer, by analogy with the dialkyldithiophosphate and bromide complexes of Bi(III).[10]

Changing from bromide as ligand to sulphur- and selenium-containing ligands gives rise to shifts of the Bi(III)-complex absorption bands to longer wavelengths. Thus the bromide, dithiophosphate and diselenophosphate complexes have singlet–triplet transitions at 373, 395[10] and 370 nm and singlet–singlet transitions at 260, 329[10] and 370 nm, respectively. Such a shift might be explained by the decreasing electronegativity of the co-ordinating atoms in the series H_2O; Cl^-; Br^-; $(RO)_2P(S)S^-$; $(RO)_2P(Se)Se^-$.[11]

The positions of the absorption bands of the bismuth diphenyldiselenophosphate complex depend on the solvent used, the shift to longer wavelength increasing in the order DMF < acetone < acetonitrile < DMSO < ethanol < methanol ~ carbon tetrachloride. In the electronic spectra

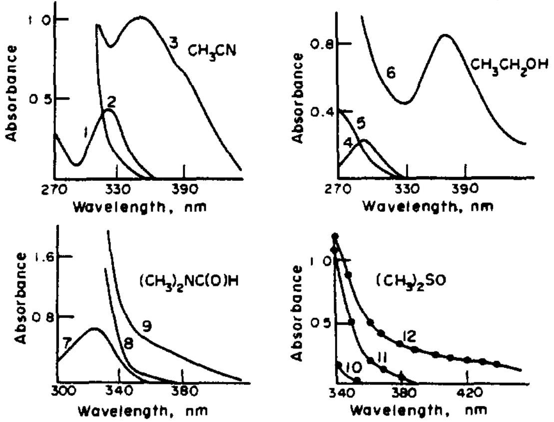

Fig. 1. Absorption spectra: 1—Bi $8 \times 10^{-5}M$; 2—L $1 \times 10^{-3}M$; 3—Bi $8 \times 10^{-5}M$ and L $1 \times 10^{-3}M$; 4—Bi $5 \times 10^{-5}M$; 5—L $1.5 \times 10^{-4}M$; 6—Bi $5 \times 10^{-5}M$ and L $1.5 \times 10^{-4}M$; 7—Bi $8 \times 10^{-5}M$; 8—L $1 \times 10^{-2}M$; 9—Bi $8 \times 10^{-5}M$ and L $1 \times 10^{-2}M$; 10—Bi $4 \times 10^{-4}M$; 11—L 1.13*M*; 12—Bi $4 \times 10^{-4}M$ and L 1.13*M*; (1—9, $l = 1$ cm; 10–12, $l = 0.1$ cm).

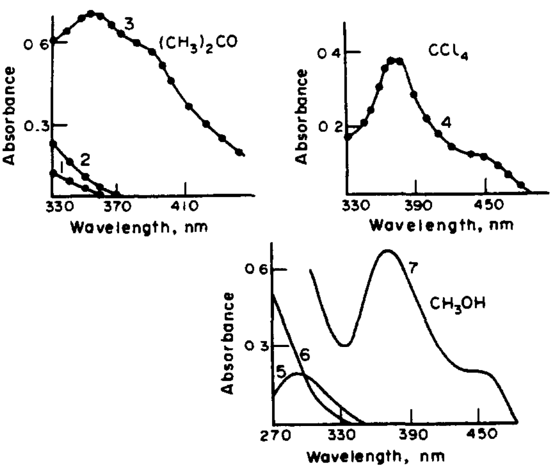

Fig. 2. Absorption spectra: 1—L $9 \times 10^{-4}M$; 2—Bi $4 \times 10^{-5}M$; 3—Bi $4 \times 10^{-5}M$ and L $9 \times 10^{-4}M$; 4—Bi $2 \times 10^{-5}M$ and L $5 \times 10^{-3}M$ (in aqueous phase); 5—Bi $4 \times 10^{-5}M$; 6—L $1.8 \times 10^{-4}M$; 7—Bi $4 \times 10^{-5}M$ and L $1.8 \times 10^{-4}M$; ($l = 1$ cm).

of the bismuth chloride solutions, the absorption maximum is also shifted depending on the solvent, but in the opposite direction. These changes are likely to be caused by different degrees of solvation in the ground and excited states of the Bi(III) compounds involved. The dependence of the wavelength of maximum absorption in the bismuth chloride and diphenyldiselenophosphate spectra on the chemical nature of the solvent was estimated by means of the Kosower *Z* parameter that characterizes the solvating ability of solvents[3] in terms of the electronic transition energy corresponding to the charge-transfer band of 1-ethyl-4-carbomethoxypyridine iodine in the particular solvent (Table 1).

For bismuth chloride a plot of the transition energy at 280–320 nm *vs.* *Z* is linear with slope close to unity (Fig. 3). This points to the excited state being more ionic than the ground state, which is in accord with the interpretation of these bands as those of charge transfer from the Cl^--ion to vacant bismuth(III) 6*d* orbitals. For the bismuth diphenyldiselenophosphate complex the charge-transfer band is almost unaffected by *Z* (Fig. 3), possibly because of screening of the bismuth ion from the solvent. On the other hand, the negative, though slight, slope of the graph shows the excited state to be more ionic than the ground state. This might be explained by the Bi–Se bond being more covalent than the Bi–Cl bond, which would make the excited state more ionic than the ground one on charge transfer (the covalent nature of the Bi–Se bond follows from comparison of the electronegativity of the atoms[12]).

Stability constants and composition of the bismuth(III) diphenyldiselenophosphate complexes were determined by the molar ratio method, with measurement at 370 nm and constant chloride concentration of 0.01*M*. Continuous-variations studies showed the complexes to contain bismuth and diphenyldiselenophosphate in 1:3 ratio. The stability constants calculated according to Schaeppi and Treadwell,[13] are shown in Table 2.

It will be seen from Table 2 that the stability constants change by about 12 orders of magnitude when the solvent is changed from ethanol to DMSO. These constants are affected both by physical characteristics, primarily the dielectric permeability, and the chemical characteristics of the solvent. The constants reported here do not correlate with the dielectric permeability of the solvents under study, presented in Table 1. The solvent effect cannot be explained, then, in terms of elementary electrostatic concepts. It might be supposed that the stability constants are mainly affected by the chemical nature of the solvent, especially by its donor strength, which is estimated from the enthalpy of formation of the iodine and phenol adducts with the particular solvent ($-\Delta H_{I_2}$, $-\Delta H_{PhOH}$), and from the donor number (DN) of the solvent, proposed by Gutmann[4] as involving the enthalpy of solvate formation between a donor solvent and a standard acceptor such as $SbCl_5$. The solvents under study cover a wide donicity range (Table 1). If the donating effect plays a dominant role there should be a correlation between the stability constants and the donor strengths of the solvents. This is because the molecules of such solvents undergo stronger

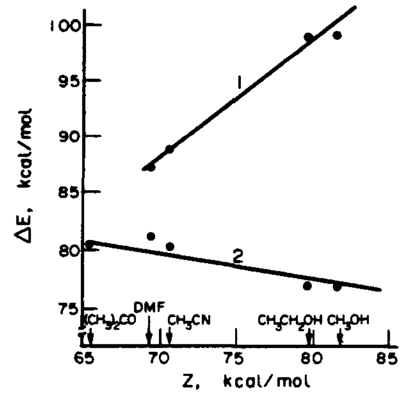

Fig. 3. Dependence (upon *Z*) of electronic transition energy corresponding to maximum absorption bands of (1) bismuth chloride and (2) bismuth diphenyldiselenophosphate complex in DMF, CH_3CN, CH_3OH, C_2H_5OH and $(CH_3)_2CO$.

Table 1. Parameters for the solvents studied

Solvent	Dielectric constant (25°C)	*Z*, *kcal/mole*	$\Delta H_{I_2\text{—adduct}}$ *kcal/mole*	DN_{SbCl_5}
Acetonitrile	36.2	71.3	2.4	14.1
Acetone	20.7	65.7	3.3	17.0
Methanol	32.6	83.6	1.9	18.9
Ethanol	24.3	79.6	2.1	17.9
DMF	36.1	68.5	3.7	26.6
DMSO	46.1	71.7	4.4	29.8

Table 2. Stability constants of bismuth(III) diphenyldiselenophosphate complexes in different solvents

	CH_3CN	$(CH_3)_2CO$	CH_3CH_2OH	CH_3OH	$(CH_3)_2NC(O)H$	$(CH_3)_2SO$
log β_3	13.11	10.50	14.40	14.30	5.20	2.22

co-ordination by the bismuth chloride, thus decreasing its ability to accept diphenyldiselenophosphate. It is seen from Figs. 4 and 5 that the logarithms of the stability constants of the bismuth(III) diphenyldiselenophosphate complex decrease linearly with increased donicity of the solvent and more negative enthalpy of iodine adduct formation with the solvent.

Our results show that all the solvents tested can be used for developing spectrophotometric methods of bismuth determination, the molar absorptivities of the complex being in the range $1.0–1.8 \times 10^4 \, \mathrm{l.mole^{-1}.cm^{-1}}$, which allows bismuth(III) to be determined over the $4 \times 10^{-6}–5 \times 10^{-5}M$ concentration range. The solvents with minimum solvating ability are preferred because of the shift of the maximum-absorption bands to longer wavelengths, which eliminates interference by ions absorbing in the near ultraviolet. Similarly, preference is given to the solvents with small donor numbers (or low enthalpy of iodine-adduct formation) because the stability constants of the Bi(III) complexes are highest in these solvents, increasing the selectivity. Thus methanol, ethanol and acetonitrile are the most useful of the solvents studied. Calibration graphs for methanol and ethanol media at potassium diphenyldiselenophosphate concentration of $5 \times 10^{-4}M$, (370 nm, 1-cm cuvettes, LiCl concentration constant at 0.01M) are described by the equations $A = (1.85 \pm 0.01) \times 10^4[\mathrm{Bi(III)}]$ and $A = (1.79 \pm 0.01) \times 10^4[\mathrm{Bi(III)}]$, respectively, over the bismuth concentration range $4 \times 10^{-6}–4 \times 10^{-5}M$. The equation for acetonitrile medium is $A = (1.51 \pm 0.02) \times 10^4[\mathrm{Bi(III)}]$ (=350 nm) for $4 \times 10^{-6}–8 \times 10^{-5}M$ bismuth. In all the solvents there is no interference from 100 times as much Pb(II), Sb(III), Cd(II) or Sn(II) as Bi(III), in contrast to the extraction–photometric method with bismuth(III) dialkyldithiophosphate.

Our suggestions about choice of the optimum solvent for the spectrophotometric determination are of a general nature, and based on the known physico-chemical properties of the solvents and their correlation with the spectral and thermodynamic properties of the complex, which is valid for a rather wide range of solvents with different chemical nature.

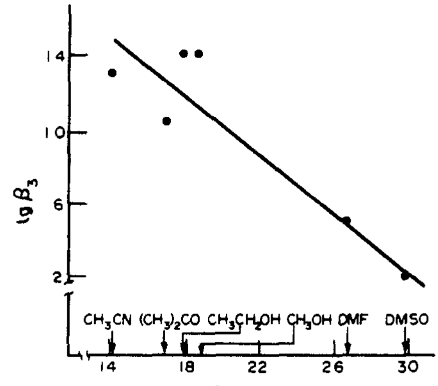

Fig. 4. Dependence of log β_3 on donor number of the solvent.

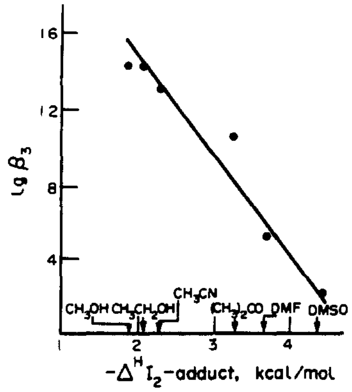

Fig. 5. Dependence of log β_3 on enthalpy of iodine adduct formation with the solvent.

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Summary—Complex formation between bismuth(III) chloride and potassium diphenyldiselenophosphate has been studied spectrophotometrically in acetronitrile, dimethylformamide, acetone, methanol, ethanol and dimethylsulphoxide media. Increased solvation ability is found to shift the maximum absorption band of the complex to longer wavelengths and there is a correlation between the stability constants and the solvent donor strength. Spectrophotometric methods for bismuth(III) determination are proposed, in methanol, ethanol and acetonitrile as media.

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SEMIMICRO DETERMINATION OF MERCAPTANS WITH COPPER(II)

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Copper(II) reacts with many mercapto compounds to yield simultaneously the cuprous mercaptide and a disulphide according to the reaction

$$4RSH + 2Cu^{2+} \rightarrow 2RSCu + RSSR + 4H^+$$

Cupric oleate,[1] acetate[2] and alkyl phthalate[3] solutions have been used as titrants on the macro-scale. The end-point is shown by the blue colour of the excess of reagent. Mercaptoacetic acid cannot be determined by this method because the deep violet cupric–cuprous mercaptide obscures the end-point,[3] but at the end-point in the reverse titration[4] the deep violet precipitate first formed changes to a permanent yellow precipitate of cuprous mercaptide.

Roth[5] suggested an indirect micro-method in which the sample is treated with an excess of cupric butylphthalate. After 5 min, the residual cupric ions are determined iodimetrically. Ellis,[2] however, says that a part of the iodine that is liberated oxidizes the mercaptide to disulphide and introduces error.

The general applicability of the reaction of mercaptans with cupric ion led us to evolve a convenient semi-micro method. Mercaptans can be determined by treating a solution of them in water, methanol, dimethylformamide or acetonitrile with an excess of cupric sulphate solution in water. After 1 min, the residual copper(II) is titrated with mercaptoacetic acid solution.

EXPERIMENTAL

Reagents

Standardized 0.1*M* copper sulphate and 0.1*M* mercaptoacetic acid standardized[6] by treatment with excess of iodine and thiosulphate back-titration.

Procedure

Weigh a sample containing 0.3–1.0 meq of mercaptan into a 150-ml Erlenmeyer flask and dissolve it in 20 ml of water, methanol, dimethylformamide or acetonitrile. Add a measured excess of 0.1*M* cupric sulphate solution and swirl for 1 min. Titrate with 0.1*M* mercaptoacetic acid from a 10-ml burette until the deep violet precipitate first formed changes to a permanent yellow. Near the end-point titrate slowly with vigorous swirling. Run a blank determination on the same volume of cupric sulphate solution.

RESULTS AND DISCUSSION

A wide variety of mercaptans, including primary, secondary and tertiary compounds, was examined. In all cases, the reaction was rapid and complete and the end-point was unaffected. Table 1 gives a comparison of results obtained by the present method and independent methods.

Table 1. Determination of mercaptans with copper(II)

	Purity, %	
Compound	Present method[a]	Comparison method
1-Dodecanethiol	98.1	98.2[b]
o-Mercaptobenzoic acid	96.6	96.5[c]
2-Mercaptoethanol	99.1	99.3[c]
p-Chlorobenzenethiol	99.3	99.5[d]
1-Butanethiol	91.0	90.8[e]
Toluene-α-thiol	98.6	98.4[f]
Allylthiol	93.5	93.6[c]
3-Mercaptopropionic acid	100.0	99.8[c]
Mercaptosuccinic acid	96.7	96.5[b]
2-Mercaptopropionic acid	95.9	95.7[e]
2-Methylpropane-2-thiol	99.0	98.9[f]
2-Naphthalenethiol	98.2	98.0[d]
p-Toluenethiol	97.6	97.6[d]
2-Diethylaminoethanethiol	98.6	98.4[e]
2-Mercaptobenzothiazole	99.2	99.0[d]
2-Mercaptobenzimidazole	97.8	97.6[d]
2-Mercaptobenzoxazole	98.9	98.8[d]
2-Butanethiol	97.9	97.8[b]
Cyclohexanethiol	95.3	95.6[c]

[a] Average of 10 determinations; average deviation in the range 0.2–0.3%.
[b] Hg^{2+} titration[9].
[c] Pb^{4+} titration[10].
[d] alkalimetry[11].
[e] iodimetry[6].
[f] acetylation[12].

The advantages of the present method over methods involving precipitation with silver or mercuric ion are its fixed stoichiometry and its simplicity. Although the iodimetric method yields more accurate results, the number of mercaptans to which it can be applied is limited, and it is reported to give over-oxidation of compounds such as 3-mercaptopropionic, mercaptosuccinic and *o*-mercaptobenzoic acid,[7] and non-stoichiometric or slow reactions with secondary, tertiary and long-chain aliphatic mercaptans,[8] all of which can be determined accurately by the present method.

Organic sulphides, disulphides, thiocyanates and unsaturated compound do not interfere. Chloride, bromide and sulphite also do not interfere. Serious interference is caused by thiourea and ions such as sulphide, thiosulphate, thiocyanate and cyanide. Like ethylenedithiol, *o*-aminobenzenethiol does not reduce copper(II), but forms a cupric mercaptide.

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Summary—A rapid and precise titrimetric method for the determination of mercaptans on the semimicro scale is described. Samples dissolved in water, methanol, dimethylformamide or acetonitrile are treated with a measured excess of cupric sulphate. After 1 min, the excess of copper(II) is back-titrated with standard mercaptoacetic acid solution. At the end-point the violet complex first formed changes to a permanent yellow. The method is applicable to a variety of mercaptans and accurate to 0.2%. It is relatively free from interferences.

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RAPID POLAROGRAPHIC METHOD FOR DETERMINING ARSENIC IN STEEL

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(*Received* 24 *June* 1975. *Accepted* 7 *March* 1976)

Many polarographic methods have been reported for determining micro- or macroamounts of arsenic in steel. They are usually based on three stages: oxidative decomposition of the sample, quantitative separation of the arsenic by extraction,[1,2] distillation[3,4] or co-precipitation[5] and subsequent determination of arsenic by a polarographic method. But none of them is sufficiently rapid, accurate and sensitive for routine analysis.

The Russian Standard Method[6] for determining arsenic in steel involves oxidative attack of the sample with *aqua regia*, treatment with $Ca(H_2PO_2)_2$ in the presence of CuCl and $CuCl_2$ to separate the arsenic in an elementary state, and its subsequent iodometric determination. With arsenic contents of 0.01–0.1% the precision of the method is about 15%.

The British Standard Method[7] is based on the evolution of AsH_3 and its absorption in silver diethyldithiocarbamate–pyridine solution. The precision is 50% and 3% for contents of 0.003% and 0.15% arsenic respectively.

This paper describes a sensitive and accurate polarographic method for determining arsenic in steel, suitable for routine control analysis.

EXPERIMENTAL

Apparatus

Polarograms were recorded with an electronic polarograph model LP-60, using a mercury electrode with a drop-time of 2.97 sec in 0.1*M* potassium chloride and a drop-rate of 4.65 mg/sec. A saturated calomel reference electrode was used for all measurements, in conjunction with a 0.033*M* sodium sulphate bridge.

Reagents and solutions

Concentrated nitric, formic and sulphuric acids; 0.1 g/ml sodium metabisulphite solution; 1% potassium iodide solution; 8% ascorbic acid solution; 0.1% Methyl Orange solution; 0.1*M* manganese sulphate; citrate buffer (1.25*M*) prepared by dissolving 53 g of citric acid monohydrate in hot distilled water, cooling and diluting to 200 ml, neutralizing with 5 g of sodium hydroxide and adjusting to pH 3.0; 40% and 20% sodium hydroxide solutions; arsenic-free iron (less than 0.0005% arsenic). Standard arsenic solution (0.1 mg/ml) was prepared by dissolving 0.132 g of arsenic trioxide in 5 ml of 5% sodium hydroxide solution, diluting to 200 ml with redistilled water and neutralizing carefully with sulphuric acid (1 + 1) (indicator litmus); the solution was then diluted to the mark in a 1000-ml volumetric flask, and standardized by the bromate method.[8]

All reagents used were analytical-reagent grade and were used without further purification.

Procedure

Weigh 0.25–1 g of steel into a 150-ml beaker, add 5 ml of nitric acid (1 + 1) and cover with a watch-glass. When the violent reaction is over, heat on a sand-bath (<200°) to complete decomposition of the sample. Add about 10–15 ml of formic acid dropwise, gradually, and heat carefully to fully expel the nitrogen oxides. Wash the watch-glass with water, cool to room temperature. Add 5 ml of concentrated sulphuric acid and heat gently almost to dryness. Then add 10–20 ml of water, heat to boiling to dissolve the salts and add 20 ml of 0.1 g/ml sodium metabisulphite solution and 1 ml of 1% potassium iodide solution. Cover with the watch-glass, wait for 15 min and

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Preparation of calibration graph

The calibration graphs are prepared by using the same quantity of pure iron as the weight of the sample of steel. The iron is dissolved and treated by the proposed procedure. Then 3.00; 2.00; 1.00; 0.50 and 0.25 ml of the standard arsenic solution are added to 25-ml aliquots in 50-ml volumetric flasks and the solutions are treated according to the procedure described above.

RESULTS AND DISCUSSION

The method is based on an oxidative decomposition of the sample to prevent loss of arsenic as arsine, followed by a reduction of As(V) and Fe(III) with sodium metabisulphite ($Na_2S_2O_5$) and potassium iodide, and subsequent polarographic determination of arsenic (III). This method is sensitive and less tedious than the other methods, and there is no interference from Fe, Si, P, Sn, Sb, Pb, Bi and Cu.

Accuracy and precision

To estimate the possible sources of errors [loss of arsenic during decomposition of the sample, incompleteness of reduction of As(V) and Fe(III), effect of supporting electrolyte composition, *etc.*] samples were prepared from high-purity iron (0.5 g), and different amounts of arsenic(III) were added before and after the dissolution, and arsenic was determined by the procedure described. Table 1 gives the currents obtained on addition of arsenic before (I) and after (II) the decomposition of the samples, for three individual measurements on separately prepared solutions. The equations of both linear calibration curves, calculated by the method of least squares,[9] were $i_I = 0.434 + 0.773C_{As}$ and $i_{II} = 0.432 + 0.799C_{As}$ where i is the current in μA and C_{As} the arsenic concentration in μg/ml. The slopes of the two lines were compared by the Student-t criterion[10] [$t = 1.1 < t(95\%, f = 7) = 2.36$]. The difference between them was found to be determined only by random errors. In addition the mean currents of the two lines at a given arsenic concentration were compared by the F- and t-tests.[9] The values of t and F (see Table 1) indicate that there is no significant difference between the two currents and consequently the dissolution process and the conditions of the reduction have no effect on the accuracy of the arsenic determination. Accordingly the two calibration graphs are identical and can be combined into $i = (0.43 \pm 0.14) + (0.79 \pm 0.06)C_{As}$. The coefficient a of the regression line was tested by the F-criterion.[9] The test $F = 115 > F(95\%, f_1 = 1, f_2 = 3) = 10.13$ shows that the intercept is not zero.

The accuracy and precision of the method were studied with samples of standard steel, containing: As 0.182%, Si 0.37%, Mn 1.68%, P 1.66%, S 0.68%. The results of the arsenic determination by the proposed method and their statistical analysis are given in Table 2.

The accuracy of the method was also studied by fitting the line $y_i = a + bx_i$ to the data, where x_i stands for the arsenic contents, y_i for the amounts found by the proposed method, and a for the initial content of arsenic in the steel (see Table 3). To 0.5-g samples of steel, containing 0.137 ± 0.008% As, 0.22% C, 0.30% Si, 0.65% Mn, 0.045% P, 0.055% S, were added different amounts of standard As(III) solution before the decomposition of the samples (x_i) and they were determined by the polarographic method (y_i = As found). The results are given in Table 3. It was found that the line $y_i = 0.133 + 1.06x_i$ fitted the data: the intercept $a = 0.133$ corresponded to the original arsenic content of the steel, the slope b of the line was unity and therefore, except for random errors, the amounts found were equal to the amounts taken. In Fig. 1 is given the statistical ellipse to test the systematic errors.[11,12]

Tables 4 and 5 consist of data for polarographic determination of arsenic in two different steels, as well as the dispersion analysis, testing possible sources of errors.[9] To

Table 1. The effect of sample pretreatment and reduction on the arsenic determination

Arsenic added, *μg/ml* in final solution	Measured mean current, *μA* (I)	(II)	Statistical tests F_{exp}	$F(95\%, f_1, f_2)$	t_{exp}	$t(95\%, f)$
6.666	5.58	5.70	2.33	19	1.14	2.78
4.444	3.80	4.03				
2.222	2.35	2.28	2.10	19	1.10	2.78
1.111	1.30	1.38				
0.555	0.74	0.70	1.32	19	0.40	2.78

Table 2. The results of polarographic determination of arsenic in standard steel samples and their statistical analysis

No.	*W*, g (sample weight)	*V*, ml (aliquot from 100 ml)	*i*, *μA* (mean)	As, %*	*S*, %As	Confid. limit (*n* = 7), %As	$t = \frac{(x - \mu_0)\sqrt{n}}{S}$	$t(95\%, f = 6)$
1′,1″	0.4433	25.00	3.86	0.195				
1‴	0.4433	20.00	3.10	0.191				
2′,2″,2‴	0.5025	25.00	4.28	0.193				
3, 3′	0.2500	direct	3.86	0.173				
4	0.2502	direct	3.80	0.170				
			Mean	0.1844	0.01179	±0.011	0.65	2.45

* As = 0.5(i-0.43)/0.79%.

estimate the precision of the method the coefficient of variation ($V\%$) is also used. The dispersion analysis of the data in Tables 4 and 5 showed equal random errors in groups A, B, C (three 25-ml aliquots of a sample of steel):

Table 4

$$\chi^2 = 2.303(f_{ji}\log S^2 - \Sigma f_i \log S_i^2)$$
$$= 2.31 < \chi^2(99\%, f = 5) = 15.1$$
$$F = \frac{S_2^2}{S_1^2} = 1.57 < F(99\%, f_1 = 2, f_2 = 17) = 6.11$$
$$\sqrt{S_1^2} = 0.0077\%; \quad \sqrt{S_2^2} = 0.0097\%$$

Table 5

$$\chi^2 = 3{\cdot}67 < \chi^2(99\%, f = 3) = 11.3$$
$$F = 2.78 < F(99\%, f_1 = 2, f_2 = 11) = 7.20$$
$$\sqrt{S_1^2} = 0.0042\%; \quad \sqrt{S_2^2} = 0.0071\%$$

Consequently the random errors of comparison $\sqrt{S_1^2}$ and of the reproducibility $\sqrt{S_2^2}$ do not differ statistically.

Selectivity

The influence of pH and the interference of some elements (Cu, Mn, Sn, Sb, Bi, Pb, Fe) have been investigated in another work.[13] It was found that Fe(II) and Mn(II) and pH affect the shape and the height of the arsenic wave. On the basis of these results we recorded all polarograms of arsenic at given Fe(II) and Mn(II) concentrations, under the following conditions: $0.045M$ ascorbic acid, $0.125M$ citric acid, $0.004M$ $MnSO_4$, $0.009M$ Fe(II). All statistical tests for systematic errors also proved that the different

Table 3. The test for systematic errors

No.	W, g	As, taken, % x_i	i, μA	As found, % $y_i = \frac{0.02i}{0.68W}$
1	0.5147	0.037	3.09	0.177
2	0.5026	0.038	2.77	0.162
3	0.4846	0.039	2.62	0.159
4	0.3173	0.060	1.95	0.180
5	0.5038	0.075	4.12	0.240
6	0.5045	0.075	4.00	0.233
7	0.5131	0.148	4.63	0.265
8	0.4948	0.154	5.34	0.317
9	0.5213	0.219	6.35	0.358

Table 4. Data for arsenic in steel by the polarographic method. As = $0.02(i-0.56)/0.79W\%$

$\longrightarrow i$

$\downarrow j$

No., m	W, g	i_1, μA	i_2, μA	i_3, μA	$\%As_1$, x_{j1}	$\%As_2$, x_{j2}	$\%As_3$, x_{j3}	%As, mean
1	0.4954	3.67_5	3.67_5	—	0.159	0.159	—	0.159
2	0.5013	3.75	3.60	—	0.161	0.154	—	0.158
3	0.4990	3.52_5	3.45	3.60	0.150	0.147	0.154	0.150
4	0.5006	3.30	3.30	3.75	0.138	0.138	0.161	0.146
5	0.5122	3.45	3.60	3.52_5	0.143	0.150	0.146	0.146
6	0.5022	3.37_5	3.15	—	0.142	0.134	—	0.138
7	0.5021	3.30	3.15	3.15	0.138	0.134	0.134	0.135
8	0.5032	3.30	3.00	3.37_5	0.138	0.123	0.142	0.134
9	0.5037	3.30	3.15	—	0.138	0.130	—	0.134
10	0.4990	3.52_5	2.85	—	0.150	0.116	—	0.133
11	0.4970	3.15	3.22_5	3.07_5	0.132	0.136	0.128	0.132
				groups	A	B	C	0.1423 ± 0.007 mean

$$S = \left(\frac{\sum_1^m \sum_1^n (x_{ji} - \bar{x}_j)^2}{n - m}\right)^{1\ 2} = 0.0087\% \qquad \Delta\bar{x} = \frac{t(P, f = 10)\cdot S}{\sqrt{mn}} = 0.007\%$$

$$n = 28 \qquad V = \frac{S\cdot 100}{\bar{x}} = 6.3\%$$

Table 5. Data for the arsenic analysis of steel by the polarographic method and their dispersion analysis

$$\%As = \frac{(i - 0.56)2\cdot 10^{-2}}{0.79\cdot W}$$

No., m	W, g	i_1, μA	i_2, μA	i_3, μA	$\%As_1$, x_{j1}	$\%As_2$, x_{j2}	$\%As_3$, x_{j3}	%As, mean
1	0.4993	1.65	1.65	1.72_5	0.0553	0.0553	0.0591	0.0566
2	0.4990	1.95	1.72_5	1.87_5	0.0705	0.0591	0.0667	0.0654
3	0.4996	1.90	1.80	1.85	0.0679	0.0628	0.0654	0.0654
4	0.5026	1.95	2.05	2.10	0.0700	0.0751	0.0776	0.0742
			Groups		A	B	C	0.0654 ±0.0048

$S = 0.00387\%$.
$V = 5.9\%$.

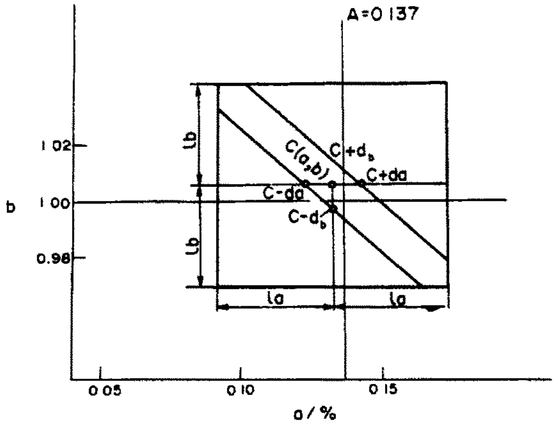

Fig. 1. Statistical ellipse for estimation of the systematic errors.

elements contained in steel do not interfere with the arsenic polarographic determination. Consequently, the proposed method, without preliminary separation of arsenic, is sufficiently sensitive, much more rapid and convenient for routine control analysis (the time of analysis is 20–30 min after the decomposition of the sample).

Sensitivity

The fact that Fe(II) and Mn(II) considerably increase the limiting current of arsenic had a favourable effect on increasing the sensitivity of polarographic As(III) determination. As a rule in the other supporting electrolytes the determination of As concentrations less than $10^{-4}M$ is difficult. The maximum on the arsenic wave in the presence of Fe(II), Mn(II) and citric acid at pH 3.0 enables us to determine As(III) at concentrations of about 10^{-7}–$10^{-6}M$ by the classical polarographic method with sufficient accuracy and precision.

The lower limit of determination was found from the equation of the calibration curve[9]

$$\mathrm{As}_{\min} = \frac{t(P,f)[S_a + \bar{x}S_b]}{b + t(P,f)\cdot S_b} = 0.311\ \mu g/\mathrm{ml}$$

where S_a and S_b are the mean-square errors of the coefficients a and b of the regression line. This lower limit corresponds to an As content of 0.0015% if a sample is dissolved and made up to 50 ml and analysed polarographically directly. For fourfold dilution and 0.5 g of steel the lower limit of determination is 0.012% As, which corresponds to the lowest measurable signal ($i_{\min} = 0.21\ \mu A$).

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INTERFERENCES IN THE ATOMIC-ABSORPTION DETERMINATION OF SILICON

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In recent years much interest has been expressed in interferences in atomic-absorption spectroscopy (AAS) determination of Si.[1–6] Enhancement by sodium was observed[1] as well as some general enhancement effects.[3–6] There is a suggestion that the effects may be dependent on the nebulizer and/or spray chamber arrangement.[6]

The present investigation was made in an attempt to establish the effects of possible interferents in amounts up to 10 mg/ml on the absorption of Si (50 μg/ml).

EXPERIMENTAL

The measurements were performed on a Perkin–Elmer Model 303 atomic-absorption spectrometer with the burner assembly from the Model 403 and a standard N_2O burner (slot 0.48 × 50 mm). The flow-rate of N_2O was 12 l./min. The flow-rate of acetylene (about 7.5 l./min) was adjusted in such a way that the upper edge of the "red feather" was 30 mm above the burner slot when water was

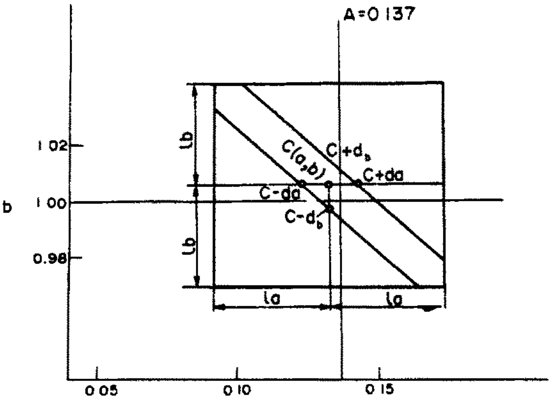

Fig. 1. Statistical ellipse for estimation of the systematic errors.

elements contained in steel do not interfere with the arsenic polarographic determination. Consequently, the proposed method, without preliminary separation of arsenic, is sufficiently sensitive, much more rapid and convenient for routine control analysis (the time of analysis is 20–30 min after the decomposition of the sample).

Sensitivity

The fact that Fe(II) and Mn(II) considerably increase the limiting current of arsenic had a favourable effect on increasing the sensitivity of polarographic As(III) determination. As a rule in the other supporting electrolytes the determination of As concentrations less than $10^{-4}M$ is difficult. The maximum on the arsenic wave in the presence of Fe(II), Mn(II) and citric acid at pH 3.0 enables us to determine As(III) at concentrations of about 10^{-7}–$10^{-6}M$ by the classical polarographic method with sufficient accuracy and precision.

The lower limit of determination was found from the equation of the calibration curve[9]

$$\mathrm{As}_{\min} = \frac{t(P,f)[S_a + \bar{x}S_b]}{b + t(P,f)\cdot S_b} = 0.311\ \mu g/\mathrm{ml}$$

where S_a and S_b are the mean-square errors of the coefficients a and b of the regression line. This lower limit corresponds to an As content of 0.0015% if a sample is dissolved and made up to 50 ml and analysed polarographically directly. For fourfold dilution and 0.5 g of steel the lower limit of determination is 0.012% As, which corresponds to the lowest measurable signal ($i_{\min} = 0.21\ \mu A$).

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EXPERIMENTAL

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The 5000-ppm silicon stock solution was prepared by dissolving silica in sodium hydroxide solution. The 10-mg/ml stock solutions of interferents other than vanadium were prepared by dissolving the high-purity metals in hydrochloric acid. The vanadium solution was made by dissolving V_2O_5 in the acid. The silicon stock solution was found to be stable for several months; the solutions measured, prepared by dilution, contained 50 ppm Si, 100 ppm Na and any interferents added. They were acidified with 4 ml of 6 *M* hydrochloric acid per 100 ml and measured within 8 hr of preparation. The silicon calibration curve was linear up to 150 ppm Si under these conditions. Non-selective absorption at the Si 243.5 nm line was tested and found negligible in all cases.

RESULTS AND DISCUSSION

Effects of acids (Fig. 2)

The acids were always added after dilution of the silicon solution to 500–1000 ppm; the addition of acids to more concentrated silicon solutions may cause the polymerization of $SiO_2 . xH_2O$. The depressive effect of sulphuric acid is not in correlation with the change in viscosity.

Effect of alkali metals (Fig. 3)

There is an inverse correlation between atomic number of the elements and the enhancement effects. Silicon is unlikely to be ionized, so the effect is most likely caused by formation of more easily volatilized mixed oxides. There is no plateau on the enhancement curve, so it is very important to keep the alkali metal concentration strictly constant in practical analysis (or below $10^{-2}M$ for Na and K). This factor may explain the somewhat higher precision of Si determination by Teflon bomb decomposition than by alkali fusion, which was recently reported.[6] However, the interference can be reduced by dilution, at the expense of sensitivity.

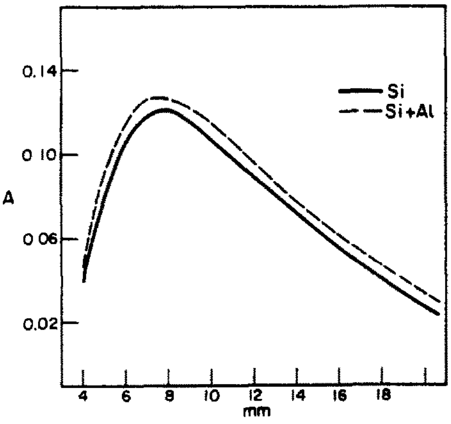

Fig. 1. Flame profile (50 ppm Si; ditto + 1000 ppm Al).

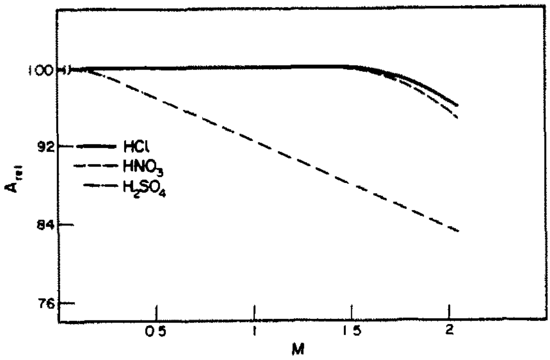

Fig. 2. Effect of acids on the absorbance of 50 ppm Si.

Effect of aluminium (Fig. 4)

This effect cannot be explained by a change in the lateral diffusion in the flame (see Fig. 5); with the same experimental arrangement a clear lateral diffusion effect by sulphuric acid was observed earlier.[7] Also the flame-height profile in presence of Al^{3+} is not changed except for a constant

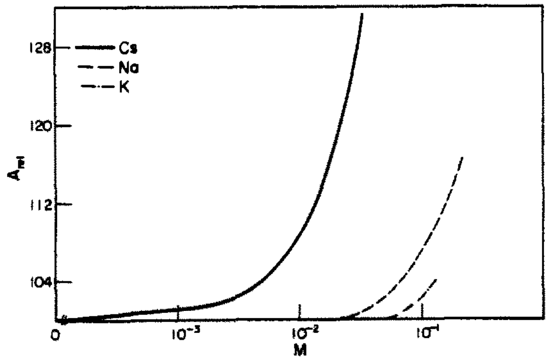

Fig. 3. Effect of alkali metals on the absorbance of 50 ppm Si.

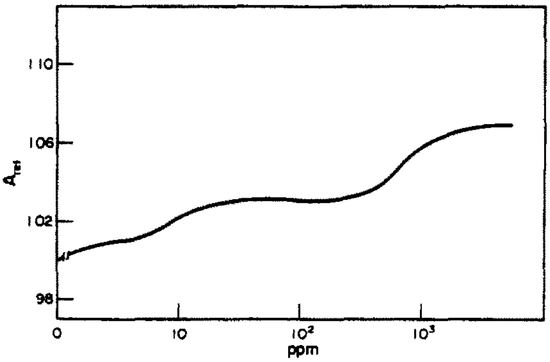

Fig. 4. Effect of Al on the absorbance of 50 ppm Si.

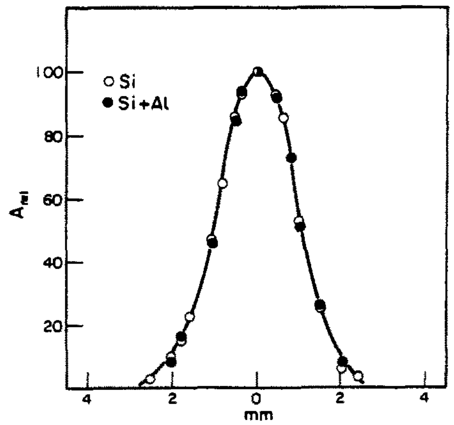

Fig. 5. Distribution of Al atoms in the flame cross-section 8 mm above the burner slot (50 ppm Si; ditto + 1000 ppm Al).

signal enhancement (Fig. 1). Thus, the enhancement effect probably takes place in the first steps of the atomization process. The two plateaux on the curve (Fig. 4) may be due to two different mechanisms.

The effect of iron, nickel, manganese (Fig. 6)

The effects of Al and Fe or Ni are additive.

The effect of vanadium (Fig. 7)

This depends on the oxidation state of the vanadium, the depression being greater with V(V) than with V(IV). The simultaneous influence of V and Fe is constant over a wide range of V:Fe ratios (7% enhancement for V:Fe < 9, falling to 2% for V alone). This situation is analytically favourable, as observed earlier in the good precision of Si determination in ferrovanadium.[8]

The effect of magnesium, etc.

The plateaux on the Mg interference curve depend on the Si:Mg ratio (Fig. 8), and the effects of Al and Mg are practically additive.

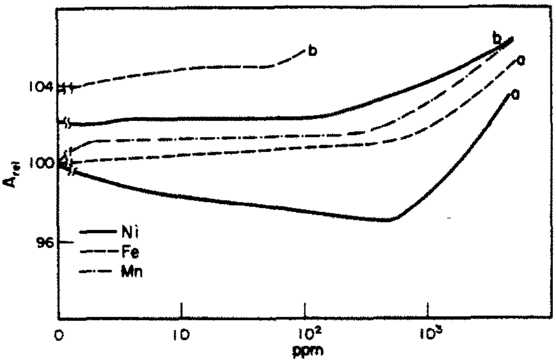

Fig. 6. Effect of Ni, Mn, Fe (curves *a*) and Ni, Fe simultaneously with 500 ppm Al (curves *b*) on the absorbance of 50 ppm Si.

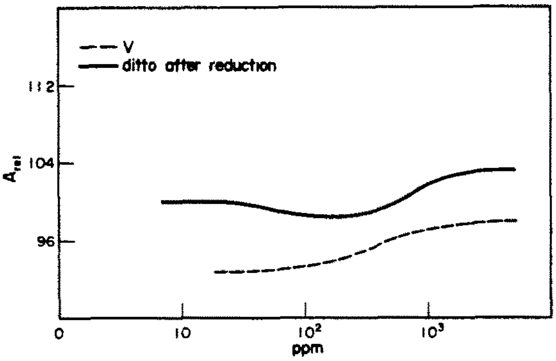

Fig. 7. Effect of V on the absorbance of 50 ppm Si (reduction with $NH_2OH.HCl$).

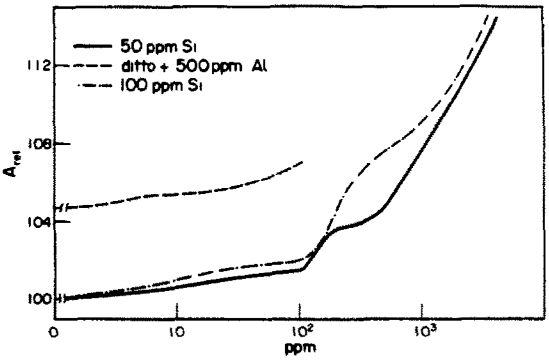

Fig. 8. Effect of Mg on the absorbance of 50 and 100 ppm Si and effect of Mg in presence of 500 ppm Al on the absorbance of 50 ppm Si.

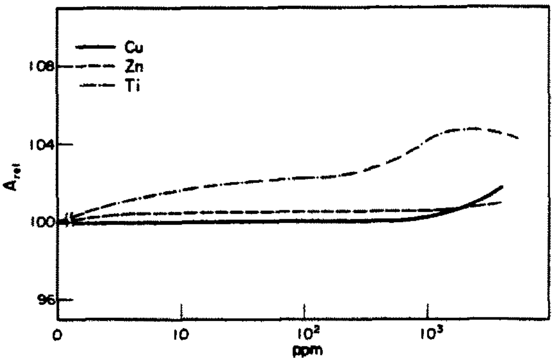

Fig. 9. Effect of Cu, Zn and Ti on the absorbance of 50 ppm Si.

In the case of Ti (Fig. 9) a higher acidity was used to prevent hydrolysis, so the decrease in interference at higher concentrations may be caused by the depressive effect of the acid. Both Ti(III) and Ti(IV) were tested, and the enhancement effect was somewhat higher with Ti(III).

The actual magnitude of the effects depends on the nebulizer and spray chamber arrangements, but the form of the interference curves is not usually changed.

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Summary—The following substances have been investigated with regard to their interfering effect in the determination of silicon by AAS: HCl, HNO_3, H_2SO_4, Na^+, K^+, Cs^+, Al^{3+}, Ni^{2+}, Mn^{2+}, Fe^{3+}, V^{5+}, Mg^{2+}, Cu^{2+}, Zn^{2+} and Ti^{4+}. Some ternary systems with aluminium have been studied to examine the additive effects. Most of the interferents enhance the silicon absorption; only nickel and the acids exert depressive effects; the interference of copper and zinc is negligible.

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FORMATION OF Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I) AND Cd(II) HEXACYANOCOBALTATES

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Some authors[1–7] have considered the reactions occurring in aqueous solution between $K_3Co(CN)_6$ and uni-, bi- and tervalent cations, but it appears that so far the reaction stoichiometries at various reagent concentrations have not been determined. We therefore decided to investigate the precipitation reactions of $K_3Co(CN)_6$ (hereafter referred to as An) with various cations Me [Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I) and Cd(II)] by means of direct and reverse titrations. The reagent concentration range examined was the widest possible, ranging from the reagent solubility down to the lowest limit detectable with the instruments used.

EXPERIMENTAL

The Me solutions were prepared from analytically pure salts, and standardized according to the usual techniques.[8]

The $K_3Co(CN)_6$ solutions were made by direct weighing of the analytically pure salt that had been dried over P_2O_5, and were stored in the dark to avoid photoreactions;[9] they were periodically checked spectrophotometrically in the 300–400 nm range, a single maximum at 310 nm confirming the exclusive presence of the hexacyanocobaltate species.[9]

The precipitations of Me with An and *vice versa* were followed by a conductometric high-frequency apparatus with digital read-out.[10] This technique was preferred because (*a*) it eliminated difficulty in choosing electrodes (an advantage over the potentiometric method), (*b*) readings could be taken immediately (zero equilibration time), (*c*) in the case of cation-exchange in the precipitates there would be a change in the solution conductivity, which could be detected even if the precipitates had similar K_{sp} values.

For each titration, the ratio between the analytical concentrations of Me and An at the equivalence point was calculated: $R = [Me]/[An]$. The volume titrated was always 100 ml, and the Me and An concentrations were allowed to vary.

Me titrations with An

Reactions occurring on addition of An to the solutions of Me always produce only $Me_3[Co(CN)_6]_n$ (n = charge on Me) except for Cd(II), for which, by further addition of An beyond the first equivalence point with $R = 1.5$, a precipitate with $R = 1.0$, corresponding to $CdKCo(CN)_6$, is obtained.

Table 1 reports the Me concentration range, R values, formulae and colours of the precipitates obtained. Titrations of 0.05–25 mmole of the cations gave results with errors ranging from −0.5 to +0.6%, average 0.3%.

Titrations of An with Me

In the reverse titrations, the stoichiometry of the precipitates was variable, depending on the nature of the precipitating cation and on the An concentration (Table 2).

Titration of 0.1–22 mmole of An with the various Me solutions gave errors ranging from −0.8 to +0.8%, average 0.2%, except for two results with zinc as titrant (± 1.2%).

DISCUSSION OF RESULTS

The interpretation of the stoichiometry of the reactions is based on the possibility of ion-pair formation between $Co(CN)_6^{3-}$ and K^+,[11,12] the concentration of the latter being three times that of the former. K_{eq} for $KCo(CN)_6^{2-}$ formation is between 17 and 30,[11,12] so ion-pairs should be the predominant species in solution and their degree

Table 1. Concentration ranges, R values, formulae and colour of compounds obtained by precipitating Me with $K_3Co(CN)_6$

Cation precipitated	Me concentration range	R value	Formula	Colour
Fe(II)	$0.90 \le pFe \le 2.92$	$1.50 \begin{vmatrix} +0.004 \\ -0.006 \end{vmatrix}$	$Fe_3[Co(CN)_6]_2$	Ivory-yellow
Co(II)	$0.69 \le pCo \le 2.70$	$1.50 \begin{vmatrix} +0.008 \\ -0.008 \end{vmatrix}$	$Co_3[Co(CN)_6]_2$	Pink
Ni(II)	$0.81 \le pNi \le 2.98$	$1.50 \begin{vmatrix} +0.004 \\ -0.009 \end{vmatrix}$	$Ni_3[Co(CN)_6]_2$	Sky-blue
Cu(II)	$0.81 \le pCu \le 3.30$	$1.50 \begin{vmatrix} +0.004 \\ -0.009 \end{vmatrix}$	$Cu_3[Co(CN)_6]_2$	Green-blue
Zn(II)	$0.70 \le pZn \le 3.02$	$1.50 \begin{vmatrix} +0.013 \\ -0.009 \end{vmatrix}$	$Zn_3[Co(CN)_6]_2$	White
Ag(I)	$0.60 \le pAg \le 3.31$	$1.00 \begin{vmatrix} +0.004 \\ -0.014 \end{vmatrix}$	$Ag_3Co(CN)_6$	White
Cd(II)	$0.73 \le pCd \le 3.16$	$1.50 \begin{vmatrix} +0.003 \\ -0.005 \end{vmatrix}$ § $1.00 \begin{vmatrix} +0.005 \\ -0.004 \end{vmatrix}$	$Cd_3[Co(CN)_6]_2$ $CdKCo(CN)_6$	White White

§ Transformation from R = 1.50 to R = 1.00 occurred in the solid phase.

Table 2. Concentration ranges, *R* values, formulae and colour of compounds obtained by precipitating $K_3Co(CN)_6$ with Me

Precipitating cation	An concentration range	R value	Formula	Colour
Fe(II)	$0.93 \le pAn \le 2.64$	$1.50 \left\lvert \begin{array}{l} +0.006 \\ -0.008 \end{array}\right.$	$Fe_3[Co(CN)_6]_2$	Ivory-yellow
Co(II)	$0.85 \le pAn \le 3.03$	$1.00 \left\lvert \begin{array}{l} +0.003 \\ -0.008 \end{array}\right.$	$CoKCo(CN)_6$	Pink
		§ $1.50 \left\lvert \begin{array}{l} +0.010 \\ -0.008 \end{array}\right.$	$Co_3[Co(CN)_6]_2$	Pink
Ni(II)	$1.46 \le pAn \le 2.85$	$1.00 \left\lvert \begin{array}{l} +0.008 \\ -0.004 \end{array}\right.$	$NiKCo(CN)_6$	Sky-blue
		§ $1.50 \left\lvert \begin{array}{l} +0.005 \\ -0.006 \end{array}\right.$	$Ni_3[Co(CN)_6]_2$	Sky-blue
	$1.26 < pAn < 1.46$	$1.50 \rightarrow 1.33$	——	
	$1.00 \le pAn \le 1.26$	$1.33 \left\lvert \begin{array}{l} +0.003 \\ -0.008 \end{array}\right.$	$Ni_4K[Co(CN)_6]_3$	Sky-blue
	$0.66 \le pAn < 1.00$	tends to 1.0	——	
Cu(II)	$0.85 \le pAn \le 3.15$	$1.50 \left\lvert \begin{array}{l} +0.012 \\ -0.006 \end{array}\right.$	$Cu_3[Co(CN)_6]_2$	Green-blue
Zn(II)	$1.55 < pAn \le 3.03$	$1.50 \left\lvert \begin{array}{l} +0.002 \\ -0.006 \end{array}\right.$	$Zn_3[Co(CN)_6]_2$	White
	$0.73 \le pAn \le 1.55$	$1.00 \left\lvert \begin{array}{l} +0.012 \\ -0.002 \end{array}\right.$	$ZnKCo(CN)_6$	White
		§ $1.50 \left\lvert \begin{array}{l} +0.008 \\ -0.008 \end{array}\right.$	$Zn_3[Co(CN)_6]_2$	White
Ag(I)	$0.60 \le pAn \le 3.31$	$3.00 \left\lvert \begin{array}{l} +0.007 \\ -0.003 \end{array}\right.$	$Ag_3Co(CN)_6$	White
Cd(II)	$0.73 \le pAn \le 3.16$	$1.00 \left\lvert \begin{array}{l} +0.006 \\ -0.003 \end{array}\right.$	$CdKCo(CN)_6$	White
		§ $1.50 \left\lvert \begin{array}{l} +0.002 \\ -0.003 \end{array}\right.$	$Cd_3[Co(CN)_6]_2$	White

§ Transformation from R = 1.00 to R = 1.50 occurred in the solid phase.

of formation should increase with increasing $K_3Co(CN)_6$ concentration.

On these premises, we can assume that in all the titrations considered, the first stage consists of the reaction of Me with $KCo(CN)_6^{2-}$ species:

$$2Me^{n+} + nKCo(CN)_6^{2-} = Me_2[KCo(CN)_6]_n \qquad (1)$$

Factors such as the nature of Me, concentration of An, order of addition of reagents, may then favour a solid phase transformation:

$$Me_2[KCo(CN)_6]_n + Me^{n+} \rightleftharpoons Me_3[Co(CN)_6]_n + nK^+ \qquad (2)$$

or, over a narrow concentration range for Ni(II) added to An, the formation of $Ni_4K[Co(CN)_6]_3$:

$$3NiKCo(CN)_6 + Ni^{2+} = Ni_4K[Co(CN)_6]_3 + 2K^+ \qquad (3)$$

In the titrations of Me with An, only the $Me_3[Co(CN)_6]_n$ species were obtained [reactions (1) and (2)] except for Me = Cd(II) where further addition of $K_3Co(CN)_6$ after the first equivalence point ($R = 1.50$) leads to formation of $CdKCo(CN)_6$ ($R = 1.00$).

In titrations of An with Me, the behaviour can be classified according to the atomic number of the metal and its position in the periodic table. For the group Fe(II), Co(II) and Ni(II), whereas Fe(II) gives exclusively $Fe_3[Co(CN)_6]_2$, Co(II) first forms the compound with $R = 1.00$ [$CoKCo(CN)_6$], which transforms into $Co_3[Co(CN)_6]_2$, and Ni(II) behaves like Co(II) with dilute An solution, but at pAn ≤ 1.26 gives a single compound with $R = 1.33$, having the formula $Ni_4K[Co(CN)_6]_3$ and being stoichiometrically equivalent to $NiKCo(CN)_6 + Ni_3[Co(CN)_6]_2$; for pAn values lower than 1.00, a trend towards quantitative precipitation of $NiKCo(CN)_6$ is observed. The stability of the compounds of $Me_3[Co(CN)_6]_2$ type, with respect to addition of potassium ions, is Fe(II) > Co(II) > Ni(II). Cu(II) and Ag(I) show identical behaviour, since they form exclusively the $Me_3[Co(CN)_6]_n$ species. Zn(II) and Cd(II) react almost identically, both forming the $MeKCo(CN)_6$ and $Me_3[Co(CN)_6]_2$ types of compounds.

The titration errors are fairly small, and the reactions can be exploited analytically for the frequentometric determination of these metal ions or, more usefully, of $K_3Co(CN)_6$, since no valid methods have hitherto been proposed for the latter.

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FLUORINE-19 MAGNETIC RESONANCE IN MEASUREMENT OF THE THERMODYNAMICS OF THE REACTION OF *o*-ALKYLPHENOLS WITH HEXAFLUOROACETONE[*]

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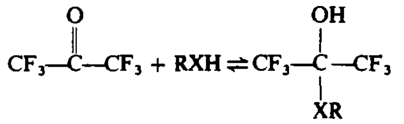
(*Received* 23 *February* 1976. *Accepted* 31 *March* 1976)

Hexafluoroacetone (HFA) has been used advantageously as a sensitive probe in the analysis of compounds containing active hydrogen. Leader[1,2] has examined HFA adducts of various alcohols, amines, mercaptans, oximes, *etc.* and found that the fluorine magnetic resonance (FMR) signals of the adducts are generally sharp and characteristic of the compounds being investigated. These signals spread over a 10-ppm range. Different functional groups in multifunctional compounds can be conveniently examined at the same time. Owing to the relatively high sensitivity of FMR (exceeded only by proton magnetic resonance, PMR) and the presence of six fluorine nuclei in each functional adduct, small samples of a few μl or mg can be easily studied. Also, use of expensive deuterated solvents is avoided.

However, the adduct reaction is an equilibrium:



$$CF_3-\overset{\overset{\displaystyle O}{\|}}{C}-CF_3 + RXH \rightleftharpoons CF_3-\underset{\underset{\displaystyle XR}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CF_3 \qquad (1)$$

where X is O, S, NH, or NR′, *etc.* Although this equilibrium generally lies far to the right,[3,4] incomplete reaction at room temperature has been observed.[2,5] Therefore thermodynamic data for it would be useful in devising analytical procedures based on it. Such data could also readily be correlated with reactivity of functional compounds, and therefore useful in correlation of reactivity parameters with structural influences or solvent effects. In this work, the equilibria of HFA with a series of *o*-alkylphenols are examined at several temperatures, and correlation of the thermodynamic data with other structural parameters is discussed.

EXPERIMENTAL

The phenols studied were reagent grade chemicals, and were further purified by fractional distillation. HFA was purchased from Pierce Chemical Co. Reagent grade ethyl acetate was dried by a Soxhlet extraction using activated 4A molecular sieves and used immediately; this procedure removed any ethanol completely and reduced the water content to below 50 ppm. It is a more effective way of removing these impurities than the alumina column reported earlier.[5] The HFA reagent in ethyl acetate was prepared in a plastic bag filled with dried nitrogen, and the general procedure in handling the reagent was as described by Leader.[1,2] The reaction in equation (1) was carried out *in situ* in a 1-ml volumetric flask. Small quantities of hexafluorobenzene were added to provide the instrument lock signal. 1,2-Difluorotetrachloroethane, obtained from PCR, Inc., and further purified by fractional distillation, was used as internal standard for integral calibration. This signal is observed 96.07 ppm downfield from that of C_6F_6.

The FMR spectra were obtained on a Bruker HFX-90 spectrometer, operated at 84.67 MHz and equipped with a variable temperature probe. The probe temperature was measured with a calibrated copper–constantan thermocouple and checked with a thin thermometer held in the spinning sample holder. The temperature was controlled within ± 1° during the measurement. Sealed tubes were used in all measurements. The equilibrium constant of equation (1) was calculated from

$$K = [c/a(b - c)] \qquad (2)$$

where a is the molar concentration of the excess of HFA (which gives a sharp peak 88.6 ppm downfield from that of C_6F_6), c is that of the phenolic adduct, measured by integration of the spectra; b is the initial molar concentration of the phenol. The adduct signals generally occurred in a region a few ppm upfield from the HFA peak and were slightly temperature-dependent.

Table 1. Comparison of log *K* with other substituent constants

ortho-substituent	log *K*	σ_{ortho}[†]	σ^*[‡]	σ^-[‖]
$-CH_3$	2.03	−0.13	0.00	−0.13
$-CH_2CH_3$	1.93	−0.13[§]	−0.10	−0.15
$-CH(CH_3)_2$	1.87	−0.23	−0.19	−0.15
$-C(CH_3)_3$	0.76	−0.52	−0.30	−0.08

[†] Apparent σ constants from reference 6, except for the ethyl compound.

[‡] Taft's constant from R. W. Taft, Jr. in *Steric Effects in Organic Chemistry*, M. S. Newman, ed., Chap. XIII. Wiley, New York, 1956.

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[*] Hercules Research Center Contribution No. 1675.

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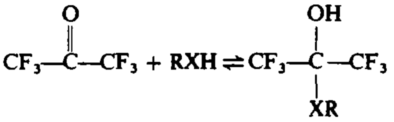

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RESULTS AND DISCUSSION

The equilibrium constants of the HFA adducts of several *o*-alkylphenols (listed in Table 1) were measured at 0–68° in ethyl acetate as solvent. The reaction was found to be truly reversible and thermodynamically controlled. Equilibrium was reached in a few minutes except in the case of *o*-tert-butylphenol at 0°, for which 1 hr was necessary. Ample time should be allowed for equilibrium to be reached before measurements are taken.

The signal from the excess of HFA increased with increasing temperature and that from the adduct decreased.

The logarithms of the equilibrium constants measured at 25° are listed in Table 1, together with several other constants reported in the literature. The enthalpies and entropies of the reaction, derived from the variation of the equilibrium constant with temperature, are summarized in Table 2.

In quantitative analyses of such functional compounds by use of FMR and HFA, knowledge of the chemical equilibrium is important. For example, the ΔH and ΔS values of *o*-ethylphenol, Table 2, show that the reaction at 40° is only 92.5% complete if $b = 0.05M$ and $a = 0.5M$. However, if the same measurement were made at 0°, the reaction would be 99.6% complete. Because the precision of the NMR integral is generally about ±2%, the reaction at 0° under these conditions can be considered virtually quantitative.

The log K values reported in Table 1 correlate fairly linearly with the apparent σ_{ortho} obtained from the pK_a values for the phenols in water at 25°,[6] and change in the same direction as those of Taft's constants within the series. However, no apparent correlation was found between log K and σ^- measured from the phenolic proton shift;[7] this can be partly attributed to the dissimilarity of the properties measured. For example, the chemical shift of *ortho*-substituted phenols in dimethyl sulphoxide was shown to be influenced by the substituents mainly through electronic effects,[7] whereas the substituent constant based on reactivity measurements includes contributions from both electronic and steric effects, as well as resonance effects. In addition, –OH chemical shifts are known to be greatly influenced by intermolecular interactions, such as hydrogen bonding and magnetic shielding by solvent molecules.

Table 2. Enthalpies and entropies of reaction of *o*-alkylphenols with HFA in ethyl acetate

ortho-substituent	ΔH, *kcal/mole*	ΔS, *cal. mole^{-1}.deg^{-1}*
$—CH_3$	-15 ± 1	-41 ± 2
$—CH_2CH_3$	-14	-38
$—CH(CH_3)_2$	-13.5	-37
$—C(CH_3)_3$	-5	-14

As expected, the thermodynamic data shown in Table 2 indicate that the reaction becomes less exothermic as the size of the *ortho*-substituent increases, suggesting the importance of steric interaction. This steric effect is very pronounced in the case of *o*-tert-butyl substituent. It is also interesting to note that within the series ΔH changes roughly linearly with ΔS, indicating the existence of an isokinetic relationship.[8]

The main attraction of the method is that it provides direct measurement of two of the parameters needed for determining equilibrium constants, but the error is about 5%.

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Summary—The reaction of several *o*-alkylphenols with hexafluoroacetone at 0–68° was followed by measuring the fluorine magnetic resonance. A knowledge of the equilibrium of the hemiacetal formation is useful in devising schemes for determination of these compounds. The enthalpy and entropy changes for the equilibrium were found to become less negative with increasing size of the *ortho*-substituents, indicating the importance of steric interaction. The equilibrium data correlate well with Taft's constant and σ_{ortho} from pK_a values, but deviate from σ^- derived from measurements of phenolic proton chemical shifts.

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SOLVENT EXTRACTION AND PHOTOMETRIC DETERMINATION OF MOLYBDENUM (VI) WITH 2-AMINOBENZENETHIOL*

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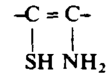
In our search for sensitive reagents containing sulphur as a donor atom for molybdenum, 2-aminobenzenethiol[1] was found to be a good colour-forming reagent. There are only a few chelating agents with the



$$\begin{array}{cc} -C = & C- \\ | & | \\ SH & NH_2 \end{array}$$

grouping that form stable complexes with metal oxo-cations such as VO_2^+, WO_2^{2+}, TiO^{2+} and MoO_2^{2+}.[2] Molybdenum usually forms stable oxo-species, *e.g.*, MoO_2^{2+}, MoO^{4+}, $MoO(OH)^{3+}$, in combination with various chelating agents in the acidic pH range. Except for instances where ligands such as dithiocarbamates reduce Mo(VI) to Mo(V), the stable chelates of oxo-molybdenum ions are reported to be formed from Mo(VI).

The present investigation shows that with 2-aminobenzenethiol, molybdenum forms a green complex which is quantitatively extractable into chloroform at pH 1.4–2.8. The colour is stable for 2 hr at room temperature and the molar absorptivity is 7.08×10^4 l.mole^{-1}.cm^{-1}. The reagent has been applied to the estimation of Mo in high-speed alloy steel containing Cr, Mo, W and V.

EXPERIMENTAL

Reagents

Ammonium heptamolybdate octahydrate was dissolved in water containing a few drops of ammonia and the solution standardized gravimetrically by the 8-hydroxyquinoline method.[3] Working solutions were prepared by appropriate dilution of the stock solution.

Chloroform was freed from alcohol by washing with dilute sulphuric acid, dilute ammonia and then twice-distilled water. Anhydrous sodium sulphate was used to free the organic phase from water.

Purification of 2-aminobenzenethiol. The reagent was fractionally distilled under reduced pressure. Because the compound is sensitive to atmospheric oxidation the distillation system was saturated with nitrogen. The product distilling at 88–91°/1 mmHg was kept frozen under nitrogen. The pure liquid is almost colourless at room temperature.

A 2% w/v solution of reagent was freshly prepared in pure chloroform before use.

Procedure

Adjust the pH of the aqueous molybdenum solution (10 ml) to 2.0. Add 5 ml of 2% reagent solution and 1 ml of pure chloroform, shake the mixture thoroughly for 5 min in a 50-ml separatory funnel, collect the chloroform layer in a 50-ml beaker and dry it over anhydrous sodium sulphate. Extract the aqueous phase with further 5-ml portions of chloroform. Transfer the combined extracts quantitatively to a 25-ml volumetric flask and dilute to volume with chloroform. Measure the absorbance at 700 nm in 1-cm cells. Construct a calibration curve similarly.

Procedure for steel analysis

Dissolve an appropriate weight of sample (1 g for 0.2% of Mo, 0.1 g for 6% Mo) in 50 ml of 3*M* sulphuric acid in a 150-ml Erlenmeyer flask and oxidize with concentrated nitric acid. Place a small funnel in the neck of the flask. Boil to reduce the volume to about 20 ml; cool, add 30 ml of water and boil for a few minutes. Cool, filter if necessary, add 0.5 g of ferrous sulphate to reduce vanadium(V) and chromium(VI), transfer to a 100-ml volumetric flask and dilute to volume. Take 5 ml of this solution, add 1 ml of saturated ascorbic acid solution and determine the molybdenum content by the procedure described above. Table 2 summarizes the results for two BAS standard steels.

RESULTS AND DISCUSSION

Characteristics of the complex

The absorption spectrum of the molybdenum–thiol complex in chloroform, extracted at pH 2.0 according to the general procedure, is reproducible for different concentrations of the metal, and has its absorbance maximum at 700 nm. The reagent does not absorb at wavelengths longer than 500 nm at the concentrations used. The system obeys Beer's law from 0.25 to 10 ppm molybdenum and a Ringbom plot[4] shows the optimum range to be 0.5–4.5 ppm. The relative error per 1% absolute photometric error for this range is 2.5%. The molar absorptivity and Sandell sensitivity of the complex were found to be 7.08×10^4 l.mole^{-1}.cm^{-1} and 0.0075 μg/cm^2 respectively.

Sufficient colour intensity is observed between pH 0.6 and 4.2, but the optimum range for the quantitative extraction of the chelate is pH 1.4–2.8. The amount of reagent necessary is at least 3 ml of 2% w/v solution for 4 ppm Mo, and 5 ml is recommended.

The optimum extraction time for 99.9% extraction is 5 min. If shaking is continued for more than 15 min the colour intensity decreases. The extracted chelate is stable for at least 2 hr at room temperature, but changes rapidly to a brown complex in presence of oxidizing agents.

Effect of other ions

The effect of diverse ions on the molybdenum determination was studied by adding 200 ppm of the ion in question to a solution containing 4 ppm of molybdenum and applying the recommended procedure. Ba, Ca, Mg, Sr, Al, Ti(IV), Sn(IV) and Sb(III) do not interfere. Tolerance limits for other ions are given in Table 1. The interference due to V(V) and Fe(III) can be eliminated by addition of hydroxylamine hydrochloride and ascorbic acid respectively. Bi(III), Sn(II), and Re(V) obtained by reduction with stannous chloride, interfere seriously.

Composition of the complex

The composition of the complex was determined by Job's method of continuous variations and was reproducible at different molybdenum concentrations.

The Job plot (Fig. 1) showed some unusual features. At the mole ratio corresponding to the MR_2 species there

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Table 1. Tolerance for foreign ions. (Molybdenum concentration: 1 ml of $1.042 \times 10^{-3} M \equiv 4$ ppm in final volume of 25 ml)

Ion added	Tolerance* limit, *ppm*	Ion added	Tolerance* limit, *ppm*
Zn^{2+}	100(a)	UO_2^{2+}	100
Cu^{2+}	100(a)	Pd^{2+}	100
Cd^{2+}	100	Pt^{4+}	50
Co^{2+}	20	Os^{6+}	50
Ni^{2+}	100(b)	Oxalate	100
Mn^{2+}	50	Tartrate	100
Fe^{3+}	50(c)	Citrate	100
Cr^{3+}	50	EDTA	100
V^{5+}	100(d)	Fluoride	100
W^{6+}	100		

* Amount causing < 2% error.
(a) Masking with 3 ml of 0.2% EDTA.
(b) Prior removal by extraction with dimethylglyoxime.
(c) No interference in presence of ascorbic acid.
(d) Using 2% $NH_2OH.HCl$ solution.

Table 2. Determination of Mo in high-speed steel (Mn—Ni—Mo—Cr—V)

Sample	Weight range studied *mg*	Mo, %	
		Certified	Found
Durgapur Steel (HSL, India) (0.49% Mn, 0.34% Mo, 1.36% Cr, 0.50% V	500–1000	0.34	0.338 0.337 0.337
BAS No. 60B	500–1000	0.43	0.427 0.427 0.429 0.429
BAS No. 64B	100–200	4.95	4.94 4.94 4.94 4.94

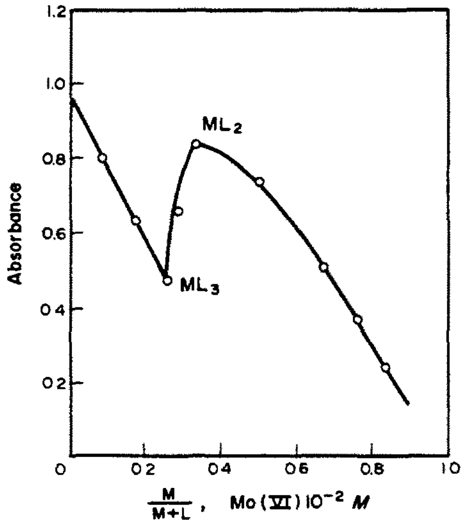

Fig. 1. Job plot, $[M] = [R] = 1.042 \times 10^{-2} M$.

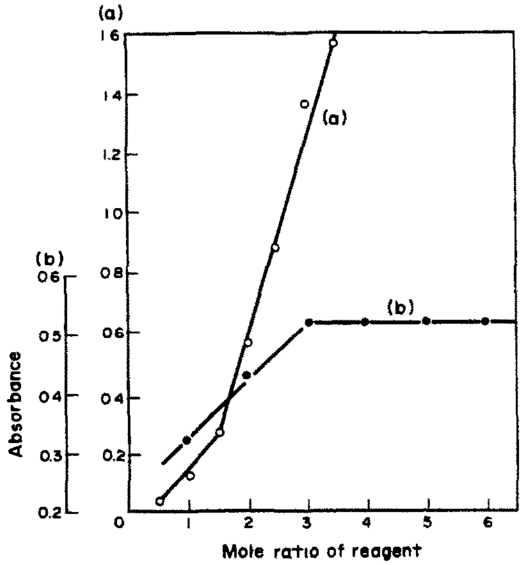

Fig. 2. Mole-ratio plots: (*a*) $[M] = [R] = 2.084 \times 10^{-2} M$; (*b*) $[M] = 1.402 \times 10^{-3} M$, $[R] = 7.01 \times 10^{-2} M$.

was a maximum in the absorbance and a sharp minimum at the ratio corresponding to MR_3. A mole-ratio plot (Fig. 2) gave a non-linear increase in absorbance up to an R:M ratio of about 3, then a steeper and linear increase followed by a maximum and constant absorbance when an R:M ratio of at least 500 was reached. This formation can be interpreted as indicating first an MR_2 complex of low molar absorptivity (2.0×10^4 $l.mole^{-1}.cm^{-1}$) followed by formation of an MR_3 complex of low stability but high molar absorptivity (found by the Bag and Chakrabarti method[5] to be 7.08×10^4 $l.mole^{-1}.cm^{-1}$). The stability constant of the MR_3 complex was evaluated as 2.0×10^8 at 25 ± 1° by Yatsimirskii's method.[6] The reaction can be interpreted as

$$MoO_2L_2 + HL \rightleftharpoons MoO(OH)L_3$$

where HL = 2-aminobenzenethiol.

The MR_3 complex was isolated for verification of its composition. Elemental analysis supported the formula $MoO(OH)L_3$. The complex gave negative tests for chloride. The infrared spectrum of the isolated complex showed a sharp absorption peak in the 3100 cm^{-1} region, suggesting the presence of an O—H stretching band. The compound also showed an Mo=O absorption band at 920 cm^{-1} (s). This again supports the existence of the $MoO(OH)^{3+}$ species. The complexes MoO_2L_2 in presence of a stoichiometric amount of ligand and $MoO(OH)L_3$ in presence of a large excess of ligand are both extractable into chloroform.

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Summary—A new extractive photometric method is described for estimation of molybdenum with 2-aminobenzenethiol. The green complex in chloroform has its absorbance maximum at 700 nm and is stable for 2 hr when extracted from a solution of optimum pH range 1.4–2.8. The extraction is quantitative. The sensitivity is 0.0075 $\mu g/cm^2$. Beer's law is obeyed over the range 0.25–10 ppm with optimum range 0.5–4.5 ppm. The molar absorptivity is 7.08×10^4 l.mole^{-1}.cm^{-1}. The overall stability constant is 2.0×10^8 at 25 ± 0.1°.

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ION-SELECTIVE ELECTRODES IN ORGANIC FUNCTIONAL GROUP ANALYSIS MICRODETERMINATION OF NITRATES AND NITRAMINES WITH USE OF THE IODIDE ELECTRODE

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Organic nitrates and nitramines have been determined by titration with various reductants.[1] However, these methods suffer from the defect that many nitrogenous and non-nitrogenous compounds interfere and the titrants need special precautions during preparation, storage and use.[2] Methods based on spectrophotometric[3] and gravimetric[4] procedures are usually time-consuming and unreliable when used on a routine basis. Gasometric reactions using inorganic[5–9] and organic[10,11] reagents have also been suggested.

Recently, the development of the nitrate-responsive electrodes[12–14] has made possible substantial improvement in the analysis of inorganic nitrates. Reduction of the nitrate ion followed by measurement of the liberated ammonia by means of the ammonium-responsive electrode has also been reported.[15] The use of both electrodes for the analysis of the nitrates by direct potential measurements requires careful adjustment of many variables and the resulting precision is not better than ± 2%.[12–15] Potentiometric titration is more accurate provided that the titrant forms either a stable complex or a precipitate, but unfortunately not many such titrants are available for nitrate or ammonia. However, diphenylthallium(III) sulphate has been applied for the titration of the nitrate ion, on the semi-micro scale only, with use of the nitrate electrode.[16]

On the other hand, the nitrate electrode is inapplicable to the determination of organic nitrates, and prior conversion of the organic nitrate or nitramine into inorganic nitrate by acid or alkaline hydrolysis is not quantitative.[17,18] The organic moiety of these compounds partially reduces the nitrate to various products such as ammonia and nitrogen oxides.

The present work describes a new finish to the determination of organic nitrates and nitramines by reaction with mercury–sulphuric acid mixture, the mercurous ions released being titrated with iodide, and an iodide electrode used to detect the end-point. Several compounds used as high explosives, industrial intermediates and vasodilators have been analysed and the results obtained are accurate.

EXPERIMENTAL

Reagents and materials

All reagents were analytical grade except where stated. Doubly-distilled water was used throughout. The nitrate and nitramine samples used were of purity not less than 99% as confirmed by the gasometric method.[5]

Apparatus

A Pye Unicam 292 MK2 pH-meter, an Orion 94-53 solid-state iodide-selective electrode and an Orion 90-02 double-junction reference electrode were used.

Procedure

Weigh accurately 2–5 mg of the ground dried nitrate, nitrite or nitramine sample and transfer it to a test-tube (10 × 21 cm). For smaller samples, transfer to the tube a portion of solution containing 0.1–1.0 mg of the sample and evaporate to complete dryness. Add 2–3 ml of 96% sulphuric acid and displace the air in the tube with pure nitrogen. Add 3 drops of mercury and shake the tube for 5–7 min at room temperature, with a continuous flow of nitrogen. Transfer the contents of the tube to a 250-ml beaker, rinsing with *ca.* 50 ml of doubly-distilled water, and stir. Insert the iodide and reference electrodes, titrate with 0.02*M* potassium iodide for sample sizes above 2 mg and with 0.002*M* solution for sample sizes below 2 mg and monitor the e.m.f. As the end-point is approached add the titrant in 0.01-ml increments. For sample sizes above 5 mg, the titration has to be conducted slowly, with efficient stirring from the beginning of the titration, since the equilibrium is reached slowly. Run a blank in the same manner.

RESULTS AND DISCUSSION

Nature of the reaction

Mercury in presence of concentrated sulphuric acid quantitatively reduces nitrates to nitric oxide,[5–9] and is itself converted into mercurous and/or mercuric ions. It is found experimentally that three moles of potassium

Table 1. Effect of temperature on the reaction of mercury with 96% sulphuric acid (reaction time 15 min)

Temperature, °C	Dissolved mercury, *μeq*
20	0.4
30	0.6
40	1.6
60	3.6
80	6.4
100	90.0

Summary—A new extractive photometric method is described for estimation of molybdenum with 2-aminobenzenethiol. The green complex in chloroform has its absorbance maximum at 700 nm and is stable for 2 hr when extracted from a solution of optimum pH range 1.4–2.8. The extraction is quantitative. The sensitivity is 0.0075 $\mu g/cm^2$. Beer's law is obeyed over the range 0.25–10 ppm with optimum range 0.5–4.5 ppm. The molar absorptivity is 7.08×10^4 l.mole^{-1}.cm^{-1}. The overall stability constant is 2.0×10^8 at 25 ± 0.1°.

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ION-SELECTIVE ELECTRODES IN ORGANIC FUNCTIONAL GROUP ANALYSIS MICRODETERMINATION OF NITRATES AND NITRAMINES WITH USE OF THE IODIDE ELECTRODE

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Organic nitrates and nitramines have been determined by titration with various reductants.[1] However, these methods suffer from the defect that many nitrogenous and non-nitrogenous compounds interfere and the titrants need special precautions during preparation, storage and use.[2] Methods based on spectrophotometric[3] and gravimetric[4] procedures are usually time-consuming and unreliable when used on a routine basis. Gasometric reactions using inorganic[5–9] and organic[10,11] reagents have also been suggested.

Recently, the development of the nitrate-responsive electrodes[12–14] has made possible substantial improvement in the analysis of inorganic nitrates. Reduction of the nitrate ion followed by measurement of the liberated ammonia by means of the ammonium-responsive electrode has also been reported.[15] The use of both electrodes for the analysis of the nitrates by direct potential measurements requires careful adjustment of many variables and the resulting precision is not better than ± 2%.[12–15] Potentiometric titration is more accurate provided that the titrant forms either a stable complex or a precipitate, but unfortunately not many such titrants are available for nitrate or ammonia. However, diphenylthallium(III) sulphate has been applied for the titration of the nitrate ion, on the semi-micro scale only, with use of the nitrate electrode.[16]

On the other hand, the nitrate electrode is inapplicable to the determination of organic nitrates, and prior conversion of the organic nitrate or nitramine into inorganic nitrate by acid or alkaline hydrolysis is not quantitative.[17,18] The organic moiety of these compounds partially reduces the nitrate to various products such as ammonia and nitrogen oxides.

The present work describes a new finish to the determination of organic nitrates and nitramines by reaction with mercury–sulphuric acid mixture, the mercurous ions released being titrated with iodide, and an iodide electrode used to detect the end-point. Several compounds used as high explosives, industrial intermediates and vasodilators have been analysed and the results obtained are accurate.

EXPERIMENTAL

Reagents and materials

All reagents were analytical grade except where stated. Doubly-distilled water was used throughout. The nitrate and nitramine samples used were of purity not less than 99% as confirmed by the gasometric method.[5]

Apparatus

A Pye Unicam 292 MK2 pH-meter, an Orion 94-53 solid-state iodide-selective electrode and an Orion 90-02 double-junction reference electrode were used.

Procedure

Weigh accurately 2–5 mg of the ground dried nitrate, nitrite or nitramine sample and transfer it to a test-tube (10 × 21 cm). For smaller samples, transfer to the tube a portion of solution containing 0.1–1.0 mg of the sample and evaporate to complete dryness. Add 2–3 ml of 96% sulphuric acid and displace the air in the tube with pure nitrogen. Add 3 drops of mercury and shake the tube for 5–7 min at room temperature, with a continuous flow of nitrogen. Transfer the contents of the tube to a 250-ml beaker, rinsing with *ca.* 50 ml of doubly-distilled water, and stir. Insert the iodide and reference electrodes, titrate with 0.02*M* potassium iodide for sample sizes above 2 mg and with 0.002*M* solution for sample sizes below 2 mg and monitor the e.m.f. As the end-point is approached add the titrant in 0.01-ml increments. For sample sizes above 5 mg, the titration has to be conducted slowly, with efficient stirring from the beginning of the titration, since the equilibrium is reached slowly. Run a blank in the same manner.

RESULTS AND DISCUSSION

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Mercury in presence of concentrated sulphuric acid quantitatively reduces nitrates to nitric oxide,[5–9] and is itself converted into mercurous and/or mercuric ions. It is found experimentally that three moles of potassium

Table 1. Effect of temperature on the reaction of mercury with 96% sulphuric acid (reaction time 15 min)

Temperature, °C	Dissolved mercury, *μeq*
20	0.4
30	0.6
40	1.6
60	3.6
80	6.4
100	90.0

iodide are required to titrate quantitatively the mercury ions produced by reaction of one mole of the nitrate or nitramine group. Consequently, the reactions of nitrates and nitramines with mercury may be

$$2\,R{-}O{-}NO_2 + 3H_2SO_4 + 6Hg = 3Hg_2SO_4 + 2NO + 2R{-}OH + 2H_2O \quad (1)$$

$$2\,R{-}NH{-}NO_2 + 3H_2SO_4 + 6Hg = 3Hg_2SO_4 + 2NO + 2R{-}NH_2 + 2H_2O \quad (2)$$

The possibility of formation of mercuric ions as shown by equation (3) leads to the same overall stoichiometry $2NO_3^- \equiv 3Hg_2^{2+} \equiv 3Hg^{2+} \equiv 6I^-$.

$$2\,R{-}O{-}NO_2 + 3H_2SO_4 + 3Hg = 3HgSO_4 + 2NO + 2R{-}OH + 2H_2O \quad (3)$$

However, qualitative identification of the inorganic reaction products, by addition of dilute hydrochloric acid and enough ethanol to give a concentration of 75% v/v, removal of Hg_2Cl_2 by filtration, then passage of hydrogen sulphide, showed that mercurous ions were the sole product.

Reaction conditions

Reaction of organic nitrates and nitramines with mercury and sulphuric acid is fast enough to ensure quantitative reduction within 5 min at 20°. Table 1 shows the blank values obtained by reaction of mercury with 96% sulphuric acid for 15 min at temperatures ranging from 20° up to 100°. Reaction at temperatures above 40° is not recommended, since the blank values tend to increase and affect the results, especially with sample sizes in the range between 100 μg and 1 mg.

Study of the effect of the sulphuric acid concentration shows that 85% v/v is the minimum concentration permissible for quantitative reduction (Fig. 1). The amount of acid actually required is determined not only by the amount needed for the reduction but also by the amount needed to give maximum solubility of mercurous sulphate during the titration. Measurements on mercurous sulphate in various concentrations of sulphuric acid show that the solubility of mercurous sulphate is maximal in the 1.5–3 *N* acid (Table 2). Consequently, the optimum volume of 96% sulphuric acid required for the reaction is 2–3 ml, which on dilution with water to *ca.* 50 ml gives a 1.5–3 *N* solution which will completely dissolve up to 33 mg of mercurous sulphate (equivalent to about 4 mg of nitrate sample containing 15% nitrogen).

It is necessary to carry out the reaction under a flow of nitrogen to remove the nitric oxide produced, because in presence of air or oxygen some nitric oxide will be oxidized, dissolve in the acid and cause oxidation of some of the mercurous ions, and possibly dissolve a little additional mercury, resulting in erratic positive errors.

Determination of mercurous ions, by using the ion-selective electrode

It has been reported that the solid-state iodide-sensitive electrode (Orion 94-53) responds to mercuric ions [20] down to 10^{-8} *M* and is useful as end-point detector in the titration of mercuric ions with potassium iodide. [21] The behaviour of this electrode towards mercurous ions has not been explored. In the present work, attempts were made to use it to determine mercurous ions by both direct potentiometry and potentiometric titration.

A test of the potential response of the iodide electrode (Orion 94-53) in conjunction with a double-junction reference electrode (Orion 90-02) at pH 2–4 in 0.1 *M* sodium perchlorate shows a more or less linear relation between the logarithm of mercurous ion concentration in the range 10^{-2}–10^{-6} *M* and the potential, but the slope is less than Nernstian, being about 45 mV/decade. Direct measurement

Table 2. Effect of sulphuric acid concentration on the solubility of mercurous sulphate at 25°C

$[H_2SO_4]$, *N*	Solubility, *g/l.*	$[H_2SO_4]$, *N*	Solubility, *g/l.*
0	0.4983	2.5	0.6644
0.1	0.4508*	3.0	0.6406
0.5	0.5457	3.5	0.6169
1.0	0.5933	4.0	0.5695
1.5	0.6406	4.5	0.5220
2.0	0.6644	5.0	0.4983

* The literature value is 0.44 g/l.[19]

Table 3. Microdetermination of some organic nitrates and nitramines by using the iodide electrode

Sample	Nitrate- or nitramine-nitrogen, % Calculated	Found*	Recovery %
Pentaerythritol tetranitrate	17.72	17.6	99.3
		17.6	99.3
		17.5	98.8
Cellulose nitrate	14.14	14.0	99.0
		14.0	99.0
		13.9	98.3
Urea nitrate	11.38	11.2	98.4
		11.2	98.4
		11.3	99.3
Guanidine nitrate	11.47	11.3	98.5
		11.3	98.5
		11.3	98.5
Nitroguanidine	13.46	13.5	100.2
		13.6	101.0
		13.6	101.0
Nitrobiuret	9.46	9.3	98.3
		9.4	99.4
		9.4	99.4
Hexogen (RDX)	18.92	18.8	99.4
		18.7	98.8
		18.7	98.8

* Based on the consumption of 3 equivalents of potassium iodide per mole of nitrate or nitramine group.

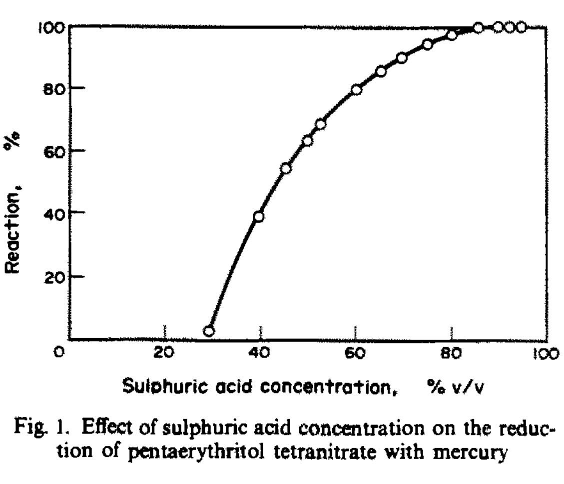

Fig. 1. Effect of sulphuric acid concentration on the reduction of pentaerythritol tetranitrate with mercury

Table 4. Microdetermination of some inorganic nitrates and nitrites by using the iodide electrode

Sample	Nitrate- or nitrite-nitrogen, %		Recovery, %
	Calculated	Found*	
Potassium nitrate	13.85	13.8	99.6
		13.7	99.3
		13.7	99.3
Barium nitrate	10.71	10.6	99.0
		10.5	98.0
		10.5	98.0
Potassium nitrite	16.47	16.0	97.1
		16.1	97.8
		16.2	98.4
Sodium nitrite	20.29	19.6	96.6
		19.9	98.1
		19.7	97.1

* Based on the consumption of one and three equivalents of potassium iodide per group of nitrite and nitrate, respectively.

of the mercurous ion concentration by using a calibration graph gives unsatisfactory results.

The use of the iodide electrode as indicator for the potentiometric titration was therefore tried. The titration curves show a sharp inflection (~400 mV) at the equivalence point. The relative standard deviation for 1 mg of mercurous ion is 0.2% and the reaction follows a 1:2 ($Hg_2^{2+}:I^-$) stoichiometry down to mercurous ion concentrations of 10^{-5} *M*.

Determination of organic nitrates and nitramines

The results obtained (Table 3) for the analysis of some nitrate esters, nitrate salts of organic bases and nitramines in the range 0.1–50 μmole show an average recovery of 99.0% and a mean relative standard deviation of 0.2%. A series of 10 replicate analysis of pentaerythritol tetranitrate and of nitroguanidine in the range 100–1000 μg showed a mean relative standard deviation of 0.3% and an average recovery of 98.3%.

The response of many nitrogenous groups to the reaction was tested. Mono-, di- and tri-nitro compounds (*e.g.*, *p*-nitrophenol, *m*-dinitrobenzene, 2,4,6-trinitrobenzoic acid and 2,4,6-trinitrophenol) as well as amides, anilides, oximes and hydrazides (*e.g.*, benzamide, benzanilide, dimethylglyoxime, sulphanilic acid and hydrazobenzene) were checked and none of these compounds responded to the reaction.

Determination of inorganic nitrates and nitrites

The applicability of the reaction to the analysis of inorganic nitrates and nitrites was also tested. The results obtained, based on the consumption of three and one equivalents of potassium iodide per nitrate and nitrite group, respectively, according to equations (4) and (5), show an average recovery of 99% for the nitrates and 97.5% for the nitrites (Table 4). The quantitative liberation of one mole of nitric oxide gas per nitrate and nitrite group[5,9] is in a good agreement with these data.

$$2NO_3^- + 4H_2SO_4 + 6Hg = 3Hg_2SO_4 + 4H_2O + 2NO + SO_4^{2-} \quad (4)$$

$$2NO_2^- + 2H_2SO_4 + 2Hg = Hg_2SO_4 + 2H_2O + 2NO + SO_4^{2-} \quad (5)$$

Advantages

The proposed procedure has advantages on the score of sensitivity, selectivity and simplicity over many of the methods used for analysis of the nitrates.[1,2] It is more than 60 times as sensitive as the micro-gasometric methods, since it is applicable to the analysis of 100 μg of the nitrates, an amount which are totally inadequate for many gasometric and titrimetric procedures: 10 μg of nitrate-nitrogen ≡ 1.07 ml of 0.002 *M* KI ≡ 0.0160 ml of NO at NTP.

It is not affected by environmental conditions such as pressure, temperature, solubility, and vapour-pressure factors, which have a direct effect on the measurement by the gasometric procedures. Also, the reagents are stable and require no special precautions such as those needed with the reductants used in the titrimetric methods. Finally, it avoids the difficulties and errors arising from the time-consuming reduction[15] and hydrolysis[22] procedures.

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Summary—A simple, selective and accurate method has been described for the rapid micro and submicro determination of organic nitrates and nitramines. It is based on reaction with mercury–sulphuric acid mixture for 5 min at room temperature followed by potentiometric titration of the mercurous ions released, a solid-state iodide-sensitive electrode being used. Three equivalents of potassium iodide as titrant are consumed per mole of nitrate or nitramine group. The results obtained, with sample sizes ranging from 1.0 to 50 μmole, are precise to ± 0.2% and the average recovery is 99%. None of the other nitrogenous functional groups responds to this reaction.

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ANALYTICAL DATA

DISSOCIATION OF THE AMMONIUM ION IN WATER–UREA AND WATER–tert-BUTYL ALCOHOL MIXTURES

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In the course of a continuing study of ion solvation in the two series of media[1] named in the title it seemed appropriate to evaluate the dissociation of the ammonium ion in order to appreciate the meaning of the thermodynamic properties of this ion, measured in those solutions.

This has been done through potentiometric measurements of the potential difference of a galvanic cell such as:

$$\text{Ag, AgCl}\left|\begin{array}{c}\text{NH}_4^+, \text{Cl}^-, \text{NH}_3\\ \text{water} + \text{solvent S}\end{array}\right|\text{H}^+, \text{glass electrode}$$

Aqueous solutions approximately equimolal in NH_3 and NH_4Cl were prepared by adding to water weighed amounts of hydrochloric acid and ammonia stock solutions of accurately known concentration. The variations δU of the potential difference U of the galvanic cell were then recorded when weighed amounts of co-solvent S were added, a Radiometer pH-meter 4, reading to 0.2 mV, being used. The solutions were kept at 25.0°; the addition of urea considerably lowered the temperature, so the measurements were taken only when the temperature had been restored to 25.0°.

The dissociation constants were calculated from δU, δU^0 (which is the change of the standard potential of the cell) and the pK_a of NH_4^+ in water (9.245).[4] Activity coefficients were estimated by using the extended Debye–Hückel equation with coefficients A and B appropriate to the media, and Bjerrum's q as distance parameter. Association of ammonium chloride was neglected and the pK_a values in mixed solvents were then obtained by using the equations

$$\mathrm{p}^{s}K_a = \frac{F(\delta U^0 - \delta U)}{RT\ln 10} + \mathrm{p}^{w}K_a + {}^{s}\Omega - {}^{w}\Omega \qquad (1)$$

where the superscript s stands for the aqueous organic mixture and w for water, and for both solvent media

$$\Omega = \log\frac{(m_s + m_{\mathrm{OH}^-})m_s}{m_b - m_{\mathrm{OH}^-}} + \frac{2A\sqrt{(m_s + m_{\mathrm{OH}^-})\rho}}{1 + Bq\sqrt{(m_s + m_{\mathrm{OH}^-})\rho}}$$

where m_b and m_s are the molal analytical concentrations of base and salt respectively (m_s = molality of acid added to the solution, $m_b + m_s$ = molality of ammonia added to the solution) and ρ is the density of the solvent medium.

The value of m_{OH^-} in water was calculated from the pK_a of NH_4^+, the ionic product of water and the analytical molality of base and salt, by using classical treatment of ionic equilibria; δU^0 was obtained by measuring the variations of the potential of the cell when co-solvent was added to pure aqueous hydrochloric acid of various concentrations. There are, then, two non-independent unknown quantities in equation (1): $\mathrm{p}^{s}K_a$ and ${}^{s}m_{\mathrm{OH}^-}$. Therefore calculations are made through successive approximations. The ionic product values used for solvent mixtures were taken from the literature.[5]

With urea, it has been observed that, taking into account the possible hydrolyses which can produce ammonium and cyanate ions, it is best to work only with fresh solutions and high enough electrolyte concentrations. With analytical salt concentrations between 5×10^{-3} and $10^{-2}\,m$,

Table 1. Molal dissociation constant of ammonium ion (pK_a) in water–urea mixtures at 25°C (pK_a in water = 9.245)[4]

m_b*	10†	20†	30†	40†
1.004×10^{-2}	8.72_6	8.43_0	8.20_7	8.02_0
9.05×10^{-3}	8.73_1	8.43_8	8.21_4	8.02_7
8.14×10^{-3}	8.72_4	8.43_3	8.20_8	8.02_1
7.07×10^{-3}	8.72_3	8.42_7	8.20_7	8.01_8
6.2×10^{-3}	8.72_5	8.42_9	8.20_1	8.01_5
Mean	8.72_6	8.43_1	8.20_7	8.02_0

* Molality of initial solution of NH_3 in water.
† Urea, % w/w.

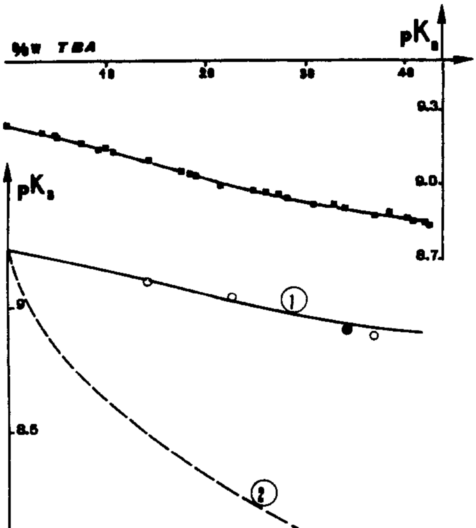

Fig. 1. Variation of the molal dissociation constant of the ammonium ion with: ■ % w/w TBA. — volume fraction of TBA, ϕ. --- volume fraction of urea, ϕ. ● volume fraction of MeOH according to ref. 6 and ○ volume fraction of EtOH according to ref. 7.

Table 2. Molal dissociation constant of ammonium ion in water–TBA mixtures at 25°C

TBA, % w/w	pK_a	TBA, % w/w	pK_a
5	9.20	25	8.97
10	9.15	30	8.94
15	9.09	35	8.90
20	9.03	40	8.87

good reproducibility of the results has been obtained (Table 1). Data concerning water–tert-butyl alcohol media are shown in Fig. 1; extrapolated data for exact concentrations of the alcohol are reported in Table 2.

It is worth noting (Fig. 1) that changes of pK_a with *volume fraction of alcohol* (ϕ) *are identical* for methanol,[6] ethanol,[7] and tert-butyl alcohol (TBA), at least in water-rich media, as if they were determined only by the actual volume of water. The same situation has been encountered for the ΔG of transfer of RbCl from water to aqueous organic media:[8] for most of the co-solvents, the variations observed are related only to the volume fraction, whereas urea produces quite different effects.

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Summary—Dissociation constants for the ammonium ion in water–urea and water–tert-butyl alcohol mixtures (0–40%) have been determined by a potentiometric method

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ANNOTATION

SOME COMMENTS ON "THE PROGRESS OF ANALYTICAL CHEMISTRY 1910–1970"

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The paper by Brooks and Smythe[1] of the title above has initiated some thoughts I consider worth while to add as comments.

The authors of this paper have tried to approach a very much up-to-date problem with methods and means applied only in very few cases to analytical chemistry. To follow the progress of analytical chemistry between 1910 and 1970, they consider the number of publications, its time-dependent growth and the distribution of publications with respect to various factors (country, language, sub-fields, elements), "in order to evaluate some of the long-term trends of this century". Now the statistical distribution and growth of scientific publications, citations and manpower has been dealt with in detail in some basic works,[2–4] and it has been shown in these that the statistical data on the number of scientific publications can be correlated to the data on new scientific achievements, although scientific achievement and scientific information are different concepts. The study of this "indicator", supplemented by several others (number of citations, number of scientists, number of institutions, funds, equipments, *etc.*) drawn from various sources (e.g., bibliographies, abstract journals, progress reviews, *etc.*) can reveal many interesting conclusions. However, one should avoid the misjudgment that the number of publications is the only and fundamental measure ("indicator") of the "size of science" or its "development" or "progress". Thus, as a title, "Progress of the literature of analytical chemistry, 1910–1970" would have been more relevant.

The growth of the number of scientific publications is exponential, as has been shown both for all science[2–4] and for several individual fields.[5] It is usual to characterize further the exponential increase by a growth rate that can be compared with the growth rate of chemistry in general or with that of some other fields.[5] A very convenient, simple, way to compare various rates of exponential growth is by means of the doubling time, the length of time required for the literature to double in size, when growing at constant rate. The problems in attempting to assess the total volume of analytical literature are so great and diverse as to cast doubts on the value of any such estimate. It seems that it is more reliable to look at and compare the rates of growth of the various techniques (see Fig. 3).

It is well known that the whole scientific literature doubles within about 15 years,[3] the literature of chemistry within 8–10 years,[6] and that of analytical chemistry within about 5–7 years[7] (for the period 1956–1972).

Another question worth consideration is whether the ranking of the countries in which analytical chemistry was carried out (*cf.* ref. 1, p. 497) is of help in the study of the general progress of analytical chemistry. It seems that a transformation of the data into a correlation with some specific factor would be more useful. If, for example, the number of publications in analytical chemistry (or its logarithm) from a given country is plotted *vs.* some indicator representing the general stage of scientific development in the country (*e.g.*, the total number of scientists or scientific authors in the country[8]), it would perhaps provide a picture of the weight of analytical chemistry within the general scientific capacity of the country. A preliminary plot of this sort is given in Fig. 1, showing data for 1970 (number of analytical publications from ref. 1, number of authors from ref. 8).

On page 500 in ref. 1, "the major (analytical) journals (each containing more than 1.0% of the world total)" are listed, based on calculations for the year 1970. The Polish nuclear journal *Nukleonika* is also mentioned. The 1% means that each listed journal published at least 184 analytical papers in 1970. Going through the 1970 issues of *Nukleonika*, it can be established that they contain *a total of 82 papers* (including nuclear physics, chemistry, biology and analytical chemistry) out of which there are only 13 dealing or related with analytical chemistry. From this it seems that this nuclear journal, excellent as it is, cannot be included in the list of major analytical journals.*

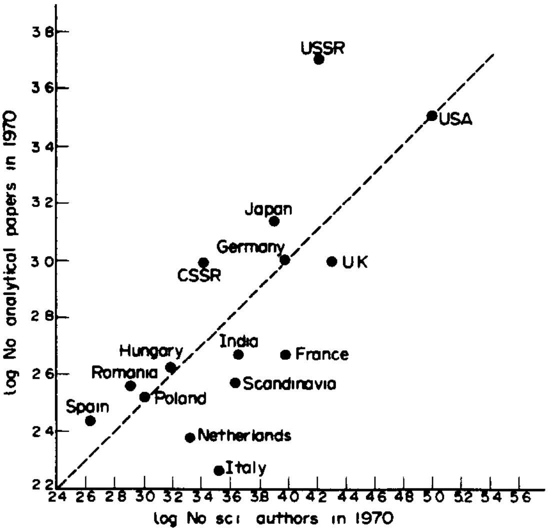

Fig. 1. Log–log scatter plot of output of analytical papers by various countries for 1970 as a function of total number of scientific authors in these countries for 1970 (slope of the regression line 1.09).

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* The authors of the original paper wish to apologise for this error; the journal itself was not available to them [Editor].

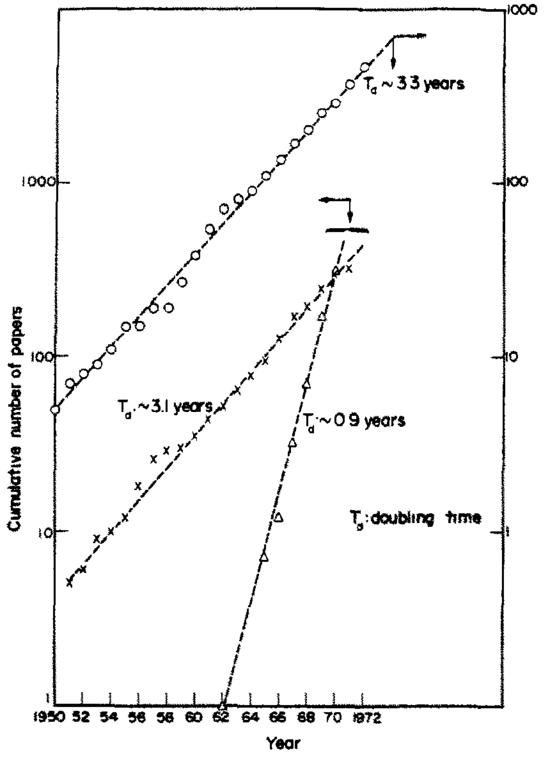

Fig. 2. Growth of papers in some sub-fields of radioanalytical chemistry. Adapted from refs. 9 and 11. ○ Prompt nuclear analysis, × Charged-particle activation analysis, △ Solid-state gamma-spectrometry.

Finally, I would like to mention that I am not convinced that "the main source for the (statistical) evaluation of methods used in analytical chemistry is the biennial reviews in Analytical Chemistry" (ref. 1. p. 500).

As a matter of fact, the basis of preparation of these reviews is not uniform and both their qualitative and quantitative contents vary over a wide range. There are some very selective critical reviews among them, and others can be considered rather as bibliographies. The latter might serve the purpose of ref. 1 but the former do not.

I have the notion that more useful data could be obtained if true bibliographies or abstract journals were used as a source, and if the number of papers published in the analytical sub-fields were plotted cumulatively as a function of time. Figures 2 and 3 shows such two illustrations from the field of radioanalytical chemistry and electroanalytical chemistry.

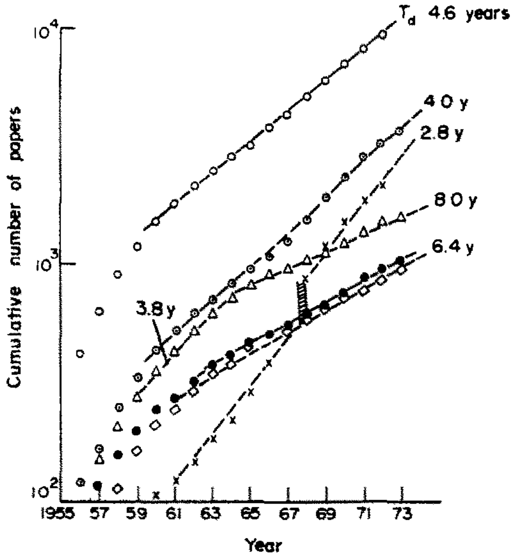

Fig. 3. Growth of papers on electroanalytical chemistry of inorganic compounds. Adapted from ref. 10. ○ Electroanalytical chemistry, total, ● Conductometry, × Voltammetry, ⊙ Potentiometry, ◇ Coulometry, △ Amperometry.

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Summary—Some means of assessment of scientific progress are proposed.

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LETTER TO THE EDITOR

Manganese in serum

SIR,

We have read the short communication by Muzzarelli and Rocchetti[1] on the atomic-absorption determination of manganese, cobalt and copper in whole blood and serum. In it they refer three times to our publications[2,3] in a wrong manner.

First. We have never stated that a high serum manganese concentration is one of the most accurate indicators of myocardial infarction as they suggest in their introduction. We have in fact examined patients with the disease but our results show that the difference in the mean serum manganese concentration between normal controls (0.57 ng/ml) and patients with acute myocardial infarction (0.64 ng/ml) is not significant ($t = 1.89$; $0.05<P<0.10$).[4] Thus, in our experience, serum manganese values do not provide an indication of myocardial damage. To the best of our knowledge, there is one publication[5] claiming that the serum manganese concentration increases after myocardial infarction, but it is apparently based on analyses of contaminated samples.[4] We found that the serum manganese concentration increases during the active phase of acute viral hepatitis (mean ± standard deviation = 2.32 ± 0.96 ng/ml), chronic aggressive hepatitis (0.84 ± 0.24 ng/ml) and posthepatitic cirrhosis (0.84 ± 0.20 ng/ml)[6] as well as in some other hepatobiliary disorders, *e.g.*, liver cirrhosis of different aetiology (0.78 ± 0.30 ng/ml) and liver metastases (1.08 ± 0.50 ng/ml).[7]

Second. In their discussion Muzzarelli and Rocchetti erroneously assert that the serum manganese concentrations they found (mean ± standard deviation = 9 ± 4.3 ng/ml; range = 5 - 16 ng/ml)[1] are in agreement with those described by us (0.57 ± 0.13 ng/ml; range = 0.38 - 1.04 ng/ml).[2]

Third. Muzzarelli and Rocchetti mention that the serum cobalt levels they determined (mean ± standard deviation = 7.7 ± 1.9 ng/ml; range = 5.6 - 9.8 ng/ml)[1] correspond to those reported by us.[3] Our paper dealt with the preparation of a multi-element serum standard. We added cobalt to give a final concentration of 6.46 ppm (μg/ml) in lyophilized serum, *i.e.*, three orders of magnitude higher than their result. The alleged agreement thus arises from a fundamental misunderstanding of the facts.

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INSTRUMENTS IN ANALYSIS—CRITICAL REVIEWS

DEVELOPMENT OF THE DIFFERENTIAL REFRACTOMETER

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When the refractive index of a solute differs from that of a solvent, then if the solution is of low absorbance and contains no suspended matter, it is possible to determine the concentration of the solute by measuring the refractive index of the solution and comparing it with those of a set of standard solutions. To take a trivial but biologically important example, the refractive index of pure water at 20° and 589 nm is 1.33299, while that of sodium chloride is 1.5442. The refractive index difference of approximately 0.22 is therefore sufficiently large to make the determination of the concentration of saline solutions by refractometry a practical proposition. A linear correlation of refractive index and concentration would be expected and solutions containing more than 1% w/v of sodium chloride can be analysed with simple apparatus.

When a solution contains more than one species having a refractive index which differs from the solvent, it may still be possible to analyse the solutions by making a pair of measurements at different dilutions or at different wavelengths. The refractive index of many substances varies substantially with wavelength and this variation is not the same for substances of different composition. Shippy and Burrows[1] derived the following equation for the calculation of the concentration of solutions containing two solutes A and B

$$\frac{\%\mathrm{A}}{100} = \frac{n(X\%\mathrm{B}) - n(\mathrm{mixture})}{n(X\%\mathrm{B}) - n(X\%\mathrm{A})}$$

where n is the refractive index and X is a concentration at which the refractive index is known for each solute in separate solutions. The same authors were the first to publish accurate values of the refractive indices of sodium chloride solutions in the concentration range 5–20% w/v. Later Brodskii and Shershever[2] analysed solutions of potassium chloride in the range 0.03–0.75% by measuring the refractive index with an interferometer. Tables of the refractive indices of dilute salt solutions have since been published by Kruis[3] and Stamm.[4]

Recently,[5] a precise study of the variation of refractive index with concentration (dn/dC) has been made for aqueous solutions of sodium chloride, potassium chloride and ammonium nitrate. The high precision made possible by the use of a helium–neon laser as a light-source revealed that the relationship was not strictly linear, but could be fitted to a polynomial. Although solutions of substances in solvents other than water do not have linear relationships between refractive index and concentration, nevertheless a wide range of solutions in organic solvents has been analysed refractometrically. Most simple refractometers rely on the critical angle principle and the Abbé refractometer is probably the most familiar. It can be used with liquids of refractive index between 1.300 and 1.700 and requires only a small sample. It can measure accurately to the third decimal place and when the temperature is kept constant to 0.2°, reliable measurements may be made to 4 decimal places. Other models such as the Pulfrich and immersion types require much larger samples and have a restricted refractive index range. Comparisons of refractive indices may sometimes be made to the fifth decimal place.

With such instruments it is thus possible to analyse solutions with a refractive index difference of 0.1 between the solute and solvent and a concentration of down to 1% w/v, with an error of 10% or better. When it is required to analyse solutions with a smaller refractive index difference between the solute and solvent, or with a lower concentration of solute, then a more sensitive instrument must be used. In many cases it is not necessary to make an absolute measurement of the refractive index with an expensive instrument such as an interferometer, but to make only a precise comparison of two similar refractive indices such as that of the pure solvent and the solution. In such cases the measurements may be made with a differential refractometer.

The principle of the differential refractometer is extremely simple. If a ray of light passes through a hollow prism which contains a liquid, the ray will be deflected (Fig. 1). If now a second identical prism is placed close to the first, thus creating a cube, the ray will now suffer no deflection if it strikes the face of the first prism normally, for any deflection experienced in the first prism will be cancelled by a deflection in the opposite direction. This condition is only fulfilled when the refractive indices of the liquids in both prisms are equal. If the refractive index of the liquid in the second prism changes by a small

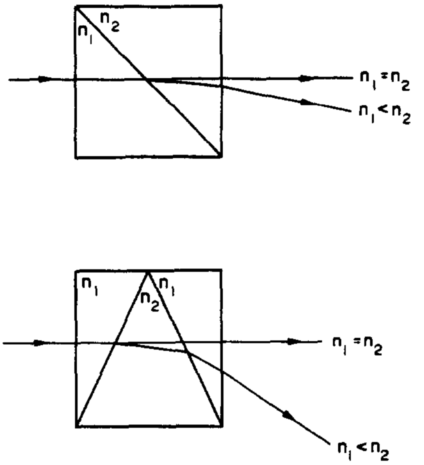

Fig. 1. Principle of the differential refractometer.

amount, then the ray of light suffers a correspondingly small deflection. For small changes in refractive index, the linear deflection of the ray of light will be proportional to the difference in refractive index and to the distance of the observer from the prism assembly. The sensitivity of the system is thus determined by the length of the optical lever and the accuracy with which the position of a spot of light can be determined. The only methods of increasing the sensitivity are to replace the double prism with a hollow right-angled prism within a rectangular tank, or to increase the number of times that the ray of light traverses the prism assembly, by the use of suitably placed mirrors.

The differential refractometer was first described many years ago, but the instrument was not used widely until the advent of chromatography, and then only when large numbers of samples had to be examined by a routine method. In this application it competes favourably with interferometry, but is often less sensitive or rapid than colorimetry when specific reagents are available.

The early differential refractometers were visual devices in which the displacement of the beam was measured optically. An excellent example of this type of instrument was designed by Brice[6] in 1951 and marketed by the Phoenix Precision Instrument Co. in America. The main problem with visual instruments is that they are tiring to use and this difficulty was overcome by Brice in a later design in 1957. Here the displacement of the light-beam was detected photoelectrically. A modern modification of the Brice–Phoenix design described by Pittz and Bablouzian[7] uses a monochromatic light-beam provided by a mercury vapour lamp and a 435.8 nm filter. The displacement of this beam is detected by the use of a pair of selenium half-cells (cut from a single cell) mounted 0.8 mm apart on a carriage. The outputs of the half-cells (about 100 mV) are connected, in opposition, to a microvoltmeter. The reading on the microvoltmeter is reduced to zero by moving the carriage in a direction at right angles to the light-beam, so that each half-cell is equally illuminated by the slit image. The extent of the deflection is read directly from a counter attached to the micrometer drive.

One disadvantage of the differential refractometer is that the glass interface between the sample and standard liquids is at an angle to the incident light-beam. This sets a limit to the refractive index of the solvent which may be used. Thus, in the original commercial cell of the Brice–Phoenix instrument, the glass interface had a refractive index of 1.52 and this restricted the choice of solvents to those having a refractive index of less than 1.62. This drawback was recognized by the manufacturers,[8] who recommended that the cell should be rotated through 90° when using highly refractive solvents (such as α-bromonaphthalene). Unfortunately, this results in a deterioration of performance, the sensitivity being only one-seventh of the initial value. Recently, Kratochvil and Babka[9] have reduced the problem of total internal reflection at the interface within the cell by constructing a modified design, in which the interface is made of highly refractive glass[10] ($n = 1.62$).

As a routine control instrument, the differential refractometer has been exploited most successfully by Jones,[11] who used it in the difficult problem of the determination of the isomers of benzene hexachloride.

Another elegant application is the study of adsorption from solution onto particulate matter. Ash, Brown and Everett[12] circulated a solution of cyclohexane in benzene through a bed of carbon black and through one side of the cell. A second stream of solution was circulated through the other side, the whole assembly being mounted in a thermostat. Adsorption on the carbon black was detected by the change in refractive index and a precision of 3 nmole/m^2 was achieved for adsorption on the carbon. When the differential refractometer is used to study the changes in the effluent from a chromatographic column or a bleed from a plant stream, then the problem of recording arises and this is a difficult problem to surmount because of the very small signals which the refractometer can provide. This difficulty has been the main obstacle to the widespread application of differential refractometry to plant control.

The first solution to the recording problem was made by Tiselius and Claesson[13] in their work on adsorption chromatography. In their design, the beam of light passing through the refractometer struck the apex of a hexagonal prism acting as a beam-splitter. The two beams then fell upon two photocells arranged in opposition so that when they were equally illuminated, no output signal was observed. When, as a result of change in refractive index in the contents of one of the refractometer cells, the incident beam was deflected, the intensity of illumination on the two photocells changed, and the galvanometer was deflected. The movement of a spot of light reflected from a mirror on the galvanometer suspension was recorded photographically, and by using a fairly long optical lever, a sensitivity of 3×10^{-5} refractive index units was achieved and this permitted the recording of changes in solute concentration of the order of 0.1%. As a further refinement, the instrument was made to record an elution curve directly, by collecting the eluate in a vessel on a spring balance and allowing the movement of this to be transmitted to the light-beam by means of a second mirror. The device of connecting the matched photocells to a galvanometer and studying the deflection of the secondary light-beam reflected from a suspended mirror has been used by a number of workers[14] to obtain the necessary sensitivity and modern spot-followers can be used to record the deflection of the secondary beam. The whole assembly, however, is very sensitive to mechanical vibration because of the number of mirrors involved and the length of the optical levers, so that its use is strictly limited.

The use of two matched photocells is expensive and most workers have preferred to use a single photocell with a split cathode, the two halves being arranged in opposition. Such a device was first used by Stamm[4] who also incorporated in his instrument an arrangement making it suitable for automatic operation. The deflection of the primary beam was neutralized by the rotation of a parallel-sided slab of glass placed before the split-cathode photocell. This was achieved with the aid of a micrometer screw and monitored by the deflection on a galvanometer attached to the photocell. Later models have used servo systems to couple the rotational movement of the compensating glass block to the photocell output. Alternatively, the output of the photocells may be recorded directly as in the instrument described by Zaukelies and Frost.[15] This design, which is extremely simple in construction, involves only a light-source and associated optical system, a refractometer cell and a twin-cathode photocell. The limiting factor in its sensitivity was noise in the photocell output, corresponding to 2×10^{-6} refractive index units. Recently an improved version of this instrument has been described in which great attention has been paid to the elimination of all sources of noise.

Much of the photocell noise was eliminated in a refractometer design due to Trenner,[16] by ensuring that the output signal from the sensing device was a.c. This is probably the most complex differential refractometer yet to be constructed and used the hexagonal prism beam-splitter in a novel fashion. Light from a slit source was focused on the apex of the hexagonal prism, which was mounted on a platform and could move in a direction at right angles to the path of the incident light. The two beams emerging from the other end of the prism were of equal intensity when the prism was precisely aligned. The beams were chopped alternately by a 60-Hz chopper and then entered an integrating sphere. Here the light was received by a photomultiplier. At balance, the light inside the sphere had no 60-Hz component. A change in refractive index in the refractometer cell caused a movement of the slit image from its position on the apex of the hexagonal prism and caused a change in the relative intensity of the two beams, so that the light in the integrating sphere then had a 60-Hz component. The corresponding a.c. output from the photomultiplier was fed to a recorder and also to the drive of a motor returning the hexagonal prism to the null position. Full-scale deflection of the recorder corresponded to approximately 1.5 mm movement of the prism and one division corresponded to a movement of 7 μm at the detector. The resulting sensitivity was 3.6×10^{-6} refractive index units. To attain this sensitivity very great care was exercised to eliminate thermal drift, the whole assembly being mounted in an air-conditioned room and all motors and sources of heat mounted outside an enclosed optical system.

The first successful recording differential refractometer for the analysis of plant streams was described by Miller.[17] This is a robust and stable but not highly sensitive design which has been produced commercially for use in the petroleum industry. Once again, a beam-splitter and a double photocell are used and the output from the sensing system is amplified and fed to a servo mechanism. This moves a reflecting prism in such a way that the light-beam is restored to its original position after a change of refractive index has occurred. Although the optical lever was quite long, the instrument was kept compact by the use of two reflecting prisms to return the light to a detector situated close to the light source. Full-scale deflection with this instrument was approximately 1×10^{-3} refractive index units, sufficient for the monitoring and control of hydrocarbon distillations. In the separation of cyclohexane and methylcyclopentane from n-pentane, the instrument maintained the refractive index of the sample within 3×10^{-4} units.

In a more sensitive design by Campbell,[18] the vacuum photocells were replaced by selenium cells and this made it possible to restore balance in the system by moving the compact photocell assembly. The refractometer cell consisted of a hollow prism within a cylindrical glass container, the whole serving as a cylindrical lens producing an image of the illuminated slit on the photocells. The output from the photocells was amplified and recorded and the signal used to drive a servo system moving the photocells to the position where they were equally illuminated. Full-scale deflection on this instrument corresponded to a change in refractive index of 3×10^{-4} units. The limit of detection was 3×10^{-6} units.

A new recording differential refractometer has been described by Vandenheuvel and Sipos.[19] It is an improved version of the original design due to Zaukelies and Frost. In their investigation every care was taken to reduce noise to a minimum. Mechanical noise was controlled by sturdy construction, electrical noise by shielding and choice of components, thermal noise by use of a thermostat and noise due to flowing liquid by accurate flow-control. Significantly, the authors did not stress the necessity to reduce convection currents in the optical path by enclosing it closely in a metal shield. The instrument was capable of a maximum sensitivity of 1 × 10^{-4} refractive index units for full-scale deflection, with a noise level of 5 × 10^{-7} and an error of 0.5%. A record of the separation by reverse-phase adsorption chromatography of a mixture of methyl laurate and methyl myristate showed two very well defined peaks, although the difference in refractive index at the tip of the largest peak was only 5 × 10^{-5}. While most of the instruments so far described have used vacuum photocells as the detectors, these require stable power supplies and electronic equipment and are often noisy at the levels of sensitivity at which they must be operated. There is an advantage in using detectors of the semiconductor type and an excellent example of this type of instrument was described by Jones,[20] who employed a pair of cadmium selenide photoconductive cells. The output from these was amplified by means of a high-gain solid-state amplifier and the sensitivity was further increased by placing graticules in the paths of the beams illuminating the detector, in such a way that when one graticule completely obscured one half of the detector, the other half experienced maximum illumination. At full sensitivity, this remarkable instrument, with an optical lever of only 20 cm, permits detection of changes in refractive index as small as 1 × 10^{-9}. An optical lever of this type is illustrated in Fig. 2.

The use of solid-state devices as differential refractometer detectors has now become standard. They have the great advantages of cheapness, stability, compact size and ease of replacement and do not require the use of expensive stable power supplies. The detectors may be of the photoconductive or photoemissive types. Suitable photoconductive cells have cadmium sulphide as the photosensitive element and a pair are used in opposition. They have the advantage over photoemissive types that they are sensitive to quite low light-levels, but do require a separate power supply.

Recently, very small light twin-photodiodes have become available. These may be of the silicon or germanium type and give a signal voltage when the two halves of the assembly are unequally illuminated. With such devices, it is a simple matter to measure deflections of the order of 10^{-7} rad so that they are highly suitable as detectors in differential refractometry. Furthermore, the output can be fed directly to a potentiometer recorder without further amplification. With the most primitive optical system it is possible to attain a sensitivity of 0.001 refractive index units for full-scale deflection. The full use of the ability of these detectors to measure deflection is limited by the necessity of providing adequate illumination. For full sensitivity an illumination of 0.03 lumens is required at the detector and this involves the use of large apertures or light-sources of high luminosity per unit area.

The development of stable robust differential refractometers has been stimulated over the past few years by the increasing interest in the newer forms

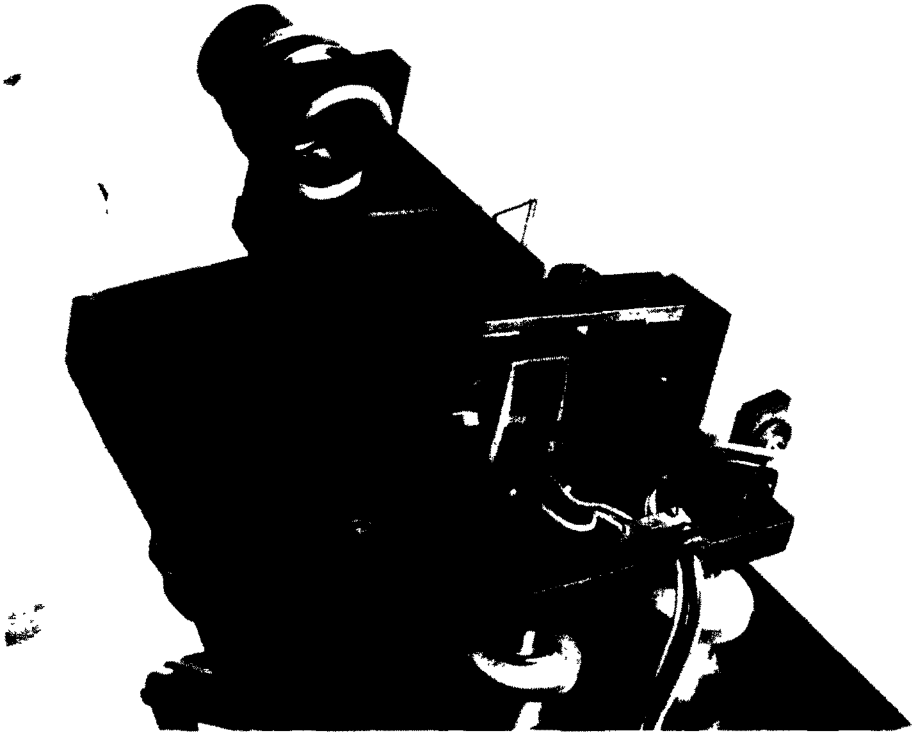

Fig. 2. A sensitive optical lever.

of column chromatography such as high-pressure liquid and gel-permeation chromatography. There are certain difficulties remaining in the use of these devices as detectors at the base of columns. It is necessary to avoid any degassing of the solvent as it passes through the refractometer cell. The appearance of small bubbles of air often accompanies a modest rise in temperature of the flowing liquid and this results in rapid oscillations of the light intensity reaching the detector, with a resulting noisy record. It is better, where possible, to ensure that the refractometer cell is maintained at a temperature slightly below ambient and to use a recording system with a long time-constant, which does not respond to rapid oscillations in detector output. The most serious problem is, however, the fluctuation in temperature between the reference liquid and the sample liquid. If one wishes to measure a refractive index to one part in a thousand then it is necessary to maintain the temperature to better than ± 1°. This requirement for temperature stability rises to ± 0.1° for measurements of refractive index reliable to the fifth decimal place. Fortunately, it is not necessary to maintain the temperature of the whole of the instrument constant, but merely to ensure that the temperatures of the two liquids do not vary differentially by more than this amount. The requirement is normally met by passing both liquids through two channels in an efficient heat-exchanger before they enter the refractometer cell and to ensure that the membranes separating the sample and reference liquids are thin and allow rapid heat transport. A simple refractometer cell which fulfils these requirements may be made by clamping microscope cover slips between drilled polished brass blocks to provide the dividing membranes. When a separate heat-exchanger is used it is important to design it so as to provide minimum hold-up and peak broadening.[21]

The Waters' Model R-4 differential refractometer is a good example of a modern instrument and illustrates many of the concepts discussed earlier. A collimated parallel beam of light passes through the cell, which is a hollow prism with an outer reference compartment, and is reflected back again through the cell to a detector close to the light-source. The detector assembly comprises a beam-splitter and a pair of cadmium sulphide photocells which are illuminated equally when the inner and outer refractometer cell compartments contain liquids of the same refractive index. Manipulation of the light-beam to achieve the null position is accomplished by the rotation of parallel-sided glass blocks in the path of the beam, giving the light-beam a transverse movement. Noise in the detector output other than electrical noise is minimized by reducing temperature fluctuations, keeping the flow-rate of the sample solution low to avoid turbulence and maintaining the temperature below ambient to avoid deaeration. The temperature of the sample and reference liquids is made identical by passing them through a heat-exchanger before they are admitted to the cell compartment. The maximum sensitivity is 1×10^{-5} refractive index units for full-scale deflection on the record.

Detectors for liquid chromatography must fulfil two requirements: they must be sensitive to very small differences in analytical properties of the solute and solvent so that total quantities of solute ranging between 10^{-3} and 10^{-8} g may be detected, and they must not reduce the efficiency of the column by peak broadening, *i.e.*, increasing the HETP. These two requirements are not independent and both are influenced by the size of the detector cell. If we assume that the slope of the elution curve is Gaussiam then the cell volume should be a fraction (1/3) of the total peak-width as calculated from the HETP and cross-section of the column. Commercially available refractometer cells having a volume in the range 5–10 μl may be used with high-efficiency liquid chromatography columns. Recently[22] the performance of two differential refractometers was compared. The first of these was a conventional beam-deflection type and the second was of the Fresnel type in which the intensity of the reflected beam, which depends upon the refractive index and the angle of incidence, is measured.[23] It can be seen from Table 1 that there is no great difference in the characteristics of the two detectors. A comparison of the differential refractometer with other types of detector shows that it is more sensitive than the ultraviolet spectrophotometer, but much less sensitive than transfer devices of the disc and wire type coupled to a flame-ionization detector.

Munk,[24] however, has shown that in comparisons of the differential refractometer with the ultraviolet absorption detector, if solutes giving maximum detector response are used, then this order may be reversed. Thus, the detection limit for a solution of sucrose in water was 3×10^{-9} g/sec for the differential refractometer,[25] while that for a solution of adenosine (molar absorptivity 1.40×10^{4} $\mathrm{l.mole^{-1}.cm^{-1}}$ at 254 nm) was 2×10^{-11} g/sec for the ultraviolet absorption detector.

The great advantage of the differential refractometer over the more sensitive interferometer in the measurement of small differences in refractive index has been its comparative simplicity and compact size. The use of lasers as light-sources makes it possible to design much smaller interferometers which can be used to monitor column effluents. An interferometric detector with a cell volume of only 4 μl has been reported by Hazebrook.[26] A helium–neon laser operating at a wavelength of 632.8 nm was used as a light-source. After polarization the beams were passed through the standard and reference cells and combined, the fringes being detected by silicon photodiodes. The large dynamic range (5000:1), rugged construction and small size make it suitable for such tasks as high-pressure capillary liquid chromatography or supercritical fluid phase separations. Although the limit of detection quoted was of the same order

Table 1. Comparison of detectors for column chromatography

Detector	Cell volume, *μl*	Sensitivity	Maximum detection, *mole/sec*	*mole/ml*
Refractometer (Laboratory Data Control)	5.0	2.87×10^{-7}	5.67×10^{-11}	2.67×10^{-8}
Refractometer (Waters Associates)	10.0	4.06×10^{-7}	9.86×10^{-10}	9.13×10^{-8}
UV detector ($l = 1$ mm)	27.2	8.68×10^{-3}	4.73×10^{-10}	5.69×10^{-8}
Wire detector	—	3.9×10^{-13}	3.93×10^{-8}	8.89×10^{-6}

as that for a sensitive differential refractometer, the ultimate sensitivity of an interferometer is theoretically much greater. It seems possible therefore that in the future these two devices will be in competition as detectors in liquid chromatography.

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PRELIMINARY COMMUNICATION

THE RAPID SEPARATION AND DETERMINATION OF RARE EARTH ELEMENTS BY USE OF THE LIGAND VAPOUR GAS-CHROMATOGRAPHIC METHOD*

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In our laboratory, a new gas-chromatographic technique called the "ligand vapour gas-chromatographic (LVGC) method" has been developed and successfully used for the determination of the trifluoroacetylacetone (HTFA) chelates of thorium and other metals.[1] Recently we have applied the LVGC method to the consecutive separation and determination of 4f rare earth elements. After thorough investigation of the experimental conditions, especially with respect to the composition of the stationary phase, it became possible to separate most of the neighbouring rare earth elements in one step, as demonstrated in the example shown in Fig. 1.

Sievers and others[2,3] have made extensive studies of the higher homologues of β-diketones which form thermally stable chelates when combined with the rare earth elements, but have not as yet reported a separation of the neighbouring elements.

A full report of the present work will be made later.

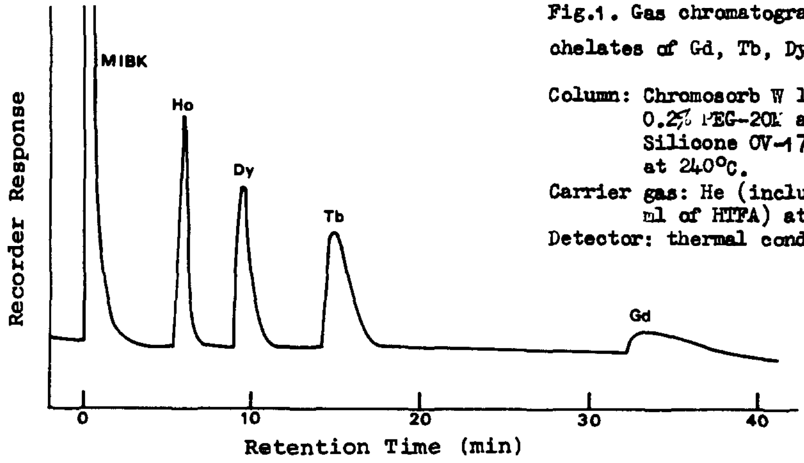

Fig.1. Gas chromatogram of TFA chelates of Gd, Tb, Dy and Ho.

Column: Chromosorb W loaded with 0.2% PEG-20M and 1.8% Silicone OV-17 and kept at 240°C.
Carrier gas: He (including 0.41 ml of HTFA) at 41 ml/min.
Detector: thermal conductivity.

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TALANTA MINI-REVIEW*

THE DETERMINATION OF VANADIUM

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Summary—A review is given of the developments in the analytical chemistry of vanadium that have taken place in the last 15 years.

The importance of vanadium in modern science and technology is reflected in the growing number of publications dealing with the analytical characterization of vanadium: over 1000 have appeared in the past 15 years. The earlier literature has been covered by Grady.[1] Our intention in writing this paper is to give some guidelines to the analytical chemist who wishes to select a method for a particular problem. To this end, we quote only those papers that seem to us to have something new and important to say, but this must not be construed as meaning that the literature omitted is without value. The material is classified according to the techniques by which vanadium is determined. First classical, then electroanalytical, optical and finally other instrumental methods are described. This classification is, we hope, in accordance with the demands of the practising analytical chemist, who may have only a limited number of techniques at his disposal when choosing his method.

QUALITATIVE TESTS FOR VANADIUM

Of the many reagents mentioned in the literature kojic acid should be recommended first:[2] under the correct conditions 0.5 μg of vanadium in a 2-ppm solution may be detected in the presence of numerous cations and anions. Ferron has been investigated by the same authors,[3] while others[4] found the Schiff-base formed from anthranilic acid and salicylaldehyde to be an equally selective and sensitive reagent for vanadium.

QUANTITATIVE SEPARATION OF VANADIUM

Solvent extraction techniques

These may be based on direct extraction with a substance serving both as complexing agent and as the water-immiscible solvent. The efficiency of such separations depends on the pH of the aqueous phase. Among such reagents 4-methylpentan-2-ol[5] and mesityl oxide[6] can be mentioned. More suitable, however, are extractions based on binary or ternary systems. The binary systems consist of a reagent and a solvent; the ternary may have two reagents with one solvent or one reagent with a mixture of two solvents. Their use gives a wider choice of experimental conditions and the separations are generally sharper and more specific. 8-Hydroxyquinoline with chloroform[7] or isobutyl methyl ketone[8] gives a good separation; so does a ternary system based on 8-hydroxyquinoline, benzyldimethyltetradecylammonium chloride and chloroform.[9] Another long-chain alkylamine is the ion-exchanger Amberlite LA-2 which, when dissolved in chloroform, is a powerful extractant for vanadium.[10] Vanadium(III) can be extracted with ammonium thiocyanate and ethyl methyl ketone;[11] tin(II) chloride can be used for preliminary reduction of the vanadium. Thiocyanate combined with tributyl phosphate[12] is suitable for extracting vanadium(IV), and the tributyl phosphate also reduces any vanadium(V) present. Tributyl phosphate alone in hydrochloric acid solution is an effective reagent; both the theoretical and the practical aspects of this separation have been investigated.[13]

β-Diketones, such as acetylacetone (with butanol)[14] and 2-thenoyltrifluoroacetone with isopentyl or butyl acetate,[15] butanol,[16] chloroform[17] or a chloroform–benzene mixture[18] have also been recommended. Hydroxamic acids are well-known reagents for vanadium; they may be used as selective extractants with various solvents, 4-Methoxybenzothiohydroxamic acid,[19] *N*-phenylbenzohydroxamic acid[20,21] and *N*-phenyl-2-naphthohydroxamic acid[22] are the most suitable. Normally chloroform is the solvent, but the sensitivity may be increased by adding ethanol to it.[20] α-Benzoinoxime in chloroform,[23] quinaldinic acid in a mixture of pyridine and chloroform[24] and 1,2,3-phenyloxyamidine[25] in ether are also powerful combinations. A thorough study of some ternary systems containing di(2-ethylhexyl) hydrogen phosphate, kerosene and, as the third component, sodium fluoride or thiosalicylic acid,[26] led to a procedure for the quantitative extraction of vanadium(IV) and its separation from vanadium(III). The choice of the third partner depends on the composition of the matrix.

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* For reprints of this Mini-Review, see Publisher's announcement near the end of this issue TALMR 4.

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Another system for extraction of vanadium(IV) is 3-methylcatechol and lauryltrimethylammonium bromide in 1,2-dichloroethane.[27]

Chromatographic methods

As vanadium may be present in solution either as a cation or as an anion, depending on the oxidation state and the acidity, there are several possibilities on which separations may be based. The simplest way of removing small amounts of vanadium for a solution is co-precipitation, where aluminium hydroxide,[28,29] zirconium oxide[29] or iron(III) hydroxide[30] may serve as carriers. The theoretical aspects of the separation of vanadium and other metals by cation- or anion-exchangers have been elucidated in a series of papers.[31] Cation-exchangers retain vanadium(IV) or (V) from strongly acid solutions.

With Dowex 50 W-X8 (H^+-form) small amounts of vanadium can be separated quantitatively from 25 other metal ions.[32,33] In the presence of titanium the cation-exchanger KY-3 (H^+-form) has been used,[34] while in the analysis of ferrovanadium or iron ores[35] the cation-exchanger KU-2 can be used to advantage. Dowex-1 anion-exchanger, with an excess of fluoride,[36] chloride,[37,38] thiocyanate[39] or acetate[40] in the solution, is the most widely applicable.

The combined use of Dowex-1 anion-exchanger and Dowex-50 cation-exchanger facilitates the quantitative separation of six metals, including vanadium, from one another.[41] The anion-exchanger EDE 10 P with hydrochloric acid,[42] lithium chloride[43] or hydrogen fluoride[44] can also be used. The Chelex-100 chelating ion-exchanger is specially recommended for the removal of vanadium from sea-water.[45] The liquid anion-exchanger Aliquat 336, adsorbed on XAD-2 resin, can remove peroxovanadate(V) together with other peroxo anions.[46]

Redox ion-exchangers are also available for the retention of vanadium; tetrachloroquinol (on Celite A support)[47,48] and chloranil[49] (on polyurethane foam) are the most suitable.

Paper chromatographic separations with various solvents[50,51,52] and with impregnated papers[53,54,55] are also available, though thin-layer chromatographic methods[56,57,58] usually offer sharper separations.

Paper electrophoretic[59,60] and gas-chromatographic[61–64] methods are also available; the latter will be discussed again in more detail.

GRAVIMETRIC DETERMINATION

Some of the old methods have been improved. Vanadium sulphide can be precipitated from homogeneous solution[65] with thioacetamide. A critical re-examination of the well-known precipitation in the form of silver vanadate[66] has revealed that precipitation is only quantitative and stoichiometric between pH 6.2 and 6.8. Numerous new organic reagents have also been suggested for the gravimetric determination of vanadium. Some of these, such as *o*-hydroxyacetophenone oxime,[67] *N*-(2)-hydroxynaphthyl-1-methylene ethylamine and 2-hydroxynaphthaldoxime[68] and benzoylacetanilide[69] produce a high molecular weight compound which can be dried and weighed, allowing the accurate determination of 10–50 mg of vanadium.

TITRIMETRIC DETERMINATION

Vanadium can be titrated with redox, complexometric and precipitating agents. Some of the well-known methods have been examined further, and a few new reagents have been introduced. A large number of papers deal with the application of known methods for the determination of vanadium, to various matrices. These cannot be reviewed here for lack of space, and we decided to omit contributions which contained only minor variations on well-established methods. Some authors have made a critical comparison of known methods with the aim of finding the most reliable procedure.

One critical study[70] showed that the most reliable titrimetric method is to oxidize vanadium to vanadate, remove the excess of the oxidizing agent, reduce vanadate with a known excess of iron(II) ammonium sulphate (added as the weighed solid) and back-titrate with potassium dichromate.

Another[71] compared the precision of the titration of vanadium(V) with iron(II) sulphate and the titration of vanadium(IV) with potassium permanganate and found that the reductometric process is considerably the more accurate if *N*-phenylanthranilic acid is used as indicator.

Another group of researchers[72] examined and combined redox and complexometric titrations with spectrophotometric measurements to determine vanadium, molydenum, tungsten, phosphorus and silicon in the same sample.

The titration with permanganate becomes more sensitive if vanadium is reduced not to the quadrivalent, but to the tervalent state. A bismuth reductor is most suitable for the reduction.[73] With fluoride as complexing agent the permanganate titration gives good results even if chromium(III) ions are present.[74] If dichromate is used as the titrant, the titration reaction is normally slow. An analytical study has been made of the vanadium(IV)–chromium(VI) reaction.[75] In the presence of an excess of phosphoric acid the titration with dichromate can be carried out with normal speed,[76] and mixtures of vanadium(III) and vanadium(IV) can also be titrated.[77] Mixtures of iron(II) and vanadium(IV)[78] as well as of molybdenum(V) and vanadium(IV)[79] can also be titrated under similar circumstances. Cerimetric titration can be performed with photometric[80] and potentiometric[81] end-point detection, without the addition of external indicators. The limitations of the photometric method have been examined theoretically and experimentally.[80] With ferroin,[82] tris(bipyridyl)iron(II) and Rhodamine B[83] as indicators, visual titrations are also possible. Other oxidimetric titrants have also been suggested; potassium ferricyanide in alkaline medium,[84] potassium chlorate,[85] iodine cyanide and bromide cyanide[86] are all suitable reagents. Vanadate can oxidize vanadium(III) to vanadium(IV), and therefore ammonium vanadate can be used as titrant for the determination of vanadium(III),[87] and with some modifications for separate determination of vanadium(II) and vanadium(III).

Vanadium(V) can be reduced to vanadium(IV) with iron(II). With amperometric end-point detection this titration is very accurate,[88] but the change of potential at the end-point is not large enough to ensure an accurate potentiometric determination unless a complexing agent which keeps the free iron(III) concentration low is added. Such agents are EDTA with Methylene Blue or thionine (the latter two as photosensitizers),[89] glycerol in alkaline medium[90] and phosphoric acid.[91] In syrupy phosphoric acid medium vanadium(IV) can also be reduced with iron(II),[92] and in ammoniacal solutions containing catechol, the vanadium(IV)-vanadium(III) end-point becomes extremely sharp.[93] Among other reductometric titrants potassium ferrocyanide[94] has been suggested for potentiometric micro-titrations. Chromium(II) sulphate[95] with potentiometric or photometric end-point, copper(I) chloride with visual indicators,[96] molybdenum(III) with potentiometric end-point[97] and vanadium(II) with visual indicators[98] may also be used. The last-named reduces both vanadium(V) and vanadium(IV) to the tervalent state under the given experimental conditions. Sodium thiosulphate with copper as catalyst reduces vanadium(V) and the titration can be monitored by potentiometry.[99] Hydroxylamine can also be used to determine vanadium(II) and vanadium(III) in one sample, though not as a direct titrant,[100] the excess of the reagent and the vanadium(II) being back-titrated in two stages with permanganate or cerium(IV) with potentiometric end-point detection. Hydrazine sulphate alone[101] or combined with phosphoric acid[102] can be used as reductometric titrant with photometric, potentiometric and in some cases visual indication. Binary mixtures of vanadium(V) and chromium(VI) can also be analysed with these reagents; isonicotinic acid hydrazide can also be used, with photometric end-point detection, the two inflexions of the titration curve corresponding to the two equivalence points.[103]

Vanadate can be titrated with silver nitrate, forming a precipitate, the composition of which depends on the pH of the medium[104] but is always stoichiometric, facilitating the determination of vanadium with potentiometric, amperometric or conductometric end-point detection.[105]

Vanadium(IV) and (V) react with EDTA. These reactions have been re-examined[106] and improved procedures have been recommended.[107] In addition to the usual metallochromic indicators, ferron[108] and Variamine Blue[109] are also suitable. Some new complexation reactions have been found and made the basis of a titrimetric determination: the new titrants are 2'-hydroxy-5'-methylpropiophenone oxime,[110] sodium tungstate[111] and pyridine-2,6-dicarboxylic acid in the presence of hydrogen peroxide.[112] A redox titration with Methyl Orange can be used.[113,114] With 5,7-dibromo-8-hydroxyquinoline[115] or with the di-iodo derivative,[116] heterometric micro-titrations are possible. Non-aqueous reductometric titrations of vanadium with chromium(II) acetate in dioxan can be used for the determination of micro-amounts of vanadium(IV).[117]

Vanadate forms polyanions when the solution is acidified with a strong acid. The possibility of titrating vanadate with perchloric acid, using thermometric end-point detection, has been investigated and favourable results have been reported.[118]

Coulometry and chronopotentiometry

Coulometric determinations of vanadium are based either on the reduction of vanadium(V) or on the oxidation of vanadium(IV). The two forms can be determined in the presence of each other by *controlled-potential coulometry*,[119] and with an on-line computer end-points can be predicted accurately before the completion of the experiment.[120] Vanadium(V) can be reduced in the presence of manganese and iron, but chromium(VI) interferes.[121]

With *constant-current coulometry* we have the choice of a direct determination[122] or the coulometric generation of an auxiliary reagent. Of these, tin(II),[123,124,125] and iron(II),[126,127] iron(II)-EDTA,[128] titanium(III),[130] copper(I),[131] molybdenum(IV)[132] and vanadium(III)[133] are suitable for the determination of vanadium(V), and the lower oxidation states of vanadium can be oxidized with electrogenerated iron(III),[134] dichromate,[135] and *p*-benzoquinone[136] as coulometric titrants. The controlled-potential coulometric determination of vanadium can also be carried out in a *molten salt electrolyte*, the sample being fused with a lithium chloride-potassium chloride eutectic.[137] Vanadium(V) can also be determined in molten salts by *chronopotentiometry*.[138]

VOLTAMMETRY, POLAROGRAPHY AND RELATED TECHNIQUES

The *d.c. polarography* of vanadium is usually based on the cathodic reduction of vanadium(V), though reduction from other oxidation states is also possible. Some new developments in this field include the determination of vanadium in various industrially important matrices: the determination in the presence of titanium,[139] thallium,[140] molybdenum,[141] nickel, copper and manganese,[142] iron, nickel and cobalt[143] as well as tungsten, chromium, lead, copper and arsenic[144] is now possible. An unusual method[144] for the analysis of steel is based on the reduction of vanadium(II) to the amalgam. The polarographic behaviour of vanadium in concentrated phosphoric acid has also been studied.[145] An *inverse voltammetric* determination of small amounts (0.2 μg/ml) of vanadium is possible with the carbon-paste electrode.[146] With *d.c. or a.c. oscillopolarography*, capacitor currents can be eliminated from the measured signals, thus improving the sensitivity of the determination. The addition of complexing agents makes the method not only sensitive, but also selective; tartaric, citric and trihydroxyglutatic acids,[147] fluoride,[148] ferron,[149] and thiocyanate[150,151] are the most suitable. A detailed study of the oscillopolarographic behaviour of vanadium[147] revealed that both the reduction of vanadium(V) and the oxidation of vanadium(IV) are suitable for analytical purposes.

It has been established that, when subjected to *voltammetry at a pyrolitic graphite electrode*, vanadium(V) is reduced irreversibly, though the voltammetric peaks are fairly reproducible.[152]

For the determination of vanadium by *amperometric titration* the titrimetric determination reagents already listed can normally be used. There are, however, some unusual reagents which have only been suggested for use with amperometric end-point detection. As oxidimetric titrants, pyrogallolcarboxylic acid[153] and hexa-amminecobalt(III) tricarbonatocobaltate,[154] and as a reductometric titrant vanadium(II) sulphate,[155] have been suggested, the latter reducing vanadium(IV) to the tervalent state. For a precipitation titration lead nitrate,[158] 8-mercaptoquinoline[159] and, in a reverse titration procedure, selenious acid[160] can be used. In the last method a known amount of selenite is titrated with the sample solution. For a complexometric titration 2,4-dithiobiuret[161] and Tiron[162] may be used. A number of papers, not listed here, describe the biamperometric ("dead-stop") titration of vanadium(V) with iron(II); a useful method with ascorbic acid as titrant is available for the simultaneous determination of cerium(IV) and vanadium(V).[163]

SPECTROSCOPIC METHODS

Emission spectrography

A large number of papers have been published on the determination of vanadium in different raw materials and industrial products. Usually a spark spectrum is obtained. Most frequently the line at 3185.4 Å is used, but those at 2864.4, 3093.1, 4112.0 and 4379.0 Å are also useful, depending on the nature of the matrix and the internal standard used. Though a detailed review of this field cannot be included here, some important new developments should be mentioned. A direct-reading spectrochemical determination of vanadium and other elements in silicates, with automatic background and matrix corrections (carried out by an on-line computer) is now possible with a coefficient of variation better than 5%.[164] A simplified standardization method based on varying the exposure time can be applied for metal samples.[165] Solvent extraction coupled with emission spectroscopy enhances the sensitivity and permits the use of an emission line produced by the solvent (a C–Cl line from the chloroform) as the internal standard.[166] Co-precipitation of vanadium with compounds such as cadmium or zinc hydroxide[167] or molybdenum phosphate[168] as collector can also favourably enhance the sensitivity. Specially prepared samples (fused buttons) can be used in the analysis of cast iron samples.[169] Geological materials can be analysed for vanadium after being diluted with a mixture of carbon and barium carbonate powder.[170] Solution techniques, resembling flame photometry, allow a higher degree of reproducibility. Small amounts of vanadium can be determined by spraying a solution of the sample through a capillary graphite electrode into an a.c. arc.[171] Hollow-cathode excitation can also be used for the emission spectrographic determination of vanadium.[172] Improved reproducibility and sensitivity are attainable by using microwave-induced plasma excitation,[173] especially if the vanadium is reacted to form a volatile chelate before the measurement.[174] The excitation processes of vanadium have been studied by time-resolved spectroscopy.[175]

Emission flame photometry

A detailed study of the flame emission spectrum of vanadium in a fuel-rich oxyacetylene flame revealed that the best wavelength for the determination is 4379.2 Å, the limit of detection being 3 ppm of vanadium.[176] The inter-element effects in a nitrous oxide–acetylene flame have been thoroughly studied.[177] The introduction of separated flames has increased the sensitivity of the determination of vanadium; with the nitrous oxide–acetylene flame the detection limit is 0.2 ppm,[178] but if the same flame is sheathed with argon or nitrogen, the detection limit is as low as 0.05 ppm.[179]

Atomic-absorption and atomic-fluorescence spectrophotometry

The atomic-absorption spectrum of vanadium in a fuel-rich acetylene–oxygen flame has been recorded.[180] Atomic absorption has been applied by a number of researchers to the determination of vanadium in various samples and matrices, but these applications will not be reviewed here. However, useful studies of interferences by inorganic substances[181,182] and organic solvents[183] have been carried out, and the addition of an excess of iodide[184] or aluminium chloride[185] has been suggested for eliminating these interferences. A new technique, a variation of the standard-addition method, may be used to obtain more reliable results.[186]

Microwave discharge tubes can easily be prepared in the laboratory, and can be used instead of hollow-cathode lamps as radiation sources in the determination of vanadium.[189] The use of sheathed flames[189] increases the sensitivity.

Important increases in sensitivity are achieved by using flameless techniques. A graphite, tungsten or tantalum boat,[190] with electrical resistance-heating is suitable for determining as little as 0.6 ng of vanadium. With a carbon-filament atomizer a limit of detection of 0.3 ng may be achieved,[191] while with one particular carbon-rod furnace even 6.8 pg of vanadium can be detected,[192] though another author has reported the much worse figure of 1 ng for a similar carbon-rod atomizer.[193] Much depends on the matrix, and the order in which the elements in the sample are volatilized also plays an important role.[194] With commercial graphite furnaces (cuvettes) at 2700 K the limit of detection is about 20 ng.[195] Interesting further developments in flameless atomic-absorption techniques involve the use of a high-frequency flame-like discharge,[196] a d.c. arc[197] and a plasma jet[198] as the means of atomization.

Sensitivities may be improved by using indirect techniques, which were reviewed in this journal some years ago.[199] An interesting way of determining vanadium is to produce molybdovanadophosphoric acid, extract this with an organic solvent, re-extract into water and determine the molybdenum content of the solution by atomic absorption. With an acetylene–air flame 0.5 ppm of vanadium can be determined with a coefficient of variation of 3.4%;[200] a further increase in sensitivity can be obtained with a modified procedure, using the nitrous oxide–acetylene flame.[201]

In atomic-fluorescence spectrophotometry, using separated nitrous oxide–acetylene flames for atomization and a microwave-excited electrodeless discharge tube as a radiation source, the limit of detection was 88 ng/ml; of 23 ions investigated only aluminium, cobalt and tungsten interfere.[202]

Molecular-absorption spectrophotometry in the visible and ultraviolet region

This approach seems to be the most popular for the determination of small amounts of vanadium. In the last 15 years more than 320 papers have been published that recommend new reagents or new procedures with known reagents. It is again impossible to include all these works in this review; even stringent selection of the material still leaves 150 works worthy of mention. The most important inorganic and organic reagents will be discussed first, followed by an alphabetical list of some less common, but still useful, reagents.

Inorganic reagents. Several ionic species of vanadium in different oxidation states have characteristic colours: it is therefore possible to determine vanadium spectrophotometrically by its own colour. Tervalent,[203] quadrivalent[204] and quinquevalent[205] vanadium may all be determined in this way. Peroxovanadium(V) (known also as peroxyvanadic acid) is a well-known coloured product obtained by treating vanadium solutions with hydrogen peroxide. Its use for the determination of vanadium has been re-examined and the optimal experimental conditions have been established.[206] The determination in the form of heteropoly acids has the advantage that it can be combined with an extraction procedure, enabling vanadium to be separated at the same time. When determining vanadium as the yellow tungstovanadophosphoric acid the best wavelength for the measurement seems to be 364 nm,[207] but good results can also be obtained at 392,[208] 415,[209] or 436[210] nm. Use of molybdovanadophosphoric acid may have some advantages, especially if it is measured in the ultraviolet (228 nm),[454] though measurements at 360[211] and 323[212] nm are also used. Thiocyanate, depending on the experimental conditions, may be used as a reducing[213] or a complexing[214] agent; in both cases the resulting product can be measured by spectrophotometry. Recently, the use of ferrocyanide has been recommended.[215]

Important organic reagents. The most sensitive spectrophotometric reagents for vanadium are the various di-substituted aromatic hydroxylamines of *hydroxamic acids.* Over the years a large number of derivatives have been prepared and suggested as reagents. There are really no great differences in sensitivity and selectivity among the various reagents; the limits of detection lie between 10 and 100 ng/ml in most cases, and determinations are feasible up to concentrations of 10 μg/ml. It is not easy to select a "best" reagent because of the large choice; some authors, however, have made comparative studies which may be used as guides. Thus, one research group compared 52 saturated[216] and 23 unsaturated[217] *N*-arylhydroxamic acids, finding *N*-*m*-tolyl-*p*-methoxybenzohydroxamic acid and *N*-phenyl-3-styrylacrylohydroxamic acid as best choices out of the first and second groups respectively. In a previous study, which included 27 different hydroxamic acids, the same group singled out *N*-phenylcinnamohydroxamic acid[218] as the best choice. Other comparative studies[219,220] involved fewer reagents but may serve as a basis for choosing the best for a given task.

Simple benzohydroxamic acid[221] combined with solvent extraction can be used with advantage, but the best reagents seem to be the di-substituted acids. Out of these 4-methoxybenzothiohydroxamic acid,[222] benzoylphenylhydroxamic acid,[223] *m*-nitro-*N*-phenylbenzohydroxamic acid,[224] *m*-(*p*-chlorophenyl)-*N*-benzohydroxamic acid[225] and its *o*-chloro-derivative,[226] *N*-*o*-tolybenzohydroxamic acid,[227] *N*-phenyl-2-sulphobenzohydroxamic acid,[228] *N*-*p*-tolyl-2-furylacrylo- and *N*-phenyl-2-furylacrylo- hydroxamic acids[229] and thiophen-2-carboxyhydroxamic acid[230] are recommendable. Other simple hydroxamic acids which have been studied and recommended are the hexanohydroxamic,[231] nicotinohydroxamic,[232] 2-furohydroxamic,[233] cinnamohydroxamic,[233] quinaldohydroxamic[234] and 2-naphthohydroxamic.[235]

4-(2-Pyridylazo)resorcinol, better known as *PAR*, is a well-known chelating agent, used for the separation and spectrophotometric determination of a number of metals. Under certain conditions vanadium can be selectively complexed and the product extracted with an organic solvent. The organic phase, or, after stripping, the aqueous phase, can be subjected to spectrophotometry. At 560 nm, 0–2 μg of vanadium can be determined accurately. The choice of an auxiliary complexing agent is important; recent works recommend the use of tartrate,[236] fluoride,[237] phosphate,[238] EDTA,[239] chloroacetic acid,[240,241] 1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid[242] and citrate.[243] The composition of the vanadium–PAR complex has also been studied[244] and the optimal conditions for formation of the complex in the absence of auxiliary complexing agents have been established.[245] Another reagent, similar in structure, is 1-(2-pyridylazo)-2-naphthol (*PAN*). It has been recommended as a reagent for vanadium in ores[246] and steel.[247] A new reagent of similar nature, 5-ethylamino-2-(2-pyridylazo)-*p*-cresol, together with its two bromo-derivatives, is suitable for determining 0.1–0.5 μg/ml levels of vanadium.[248] A comparative study on the PAR and PAN complexes has been made.[249]

8-Hydroxyquinoline and its derivatives are also frequently used complexing agents. They react with a number of metals by forming precipitates in aqueous media, which can then be extracted and determined by spectrophotometry. The reagents on their own are not selective, but the use of an auxiliary complexing agent and the proper choice of pH can make these determinations highly selective. With 8-hydroxyquinoline itself, EDTA,[250] phosphate,[251] phenols,[252] sodium azide[253] and zephiramine[254] are suitable masking agents for a number of determinations on different matrices. Another way of improving the selectivity is to co-precipitate vanadium with 8-hydroxyquinoline and phenylphenol.[255] Some derivatives such as 7-arylazo-8-hydroxyquinoline,[256] 8-hydroxy-5,7-di-iodoquinoline[257] and 8-aminoquinoline[258] are also suitable reagents.

Methylthymol Blue is a well-known metallochromic indicator, used mainly in complexometric analysis. It forms coloured complexes with a number of metals,[259] but under certain conditions it can serve as a selective reagent for vanadium.[260] Usually the vanadium(V) complex is measured, but the vanadium(IV) complex is also suitable for qualitative determination.[261] The latter complex can also be extracted.[262]

1,10-Phenanthroline, often used as a reagent for bivalent iron, forms a coloured complex with vanadium(II) and can be recommended for its determination by spectrophotometry.[263] In the presence of sodium azide, vanadium(V) can be determined if the complex is extracted. Vanadium(IV) does not react under these conditions.[264] Alternatively, 6-hydroxy-1,7-phenanthroline may be used.[265]

Phenylfluorone reacts with quadrivalent metals; its use for the determination of tin(IV) is well known. In the absence of tin(IV) it can also be used for the determination of vanadium(IV);[266] with 9-(3-pyridyl)-fluorone[267] a vanadium concentration as low as 5 ng/ml can be determined.

With the use of complexing agents, maltol (3-hydroxy-2-methylpyran-4-one) is a selective reagent for vanadium(V);[268] the product can be extracted into chloroform. Interferences of a number of ions can be eliminated by proper choice of the acidity.[269,270]

Other organic reagents. The following reagents, listed in alphabetical order, can also be used for the spectrophotometric determination of vanadium under certain conditions: Acid Alizarin Black SN,[271] Acid Chrome Blue K,[272] Alizarin Red S,[273] 3-amino-5-hydroxy-naphthalene-2,7-disulphonic acid,[274] *p*-anisidine,[275] Arsenazo,[276] catechol alone[277] or with a tertiary amine[278] or as its 3,4-dinitro derivative,[279] Calcichrome,[280] *p*-chloroaniline,[281] Chrome Azurol S alone[282] or combined with zephiramine,[283] 1,2-di-(2-aminoethoxy)ethane-*N,N,N′,N′*-tetra-acetic acid and hydrogen peroxide,[284] 1,2-di-(2-aminoethyl)-ether-*N,N,N′,N′*-tetra-acetic acid,[285] *o*-dianisidine,[286] β-(diantipyrinylmethyl)styrene[287] and its derivatives,[287,288] 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol,[289] 5,7-dichloro-8-hydroxyquinaldine,[290] (diethylamino)pyridylazophenol derivatives,[291] 3,3-dimethylnaphthidine,[292] 2-dimethylaminoethanethiol,[293] diphenylamine,[294] Eriochrome Cyanine,[295] Eriochrome Red,[296] Erio Green,[297] ferron,[298] formaldoxime,[299] *o*-hydroxyacetophenone,[300] 3-hydroxyflavone,[301] bis(2-hydroxyethylimino)gossypol,[302] 2-(3-hydroxy-3-phenyltriazeno)benzoic acid[303] and its sulphonated derivative,[304] *N*-hydroxysuccinic acid,[305] 2,2′-iminodibenzoic acid (Vanadox),[306] β-isopropyltropolone,[307] the reagent called MAAF II,[308] Magneson (dimethylamino-2-[3-(1-methyl-2-piperidyl)-2-pyridylazo]phenol,[309] *N*-methylanabasine-α-azo-α-naphthol,[310] morin,[311,312] murexide,[313] naphthalene-2,3-diol,[314] nicotinic acid hydrazide,[315] organic dibasic acids,[316] oxalic acid,[317] phenothiazine derivatives,[318] *o*-phenylenediamine,[319] phenylthiosemicarbazide,[320] phthalocyaninetetrasulphonic acid,[321] picramic acid,[322] picraminazo N,[323] propane-1,2-diaminetetra-acetic acid (APDT),[324] propyl-2,3,4-trihydroxybenzoate,[325] protocatechuic acid,[326] pyridine thiocyanate,[327] pyridine-2,6-dicarboxylic acid,[328] pyridine-2,4,6-tricarboxylic acid,[329] 6-(2-pyridylazo)thymol,[330] 6-2(pyridylazo)-3,4-xylenol,[331] Pyrogallol Red,[332] quercetinsulphonic acid,[333] rutin,[334] salicyalaldehyde,[335] Schiff-base,[336] Solochrome Black RN,[337] Solochrome Violet RS,[338] sulphonated derivatives of diphenylcarbazone and dithizone,[339] Sulphonazo,[340] Sulphonitrazo,[341] sulphosalicylic acid,[342] tetraphenylphosphonium chloride,[343] various thiazolylazo-compounds,[344,345] thiosalicylamide,[346] tiron,[347] tribromopyrogallol,[348] tris(2-hydroxyalkyl)amine derivatives,[349] tropolone[350] and Xylenol Orange.[351]

Infrared spectroscopy

Infrared spectroscopy is a powerful technique for the qualitative characterization of substances. Though its main field of application is organic chemistry, it can be applied for inorganic systems. In one important paper[352] all previously published infrared data on vanadium have been collected. From the infrared spectra and correlation charts it is now possible to identify ortho-, pyro-, meta-, hexa and decavanadates. A quantitative determination of vanadium in infrared spectroscopy is possible by precipitating with 8-hydroxyquinoline, making a KBr disk and measuring the characteristic absorption band.[353]

Molecular-fluorescence spectrophotometry

The great advantage of molecular-fluorescence spectrophotometry is that by selecting the wavelengths of both the excitation and emission radiation separately, one has double the confidence in the qualitative characterization. The vanadium complexes of isophthalic acid[354] and benzoic acid[355] show characteristic fluorescence and can be used for the quantitative determination of vanadium. The structure of the complexes and the mechanisms of the reactions leading to the fluorescent compounds have also been discussed.

Electron paramagnetic resonance (EPR) and electron spin resonance (ESR) spectroscopy

These techniques are seldom used for quantitative analysis. Nevertheless, it is possible to determine 0.1–200 ppm of vanadium(IV) as vanadyl aetioporphyrin by EPR spectroscopy,[356] the method being especially suitable for the determination of vanadium in crude petroleum.[356,357] At low temperatures the Q-factor of the oscillator is considerably higher than at room temperature, facilitating the EPR spectroscopy determination.[358] Quantitative determination is also possible with ESR spectroscopy.[359,360] The reaction mechanism of the formation of the vanadium(IV)–Arsenazo complex has been investigated by EPR spectroscopy.[361]

X-Ray fluorescence

As the X-ray spectra of the elements are comparatively simple, consisting of only a few strong lines, the evaluation of the X-ray fluorescence spectrum of a sample containing several elements is relatively easy. This, together with the absence of chemical interferences and dependence on oxidation state, and its applicability to nearly all the elements, has helped to ensure the popularity of XRF in spite of the costs involved and the problems of sample preparation. Usually the unresolved $K\alpha_{1,2}$ lines are used for the analysis (with an LiF analyser crystal they appear at $2\theta = 76.91°$), without the use of a titanium filter, which absorbs these lines. For the same reason, titanium and also calcium interfere if present in the sample.

More than 40 papers have appeared in the past 15 years on the determination of vanadium by this technique, about half of them dealing with the analysis of steel, rock or petroleum samples. They describe various techniques for sample preparation, and there are differences in the choice of the line measured. These papers have not been included in this review. Some special methods of sample preparation have been developed, such as a device to handle small liquid samples,[362] a borax-disk technique for fusible substances,[363] a cellulose disk method,[364] adsorption of metal ions from solutions with cation-exchangers and use of the dried solid as the sample,[365] as well as dissolving the substance in sulphuric acid, evaporating to small volume and preparing a paste with magnesium oxide,[366] which is dried and then used as the sample in the X-ray spectrophotometer. When the amount of vanadium is too small for direct determination, preconcentration by precipitation with ammonium tetramethyldithiocarbamate[367] or diethyldithiocarbamate[368] as precipitants can be applied. The determination of vanadium in samples such as ultrapure chemicals,[369] air-borne dust[370,371] and organometallic compounds[372] is also possible by X-ray fluorescence. Electron-microprobe determinations of vanadium in silicates[373] and in samples containing titanium,[374] where spectral interferences have to be eliminated, have also been described. A simple mathematical method to evaluate matrix effects in X-ray fluoresence analysis can also be applied.[375]

ACTIVATION ANALYSIS

Neutron-activation analysis is one of the most powerful techniques, capable of determining as little as 10^{-12} g of some elements. By careful choice of neutron energy, neutron flux, length of irradiation and cooling time between irradiation and measurement, the method can be adapted for the determination of vanadium in almost any matrix. The number of papers which have appeared over the past 15 years demonstrates the popularity of the technique.

Usually, thermal neutrons are used to activate ^{51}V in an n,γ reaction to give ^{52}V which gives a γ-line at 1.433 MeV suitable for measurement. The isotopic abundance is almost 100%, the cross-section is reasonably high at 4.9 barns, but the half-life is rather short at 3.76 min. The limit of detection is usually better than 10^{-9} g, though it does depend on the composition of the matrix.

Methods are available for the determination of vanadium in iron alloys,[376] iron and iron ores,[377] high-purity iron,[378] aluminium,[379] petroleum,[380] fuel oil,[381] air-pollution particles,[382,383,384] rocks and meteorites,[385,386] cement,[386] nuclear graphite,[387] lunar samples,[388] human bone,[389] biological materials,[390] tissue[391] and plants.[392] Sometimes a chemical preconcentration or separation step is needed before activation analysis; this can be done with ion-exchangers,[393] extraction with 2-nonylpyridine N-oxide[394] or precipitation with 8-hydroxyquinoline.[395] Moderated fast neutrons[396] and charged particles[397,398] can also be used for the activation analysis of vanadium. A special technique called "re-activation analysis" can also be used[399] and a precipitation–exchange technique, based on the measurement of ^{110}Ag, has also been described.[400]

CATALYTIC ANALYSIS

There are two main advantages of catalytic methods of analysis. First, they allow the selective and sensitive determination of trace amounts (as low as 10–100 ng) with simple, cheap equipment. Secondly, they produce an analytical signal from a kinetic system which is moving towards equilibrium; this signal is different in principle from almost all other analytical signals, obtained from equilibrium systems. The rate of a reaction between two reactants, present in macro amounts, is measured; this depends on the analytical concentration of the catalyst present. Vanadium catalyses several redox processes in homogeneous solution; at least 50 papers have been published on its catalytic determination. The optimum concentration range is usually 0.1–1 ppm with a detection limit of 0.02 ppm (20 ng/ml). The methods reviewed here will be classified according to the oxidizing agents applied. Vanadium catalyses the bromate oxidation of iodide,[401,402] thiocyanate,[403] amidol,[404] 4-amino-5-hydroxynaphthalene-2,7-disulphonic acid,[504] Bordeaux Red[406] (this method being also adapted for the determination of vanadium in steel),[407] Bromopyrogallol Red,[408] Eriochrome Blue P,[409] Indigo Carmine,[410] 4-aminodiphenylamine-2-sulphonic acid,[411] *p*-phenetidine[412] and Solochrome Violet.[413] With chlorate as oxidizing agent, traces of vanadium can be determined by using *p*-aminodiethylaniline,[414] aniline,[415] benzidine,[416] 4-hydrazinobenzenesulphonic acid[417] or *p*-phenetidine[418] as the reducing agent. Hydrogen peroxide oxidizes iodide,[419,420] aniline[421] (this reaction can be adapted for the determination of vanadium in rocks),[422] benzidine[423] and diphenylcarbazide[424] in slow reactions which are catalysed by trace of vanadium. Oxidations with peroxodisulphate are also catalysed by vanadium; catechol[425] and gallic acid[426] can serve as reducing agents. With the latter, vanadium can also be determined in sea-water.[427] The oxidative coupling of 4-hydrazobenzenesulphonic acid with 1-naphthylamine is also suitable as a main reaction for the catalytic microdetermination of vanadium.[428] When Landolt reactions are used as the slow reaction, a simple visual procedure can be adapted, reaction times being measured with a stop-watch. Landolt systems involve one oxidizing and two reducing agents. With the bromate–iodide–ascorbic acid system 0.1 ppm of vanadium can be determined selectively in the presence of 22 foreign ions.[429] Good results are also obtainable with the bromate–bromide–ascorbic acid,[430,431] the chlorate–chloride–ascorbic acid[432,433,434] and the chlorate–bromide–ascorbic acid[435] systems. Chemiluminescence reactions are also catalysed[436,437] or quenched[438] by traces of vanadium, and these reactions can again be used for its determination.

MASS SPECTROMETRY

Although not a cheap technique, mass spectrometry produces an easily distinguishable analytical signal, and can be adapted for the qualitative and quantitative characterization of an element, such as vanadium, with a relatively low atomic weight. Spark-source mass spectrometry is normally used. ^{51}V is present in almost 100% abundance and the ^{51}V line is well separated (in an organic matrix no other line appears between mass numbers 50 and 52). The limit of detection is about 0.01 ppm, with 0.1–10 ppm the optimum concentration range.

The method can be adapted for various matrices, mass spectrometric determinations of vanadium in iron and steel,[439,440,441] other metals,[442,443] rocks,[444] coal ash,[445] marble[446] and titanium dioxide[447] having been described.

GAS CHROMATOGRAPHY

Some metal chelates with organic ligands are easily volatilized. This fact can be utilized for the gas chromatographic separation of vanadium from other metals and its determination. As chelating agents trifluoroacetylacetone,[61] thenoyltrifluoroacetylacetone,[62] bis(trimethylsilyl)trifluoroacetylamide[63] and salicylaldimine[64] have been suggested. Usually, the separated components are condensed and the vanadium is determined by spectrophotometric methods.

MISCELLANEOUS TECHNIQUES

Separations based on the ring oven technique coupled with spectrophotometry,[448] fluorescence measurements,[449] segment colorimetry[450] and the related technique of annular colorimetry[451] are also suitable for the qualitative and quantitative characterization of traces of vanadium. Thermogravimetric studies on vanadium precipitates[452] and alums containing vanadium(III)[453] have also been made.

As interest in the determination of vanadium seems to grow, the authors hope to prepare a further critical review when enough new material, worthy of appraisal, becomes available.

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ACID–BASE TITRATIONS BY STEPWISE ADDITIONS OF EQUAL VOLUMES OF TITRANT WITH SPECIAL REFERENCE TO AUTOMATIC TITRATIONS—I

THEORY, DISCUSSION OF THE GRAN FUNCTIONS, THE HOFSTEE METHOD AND TWO PROPOSED METHODS FOR CALCULATING EQUIVALENCE VOLUMES

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Summary—The range of acid stability constants over which the Gran functions are applicable in evaluating acid–base titrations at normal concentrations is studied and found to be quite narrow. Alternatively, the titrations can be evaluated by using non-approximative methods based upon an equation that is derived without making the simplifying assumptions leading to the Gran functions. One such method, introduced by Hofstee, is discussed and the results of a study of the effects of a systematic error in the pH-determinations upon the determination of the equivalence volume are given. Two other non-approximative methods for evaluating acid–base titrations that are particularly suitable for use in automatic titrations of many similar samples are also described. These methods yield correct values of the equivalence volume regardless of a possible systematic error in the pH-values and are particularly useful for titrations of moderately strong and very weak acids (stability constants up to 10^{10}–10^{11} at $0.01M$ concentration) where the Gran functions cannot be used.

Over the years, the so-called Gran curves[1,2] have attracted the interest of analytical chemists. This interest has been intensified by the introduction of several new ion-selective electrodes. The Gran functions (founded upon an idea of Sørensen's[3]) represent one of the first attempts to linearize titration curves, thereby making it possible to calculate the equivalence volume by using several points on the titration curve instead of only the inflexion point. As shown by Johansson and Pehrsson[4] it is simple to design an apparatus for performing titrations automatically along the principles developed by Gran.

The Gran functions for titrations of acids with strong base are summarized in Table 1. Similar functions may be derived for titrations of bases and for compleximetric titrations, *e.g.*, of fluoride ions.[5]

The titrant is in each case assumed to be a strong base. V_0 is the volume of the sample solution before the titration is started, V the volume of titrant added, and k, k' are arbitrarily chosen constants. If the functions are plotted against V, straight lines are obtained that intersect the V-axis at V_e, the equivalence volume.

The great advantage of the Gran functions is that it is not necessary to determine absolute [H]-values (charges are omitted for simplicity). It suffices to determine values proportional to [H] which means that it is not necessary to calibrate the electrode system. However, the use of the traditional Gran curves is restricted to a limited range of acid strengths. The Gran function $(V_0 + V)10^{(k-\mathrm{pH})} = f(V)$ gives a straight line only when a strong acid is titrated. As shown below, $V\,10^{(k-\mathrm{pH})}$ will not give a completely straight line for any acid. However, for moderately weak acids, HA, having logarithmic stability constants

$$\log K_{\mathrm{HA}} = \log[\mathrm{HA}] - \log[\mathrm{H}] - \log[\mathrm{A}]$$

lying in the range 5.0–8.5, more than 50% of the function will lie on a straight line intersecting the V-axis at $V = V_e$ (assuming concentrations of the order of $0.01M$). There is a range of acids between strong and moderately weak within which neither of these simple functions will yield satisfactory results and this has not been generally recognized. When the acids are

Table 1. Gran's second method

Substance titrated	Gran functions	
	On the acid side of the equivalence point	On the alkaline side of the equivalence point
Strong acid	$(V_0 + V)10^{(k-\mathrm{pH})} = f(V)$	$(V_0 + V)10^{(\mathrm{pH}-k')} = f(V)$
Weak acid	$V10^{(k-\mathrm{pH})} = f(V)$	$(V_0 + V)10^{\mathrm{pH}-k'} = f(V)$

very weak, the Gran function $V\,10^{(k-\mathrm{pH})} = f(V)$ gives incorrect results.

Ingman and Still,[6] and Johansson,[7] have derived the following equation that is valid throughout the range of acidic strengths without approximations:

$$V_e = V + K_{HA}\left\{V[H] + \frac{V_0+V}{C}[H]^2 - \frac{V_0+V}{C}K_w\right\} + \frac{V_0+V}{C}\left\{[H] - \frac{K_w}{[H]}\right\} \qquad (1)$$

K_w is the ion-product of water and C the concentration of the titrant solution. This equation requires use of concentrations and concentration constants determined at the ionic strength in use. The different terms in equation (1) all have the dimension of volume and may be interpreted as being contributions in different pH-ranges to the equivalence volume of the acid. This makes it quite easy to judge whether a term is negligible or not. A similar equation can be derived for titrations of bases with strong acids.

It is easily seen that the Gran functions mentioned in the introduction may be obtained from equation (1) by making the appropriate simplifying assumptions. In strongly acidic solutions, in other words when a strong acid is being titrated, all other terms in equation (1) may be neglected in comparison with the term $(V_0 + V)[H]/C$ and so the Gran function for titrating strong acids is obtained. When a weak acid is titrated, the dominant term will be $K_{HA}V[H]$, thus yielding the Gran function for titrating weak acids. Finally, if the value of K_{HA} is not too high, equation (1), for strongly alkaline solutions, will be reduced to

$$(V_e - V) = -\frac{(V_0+V)}{C}\frac{K_w}{[H]}$$

which is the Gran function to be used after the equivalence point when base is being added in excess to the solution.

The aim of the first part of the present paper is to study the conditions under which titration data will give correct equivalence volumes when treated according to Gran. In the second part of the paper, a method given by Hofstee[8] is discussed. This method is based upon equation (1) and is thus non-approximative, but it requires knowledge of absolute [H] values and not simply values proportional to [H]. In this case it is consequently necessary to calibrate the electrode system. In the third part, two alternative non-approximative methods of calculating equivalence volumes from titration data are presented. The equivalence volumes are determined by using equation (1) and simple numerical methods. It is shown that even large systematic errors in the determination of the pH values can be tolerated without sacrifice in the accuracy of the results. A very rough calibration of the electrode system is therefore enough. An apparatus for automatic titration utilizing the principles put forward in this paper will be presented in a forthcoming communication.

MEASURING HYDROGEN-ION CONCENTRATIONS

The most common method of measuring hydrogen-ion concentrations is potentiometrically with the glass electrode. Though the electrode in principle responds to activity, it may be calibrated with known concentrations if precautions are taken in order to keep the activity factors constant. This can be done by using ionic media of constant ionic strength. Equation (2) relates the measured potential to the concentration of hydrogen ions in the solution:

$$E = E'_0 + Q\log[H] + E'_j \qquad (2)$$

Here, E'_0 stands for the standard potential, including the reference potential and the part of the activity coefficients and the junction potential that is independent of the acidity. $Q = RT\ln 10/nF = 59.2$ mV at 25°. In our experience, good glass electrodes do not deviate from this value in a thermostatically controlled system. $E'_j = j_H[H] + j_{OH}[OH]$ accounts for the acidity-dependent part of the activity coefficients and the junction potential. The constants j_H and j_{OH} are characteristic of the ionic medium.

In the following we denote $-\log$ [H] by ph to distinguish it from $-\log\{H\} = $ pH, where $\{H\}$ is the hydrogen-ion activity. Our experience shows that the main cause of errors in the determination of ph is the difficulty of obtaining a correct value of E'_0. The most accurate way to determine E'_0 seems to be by a so called E'_0-titration (see below). First, however, the values of j_H and j_{OH} must be determined.

The value of j_H may be determined once and for all by titrating a known amount of a rather concentrated solution of strong acid with strong base. The concentrations of the acid and base must be known. The base is added stepwise and E and V are measured after each addition of titrant. A plot of $E - Q\log[H]$ against [H] yields j_H as the slope and E'_0 as the intercept with the y-axis;[9] j_{OH} is similarly calculated from titration points taken after the equivalence point.

When j_H has been determined, E'_0 is preferably determined by titrating a more dilute solution of strong acid ($C_{HA} = 0.01$–$0.001M$) in order to minimize the effect of an error in j_H. For each titration, several values of E'_0 can be calculated by using equation (2) and the E'_0 value to be used is taken as the mean. Normally, an E'_0-titration is run in a separate vessel before the titration of the unknown in another vessel. A small change in E'_0 (of the order of a few tenths of a millivolt) may result when the electrode is transferred from one solution to another. This source of error can be eliminated by running the E'_0-titration before the determination of the unknown, which is then added to the same solution. This procedure is, however, time-consuming and is only used when a very high degree of accuracy in the determination of E'_0 is necessary.

The simplest, though less accurate, method of determining E_0' is to use a calibration solution of known hydrogen-ion concentration.

A change in E_0' also seems to take place in some glass electrodes on going from the acid to the alkaline pH-range. This change may amount to a few millivolts. An electrode system that is to be used on the alkaline side of this region should therefore be calibrated in alkaline solution and points that lie in the critical range should not be used in the evaluation of titrations.

THE GRAN FUNCTIONS

Since their appearance, the Gran functions have been discussed and further developed by several authors. In their monograph on computer calculations in analytical chemistry, Dyrssen and coworkers[10] discussed the approximations that need to be made in order to obtain the Gran functions for titration of bases with strong acids. They gave some rather crude rules for deciding when the Gran functions $V/[\mathrm{H}]$ and $(V_0 + V)[\mathrm{H}]$ may be expected to yield correct results. They also discussed the functions from the statistical point of view and devised methods for estimating the precision of the determination of the equivalence volume from the titration points and for deciding whether a point should be disregarded or not. Hansson and Jagner[11] modified the Gran plots for titration of the total alkalinity and carbonate content in ocean water by accounting for the interfering side-reactions of other species in sea-water.

Ebel and Krömmelbein[12,13] have discussed experimental sources of errors in the use of Gran functions. According to them, a 1% error in the slope of the electrode response will result in a titration error of 0.3% for a titration of strong acid with strong base. No such error has, however, been observed by the present authors if the temperature is properly controlled. Ebel and Krömmelbein have also shown[14] that the Gran function $V[\mathrm{H}]$ represents a poor approximation of the complete equation (1) for some ranges of K_{HA} values. Therefore, they applied orthogonal polynomials to approximate equation (1) but exchanged the (x,y)-values for (y,x)-values in the curve-fitting procedure. This was later commented upon by Wahbi[15] who considered it to be mathematically incorrect.

McCallum and Midgley[16] have discussed the effect of changes in activity coefficients upon the Gran functions during a titration. They took these changes into account by an iterative computer technique using the Debye–Hückel equation. They thus assumed that no attempts are made to keep the ionic strength of the solution constant during the course of the titration. In a second paper[17] the same authors have shown that the Gran function $V[\mathrm{H}]$ gives poor results for acids having $C_{\mathrm{HA}}K_{\mathrm{HA}} < 10^3$. They have also extended the equation given by Ingman and Still to make it valid for titrations of acids in the presence of a weak base. Furthermore, they have given an equation for evaluating titrations of biprotic acids. The main drawback of these methods is that it is necessary to know the stability constants of both the acids and the bases as well as the E_0' of the electrode system.

The principal advantage of the simple Gran function is that it is not necessary to compute [H] from the measured emf data by using equation (2). As soon as E_j' is negligible it will be possible to plot for example $(V_0 + V)10^{(E-k)/Q}$ (that is, $(V_0 + V) \times$ constant $\times$ [H]) instead of $(V_0 + V)[\mathrm{H}]$ against V, where k is a constant that may be chosen arbitrarily. This is a distinct advantage since it is rather easy to measure E with good precision but an accurate determination of E_0' (and thus of [H]) is considerably more difficult.

One case where E_j' is frequently negligible is when weak acids are titrated at ionic strengths equal to or exceeding 0.1. However, when strong acids are titrated, it is often not possible to neglect E_j'. To give an example: in 0.5M potassium chloride, $j_{\mathrm{H}} \approx -90$ mV and $j_{\mathrm{H}}[\mathrm{H}]$ will vary from 0.9 mV to negligible values for a titration of 0.01M hydrochloric acid; this will result in a curved Gran plot.

When a strong acid is titrated and E_j' cannot be neglected, iteration provides one way of calculating values that are proportional to [H] though E_0' may be unknown. An approximate value of the equivalence volume V_e is then first calculated by using $E_j' = 0$. Subsequently, E_j' is computed from j_{H} and approximate [H] values obtained from the approximate V_e value. Corrected relative values of [H] may then be calculated for each pair of $(E - E_j', V)$ data. It is only rarely necessary to repeat the iteration.

The limitations of the Gran functions

These have been studied for different values of K_{HA} by computing theoretical titration curves and using these data ([H], V) to test the Gran functions. The calculations were done for titration of 0.01M acid with 0.1M sodium hydroxide, and for titration of 0.001M acid with 0.01M sodium hydroxide. The results are shown in Table 2. The first column in the table gives the initial concentration C_{HA}^0 of the acid, the second column gives log K_{HA} and the other columns list the range of the titration parameter a (defined by $a = VC/V_0C_{\mathrm{HA}}^0$), within which the Gran functions yield straight lines that intersect the V-axis at $V_e \pm 0.1\%$. (An arbitrary criterion of linearity was chosen, *viz.* the ordinate value of the function should not deviate from the corresponding ordinate of the extrapolated linear portion of the function by more than 0.1% of the straight line ordinate at $V = 0$.)

As can be seen from Table 2, the Gran function $V[\mathrm{H}]$ (or $K_{\mathrm{HA}}V[\mathrm{H}]$) which is used to evaluate titrations of weak acids does not yield a straight line within the specified error limits in the entire range $a = 0$–1 for any value of the stability constant. In the following, three specific examples will be discussed in some detail.

Table 2. The range $a(=VC_B/V_0C^0_{HA})$ within which the Gran functions yield straight lines that intersect the V-axis at $V_e \pm 0.1\%$ for different values of K_{HA}. (see text for explanation.)

C^0_{HA}, M	log K_{HA}	$(V_0+V)[H]$ a	$V[H]$ a	$(V_0+V)/[H]$ a
0.01	−10	0.00–1.00		1.00–2.00
	1.0	0.00–1.00		1.00–2.00
	1.5	0.75–1.00		1.00–2.00
	2.0	0.90–1.00		1.00–2.00
	2.5			1.00–2.00
	3.0		0.90–1.00	1.00–2.00
	3.5		0.85–1.00	1.00–2.00
	4.0		0.75–1.00	1.00–2.00
	4.5		0.65–1.00	1.00–2.00
	5.0		0.50–1.00	1.00–2.00
	5.5		0.40–1.00	1.00–2.00
	6.0		0.25–1.00	1.00–2.00
	6.5		0.15–0.99	1.01–2.00
	7.0		0.10–0.99	1.01–2.00
	7.5		0.05–0.97	1.03–2.00
	8.0		0.03–0.90	1.10–2.00
	8.5		0.02–0.75	1.25–2.00
0.001	−10	0.00–1.00		1.00–2.00
	2.0	0.00–1.00		1.00–2.00
	2.5	0.75–1.00		1.00–2.00
	3.0	0.90–1.00		1.00–2.00
	3.5			1.00–2.00
	4.0		0.90–1.00	1.00–2.00
	4.5		0.85–1.00	1.00–2.00
	5.0		0.80–1.00	1.00–2.00
	5.5		0.70–0.99	1.01–2.00
	6.0		0.55–0.99	1.01–2.00
	6.5		0.40–0.97	1.03–2.00
	7.0		0.25–0.90	1.10–2.00

Example 1. An acid having log $K_{HA} = 3.0$. Figure 1 shows a plot of $V[H]$ against V compared with a plot of $(V_e - V) = f(V)$ calculated from the complete equation (1) for a titration of 100 ml of $0.01M$ solution of an acid having log $K_{HA} = 3.0$, with $0.1M$ sodium hydroxide. As said above, all the terms in equation (1) have the dimension of volume. During the course of the titration different terms will be predominant in different pH-regions. In Table 3 the values of the terms $K_{HA}V[H]$, $K_{HA}(V_0 + V)(H)^2/C$, $(V_0 + V)[H]/C$, $K_{HA}(V_0 + V)K_W/C$ and $(V_0 + V)K_W/C[H]$ in equation (1) are listed for different values of a. It is seen from the table that the second and third terms listed above are not negligible in comparison with the first term at the beginning of the titration. However, as the equivalence point is approached the predominance of the first term grows and for the titration shown in Fig. 1, a straight line will result for $a = 0.9$–1.0. After the equivalence point all other terms are negligible in comparison with $(V_0 + V)K_W/C[H]$ and a plot of this function *vs.* V will therefore yield a straight line that intersects the V-axis at the equivalence volume.

Example 2. An acid having log $K_{HA} = 10$. Figure 2 shows a titration of 100 ml of $0.01M$ acid having log $K_{HA} = 10.0$, with $0.1M$ sodium hydroxide. According to Table 4 it is not possible to neglect the terms $K_{HA}(V_0 + V)K_W/C$ and $(V_0 + V)K_W/C[H]$ in comparison with $K_{HA}V[H]$ before the equivalence point. It is also necessary to consider all three terms after the equivalence point.

Example 3. An acid having log $K_{HA} = 7.5$. As is clear from Table 2, the best results will be obtained with the Gran function $V[H]$ in the range $6.0 \leq \log K_{HA} \leq 8.0$ at normal concentrations ($\approx 0.01M$). A plot of this function against V is shown in Fig. 3, assuming that 100 ml of $0.01M$ acid having log $K_{HA} = 7.5$ is titrated with $0.1M$ sodium hydroxide. As is seen from Table 5, The term $K_{HA}V[H]$ predominates over all other terms in equation (1) in the interval $0.1 < a < 0.9$.

Systematic titration errors

As seen from the preceding discussion, in many cases the lines that result from plotting the Gran func-

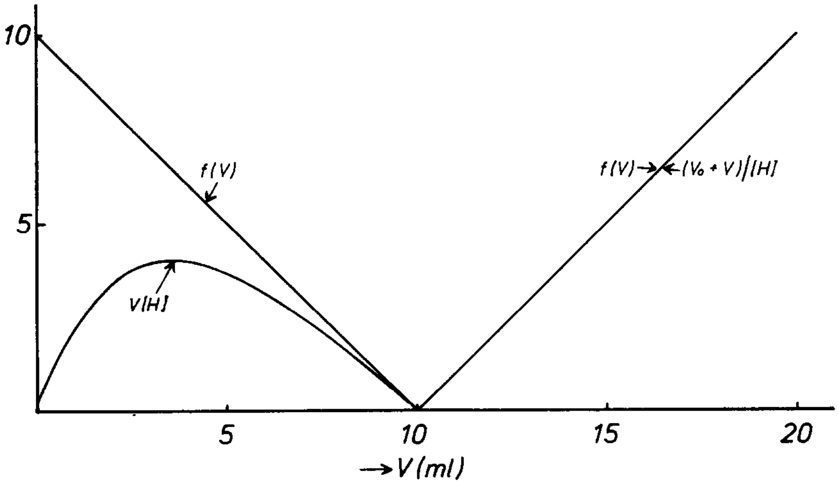

Fig. 1. Gran plots ($V[H]$ and $(V_0 + V)/[H]$) and a plot of $(V_e - V) = f(V)$ calculated from equation (1) against V for a titration of $0.01M$ solution of an acid having log $K_{HA} = 3.0$, with $0.1M$ NaOH.

Table 3. The table lists the contributions of the different terms in equation (1) to the equivalence volume at different values of a. It is valid for a titration of 100 ml of 0.01M solution of an acid having log K_{HA} = 3.0, with 0.1M NaOH

a	$K_{HA}V[H]$	$K_{HA}\frac{V_0+V}{C}[H]^2$	$\frac{V_0+V}{C}[H]$	$K_{HA}\frac{V_0+V}{C}K_w$	$\frac{V_0+V}{C}\frac{K_w}{[H]}$
0	0.000	7.300	2.702	0.000	0.000
0.1	2.152	4.676	2.173	0.000	0.000
0.2	3.374	2.903	1.721	0.000	0.000
0.3	3.910	1.749	1.342	0.000	0.000
0.4	3.955	1.017	1.028	0.000	0.000
0.5	3.666	0.564	0.770	0.000	0.000
0.6	3.151	0.292	0.557	0.000	0.000
0.7	2.485	0.135	0.380	0.000	0.000
0.8	1.718	0.050	0.232	0.000	0.000
0.9	0.883	0.010	0.107	0.000	0.000
1.0	0.000	0.000	0.000	0.000	0.000
1.1	0.000	0.000	0.000	0.000	−1.000
1.2	0.000	0.000	0.000	0.000	−2.000
1.3	0.000	0.000	0.000	0.000	−3.000
1.4	0.000	0.000	0.000	0.000	−4.000
1.5	0.000	0.000	0.000	0.000	−5.000
1.6	0.000	0.000	0.000	0.000	−6.000
1.7	0.000	0.000	0.000	0.000	−7.000
1.8	0.000	0.000	0.000	0.000	−8.000
1.9	0.000	0.000	0.000	0.000	−9.000
2.0	0.000	0.000	0.000	0.000	−10.000

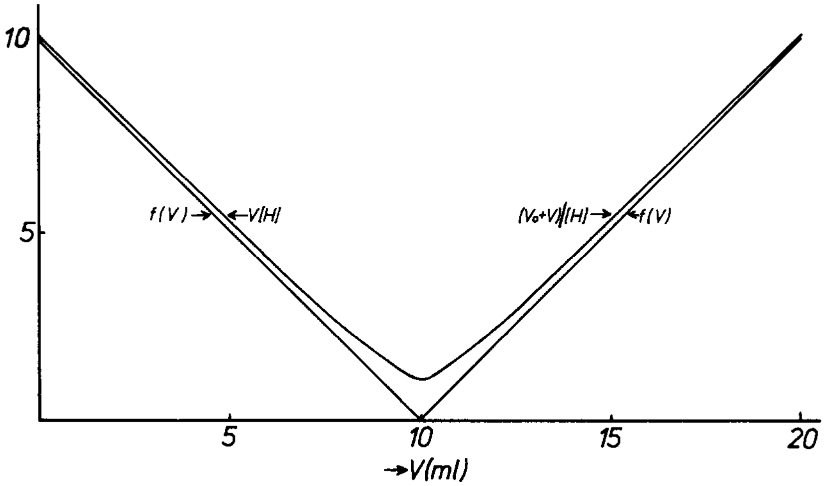

Fig. 2. As Fig. 1 but log K_{HA} = 10.0.

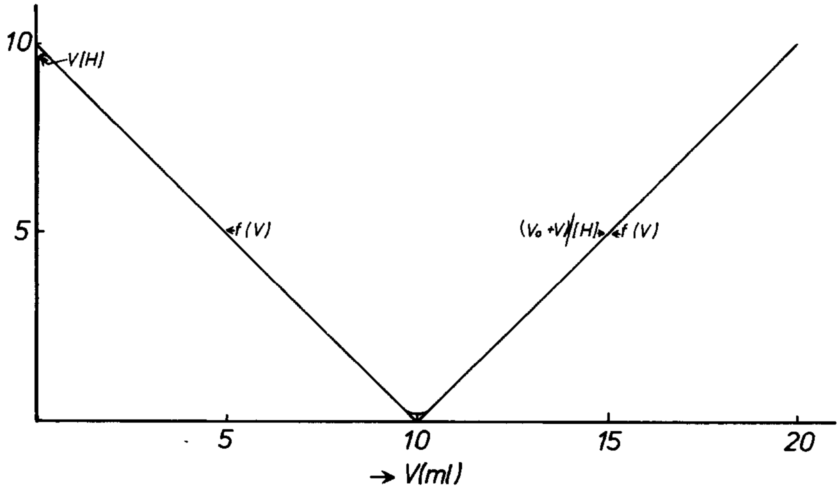

Fig. 3. As Fig. 1 but log K_{HA} = 7.5.

Table 4. The table lists the contributions of the different terms in equation (1) to the equivalence volume at different values of a. It is valid for a titration of 100 ml of 0.01M solution of an acid having $\log K_{HA} = 10.0$, with 0.1M NaOH

a	$K_{HA}V[H]$	$K_{HA}\frac{V_0+V}{C}[H]^2$	$\frac{V_0+V}{C}[H]$	$K_{HA}\frac{V_0+V}{C}K_w$	$\frac{V_0+V}{C}\frac{K_w}{[H]}$
0	0.000	10.097	0.001	−0.100	−0.000
0.1	9.111	0.000	0.000	−0.101	−0.011
0.2	8.127	0.000	0.000	−0.102	−0.025
0.3	7.146	0.000	0.000	−0.103	−0.043
0.4	6.172	0.000	0.000	−0.104	−0.067
0.5	5.205	0.000	0.000	−0.105	−0.101
0.6	4.255	0.000	0.000	−0.106	−0.149
0.7	3.332	0.000	0.000	−0.107	−0.225
0.8	2.459	0.000	0.000	−0.108	−0.351
0.9	1.689	0.000	0.000	−0.109	−0.581
1.0	1.105	0.000	0.000	−0.110	−0.995
1.1	0.747	0.000	0.000	−0.111	−1.636
1.2	0.551	0.000	0.000	−0.112	−2.439
1.3	0·441	0.000	0.000	−0.113	−3.328
1.4	0·375	0.000	0.000	−0·114	−4.260
1.5	0.331	0.000	0.000	−0.115	−5.216
1.6	0·300	0.000	0.000	−0.116	−6.184
1.7	0.278	0.000	0.000	−0.117	−7.161
1·8	0·261	0.000	0.000	−0.118	−8.142
1.9	0.248	0.000	0.000	−0.119	−9.129
2.0	0.237	0.000	0.000	−0.120	−10.116

tions will not be perfectly straight and this may lead to a systematic titration error. The magnitude of this error depends upon how large a part of the function is used for calculating the equivalence volume V_e. The theoretical systematic titration errors resulting when titrations of 0.01M solutions of acids of different strengths with 0.1M sodium hydroxide are evaluated by the diverse Gran functions have been collected in Table 6. It was assumed that the titrations were performed by stepwise additions of equal volumes of titrant in the range $a = 0$–1.0 so that $\Delta a = 0.1$. The equivalence volumes were calculated from not less than five titration points. If the only way to obtain an acceptable result is to use less than five points in the Gran evaluation, one of the methods presented below is definitely prefereable to the Gran method.

The applicability of the Gran functions

If it is desired that a Gran function should give a line that is straight over at least 50% of its course and such that the extrapolated straight-line portion intersects the V-axis at V_e with a maximum relative

Table 5. The table lists the contributions of the different terms in equation (1) to the equivalence volume at different values of a. It is valid for a titration of 100 ml of 0.01M solution of an acid having $\log K_{HA} = 7.5$, with 0.1M NaOH

a	$K_{HA}V[H]$	$K_{HA}\frac{V_0+V}{C}[H]^2$	$\frac{V_0+V}{C}[H]$	$K_{HA}\frac{V_0+V}{C}K_w$	$\frac{V_0+V}{C}\frac{K_w}{[H]}$
0	0.000	9.982	0.018	0.000	0.000
0.1	8.998	0.003	0.000	0.000	0.000
0.2	7.999	0.001	0.000	0.000	0.000
0.3	7.000	0.000	0.000	0.000	0.000
0.4	6.000	0.000	0.000	0.000	0.000
0.5	5.001	0.000	0.000	0.000	0.000
0.6	4.001	0.000	0.000	0.000	−0.001
0.7	3.001	0.000	0.000	0.000	−0.001
0.8	2.002	0.000	0.000	0.000	−0.001
0.9	1.003	0.000	0.000	0.000	−0.003
1.0	0.059	0.000	0.000	0.000	−0.059
1.1	0.004	0.000	0.000	0.000	−1.003
1.2	0.002	0.000	0.000	0.000	−2.002
1.3	0.002	0.000	0.000	0.000	−3.001
1.4	0.001	0.000	0.000	0.000	−4.000
1.5	0.001	0.000	0.000	0.000	−5.001
1.6	0.001	0.000	0.000	0.000	−6.001
1.7	0.001	0.000	0.000	0.000	−7.000
1.8	0.001	0.000	0.000	0.000	−8.000
1.9	0.001	0.000	0.000	0.000	−9.000
2.0	0.001	0.000	0.000	0.000	−10.000

Table 6. The systematic titration errors that result when linear regression is used to fit a straight line to calculated titration data (V,[H]) according to Gran's method. (See text for explanation.) Different values of the stability constant of the acid were assumed, and $C_{HA} = 0.01M$

$\log K_{HA}$	Range of the parameter a used in calculating the equivalence volume	Gran function used	
		$(V_0 + V)[H]$ titration error, %	$V(H)$ titration error, %
−10	0.00–1.00	<0.01	
1.0	0.00–1.00	<0.01	
1.5	0.50–1.00	−0.09	
2.0	0.50–1.00	−0.6	
2.5	0.50–1.00	−4.1	+11.5
3.0	0.50–1.00		+1.8
4.0	0.50–1.00		+0.3
5.0	0.40–1.00		+0.07
6.0	0.20–1.00		+0.08
7.0	0.10–1.00		+0.14
	0.10–0.90		+0.03
8.0	0.10–0.90		+0.08
8.5	0.10–0.90		+0.3
	0.10–0.60		+0.12
9.0	0.10–0.90		+0.8
	0.10–0.60		+0.4
9.5	0.10–0.90		+2.3
10.0	0.10–0.90		+6.3

error of ±0.1%, then Table 2 can be used to formulate the following conditions for the applicability of the Gran functions.

Before the equivalence point:

$(V_0 + V)[H]$ $C_{HA} = 0.01M$ $\log K_{HA} \le 1.0$
$V[H]$ $C_{HA} = 0.001M$ $\log K_{HA} \le 2.0$
$C_{HA} = 0.01M$ $5.0 \le \log K_{HA} \le 8.5$
$C_{HA} = 0.001M$ $6.0 \le \log K_{HA} \le 7.0$

After the equivalence point:

$(V_0 + V)/[H]$ $C_{HA} = 0.01M$ $\log K_{HA} \le 8.5$
$C_{HA} = 0.001M$ $\log K_{HA} \le 7.0$

THE HOFSTEE METHOD

As is clear from the discussion above, the use of the simple Gran functions is severely restricted, which is particularly serious when using the method of stepwise additions of equal volumes of titrant. With data of good quality equation (1) should always yield good results and it is easily solved with the aid of a computer. A systematic deviation of the ph measurements was considered the most likely systematic error and a study of its effects upon the results yielded by equation (1) has been conducted.

Hofstee[8] in 1960 published a method for determining equivalence volumes which is, in principle, based upon equation (1). He used the equations for the total concentration of the acid and the electroneutrality condition in order to determine the concentration of acid and the stability constant of the acid in the following manner:

$$C_{HA} = [A] + \{H\}[A]K_{HA}$$

$$[A] = [Na] + [H] - [OH]$$

where K_{HA} in this case is a mixed constant, and $[Na] = VC/(V_0 + V)$. A plot of $[A] \approx [Na] = VC/(V_0 + V)$ against $\{H\}[A]$ yields C_{HA} as the intercept with the y-axis and K_{HA} from the slope. Hofstee used his method with the approximations shown here to evaluate titrations that could equally well have been evaluated by Gran's method ($\log K_{HA} = 7.02$ and 7.90). His method was used for titrations of moderately strong acids and very weak acids by Benet and Goyan,[18] who also pointed out that a systematic error in pH gives an incorrect value of the equivalence volume if the titration data are taken outside the pH interval 5–9. Their experiments were conducted in such a way that V was negligible in comparison with V_0.

Leeson and Brown[19] modified Hofstee's equation in order to account for dilution during the course of the titration. Briggs and Stuehr[20] used an iterative technique to allow for excess of strong acid or strong base in the solution.

Equation (1) is linear in V_e and K_{HA} and may be written in the form

$$-V_e + rK_{HA} + s = 0 \tag{3}$$

where

$$r = V[H] + \frac{V_0 + V}{C}[H]^2 - \frac{V_0 + V}{C}K_w$$

and

$$s = \frac{V_0 + V}{C}\left([\mathrm{H}] - \frac{K_w}{[\mathrm{H}]}\right) + V.$$

V and E are measured. [H] is calculated according to equation (2), by an iterative technique when E'_j cannot be neglected. (Those who have until the present time published work about the Hofstee method have determined the hydrogen-ion activity and not the concentration. In other words, they have calibrated the glass electrode for hydrogen-ion activity. For them, it has therefore been necessary to know or determine the activity coefficients.)

After calculation of r and s for each measured point on the titration curve, linear regression may thus be employed to fit a straight line to equation (3), yielding the unknowns V_e and K_{HA}. [One of the assumptions made when the method of least squares is used for regression of y on x is that there is no error in x and a normally distributed error in y. Care should therefore be exercised in order to ensure that the quantity having the greater errors is considered as y. In equation (3) both r and s are dependent upon the primary data V and [H] (or rather E). Errors in these quantities are propagated and give corresponding errors in r and s. A certain error in [H] gives a much greater relative error in r than in s. Therefore, r should be considered as y in the calculations.]

The main advantage of the Hofstee method in comparison with the Gran functions is that it is applicable to acids of any strength since it is based upon the complete equation (1), which was derived without approximations. The main disadvantage is that it is necessary to measure absolute values of [H] and not just values proportional to [H], *i.e.*, E'_0 in equation (2) must be determined. As has already been pointed out, E'_0 is difficult to determine with good *accuracy*, but it is much easier to determine E with good *precision*.

An incorrect value of E'_0 gives rise to a systematic error, Δph, in the ph value that is calculated from the measured emf data. The error at 25° is given by

$$\Delta\mathrm{ph} = \frac{\Delta E'_0}{59.155\,\mathrm{mV}}$$

A systematic error in the ph values gives rise in turn to a systematic titration error when Hofstee's method is used to calculate the equivalence volume. We have calculated this titration error for Δph = ± 0.01, corresponding to an error of E'_0 of ± 0.5 mV in the determination, and for different values of K_{HA}. The results are shown in Table 7. It has been assumed that the titrations are performed by stepwise addition of equal volumes of titrant. The calculations were made for titration of 0.01*M* (0.001*M*) solution of acid with 0.1*M* (0.01*M*) sodium hydroxide in the range $a = 0$–1.0 with $\Delta a = 0.1$.

The table shows that the titration error at constant Δph is dependent upon the stability constant K_{HA} and the concentration of the acid that is being titrated. It is seen from Table 7 and Fig. 4 that the systematic titration error obtained when the Hofstee method is used to evaluate titrations will be least for those values of the stability constant that are most suitable for evaluation with the Gran function V[H]. (The reader is referred to Table 2.) This is quite logical since, as shown above, this Gran function may be used without knowledge of the value of E'_0. In these cases, Hofstee's method will give a very nearly

Table 7. The systematic titration errors that result by Hofstee's method for different values of log K_{HA} and C^0_{HA} (0.01*M* and 0.001*M*, respectively) if a systematic error Δph = ± 0.01 is assumed in the ph values. (See text for explanation.)

log K_{HA}	Range of the titration parameter a used in calculating the equivalence volume	Titration error, %	
		$C^0_{HA} = 0.01\ M$	$C^0_{HA} = 0.001\ M$
1.0	0.00–1.00	0.03	
1.5	0.10–1.00	0.09	
2.0	0.10–1.00	0.19	0.03
	0.30–1.00	0.10	
3.0	0.10–1.00	0.27	0.19
	0.30–1.00	0.10	
4.0	0.10–1.00	0.14	0.27
5.0	0.10–1.00	0.03	0.14
6.0	0.10–1.00	<0.01	0.03
7.0	0.10–1.00	<0.01	0.01
8.0	0.10–1.00	0.01	0.04
9.0	0.10–1.00	0.04	0.19
	0.10–0.90	0.02	
9.5	0.10–1.00	0.08	
10.0	0.10–1.00	0.19	1.0
	0.10–0.90	0.14	
11.0	0.10–1.00	1.0	

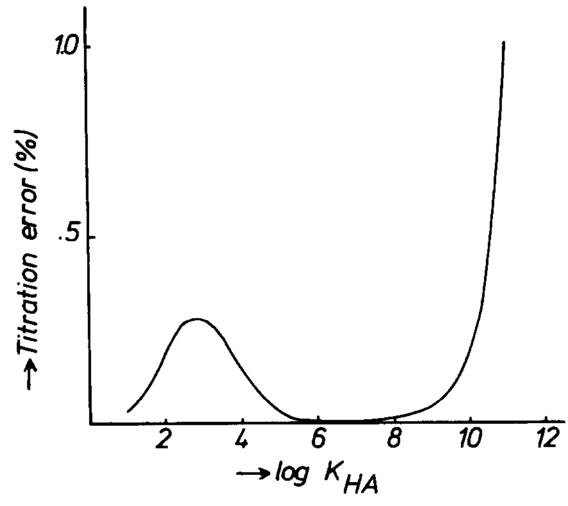

Fig. 4. The systematic titration error resulting by the Hofstee method from a systematic deviation $\Delta ph = \pm 0.01$ in the pH values as a function of log K_{HA}. The figure has been constructed for titrations of $0.01M$ acid with $0.1M$ NaOH. Ten additions of titrant were assumed so that $\Delta a = 0.1$. All points in the range of the titration parameter $a = 0.1$–1.0 were used in the evaluation.

correct value of the equivalence volume, but an erroneous value of the stability constant K_{HA} is obtained if there is an error in E_0'. In the K_{HA} range mentioned, the other terms in equation (1) are small in comparison with $K_{HA}V[H]$ and so the systematic titration error arising from an error in E_0' should also be small. It can be shown that *the titration error in most cases is approximately proportional to the error Δph in the ph values*, assuming moderate titration errors amounting at most to a few per cent. In the following, a few examples will be discussed. Titration of $0.01M$ solutions of the acids with $0.1M$ sodium hydroxide is assumed. Ten titrant additions ($\Delta a = 0.1$), all made before the equivalence point are also assumed.

Example 1. If log $K_{HA} = 7.5$ all terms in equation (1) except $K_{HA}V[H]$ are negligible in the range $0.1 \leq a \leq 0.9$ (refer to Table 5). A systematic error in the ph values will result in an incorrect value of K_{HA} but an almost correct value of the equivalence volume. $\Delta ph = +1.0$ thus yields log $K_{HA} = 8.5$ but an error in the equivalence volume V_e that is less than ±0.1%.

The largest systematic titration errors result when two or more terms in equation (1) are of the same magnitude. This is the case when values taken before the equivalence point are used to calculate the equivalence volume for titrations of moderately strong acids with K_{HA} values in the range $2.0 \leq \log K_{HA} \leq 3.5$ ($C_{HA} \approx 0.01M$). The terms $K_{HA}(V_0 + V)[H]^2/C$, $K_{HA}V[H]$ and $(V_0 + V)[H]/C$ will then all be of the same magnitude as shown by Table 3. Greater accuracy in the calculation of the equivalence volume may in such cases be achieved by omitting some of the first titration points (refer to Table 7). As shown by Table 3 the predominance of $K_{HA}V(H]$ grows as the equivalence point is approached.

At a constant value of Δph an increase in the titration error is also to be expected when very weak acids are titrated. The terms $K_{HA}(V_0 + V)K_w/C$ and $(V_0 + V)K_w/C[H]$ become increasingly important as compared to $K_{HA}V[H]$, with increasing values of K_{HA}.

The importance of the term $K_{HA}(V_0 + V)[H]^2/C$ is greatest when $a = 0$ and decreases rapidly with growing V. Because this term contains the square of the hydrogen-ion concentration, an error in [H] gives rise to a large error in the equivalence volume. This is the reason why *the point* a = 0 *should normally be disregarded* in the evaluation of the equivalence volume for weak acids.

Example 2. An acid having log $K_{HA} = 7.5$ is titrated. A Δph of ±0.01 is assumed. The titration error amounts to ±0.5% if $a = 0$ is included in the evaluation, whereas the error falls to less than ±0.01% if this point is left out.

In order to obtain good results when using the Hofstee method to compute equivalence volumes, only titration points *either* before *or* after the equivalence point should be used if there is a systematic error in the ph values. The reason for this is that for weak acids the predominant term in equation (1) before the equivalence point will be $K_{HA}V[H]$. After equivalence has been attained $(V_0 + V)K_w/C[H]$ will predominate.

Example 3. An acid having log $K_{HA} = 6.5$ is titrated. $\Delta ph = \pm 0.01$. If nine points before and nine points after the equivalence point ($\Delta a = 0.1$) are considered in the evaluation, the systematic error amounts to ±1%. With only the nine points taken before the equivalence point, the error is less than ±0.01%.

There is no reason to use the Hofstee method to evaluate titrations of acids having log $K_{HA} \leq 7.5$ and $C_{HA} = 0.01M$ (or log $K_{HA} \leq 6.5$ and $C_{HA} = 0.001M$) by using points taken after the equivalence point. The reason is that the Gran function $(V_0 + V)/[H]$ yields accurate equivalence volumes in these cases. In the same way it is best to use the Gran function $(V_0 + V)[H]$ for titrations of strong acids.

If the Hofstee method is to be used for calculation of the equivalence volume for *very weak acids*, E_0' for the electrode system should be determined in alkaline solutions. E_0' is then given by

$$\begin{aligned} E &= E_0' + Q \log [H] + E_j' \\ &= (E_0')_{OH} - Q \log [OH] + E_j' \\ &= (E_0')_{OH} - Q \log K_w + Q \log [H] + E_j' \\ E_0' &= (E_0')_{OH} + Q\,pK_w \end{aligned}$$

An error in K_w will result in an error in E_0' and thus in [H]. K_w is, however, also contained in equation (1). If the same value of K_w is used for calculation of E_0' and in equation (1), it can be shown that the errors will balance each other so that a correct value of the equivalence volume, V_e, is obtained. Consequently, in order to obtain a correct value of the equivalence volume it is not necessary to know K_w accurately *if the electrode is calibrated in alkaline solutions.* The value of K_{HA} will, however, be incorrect if the value of K_w is incorrect ($\log K_{HA}^{\text{obtained}} = \log K_{HA} + \Delta pK_w$, where ΔpK_w is the error in pK_w).

PROPOSED NON-APPROXIMATIVE METHODS NOT REQUIRING CALIBRATION OF THE ELECTRODE SYSTEM

The main disadvantage of the Hofstee method is that an accurate knowledge of E'_0 is required for certain ranges of acid strengths. It is true that E'_0 can be accurately determined by running an E'_0-titration before every analysis but this is a time-consuming and—especially in routine work—awkward procedure. Multiparametric refinement methods primarily designed for evaluating stability constants, such as Sillén's LETAGROP procedure,[21] can also be used for determining concentrations.[10] The value of E'_0 is refined by these methods during the calculations, and the problem of an E'_0 that varies from one titration to another may thus be solved. These methods are, however, rather complicated and generally require a considerable amount of computation time. Waldmeier and Rellstab[22] applied a similar technique to evaluate the concentration of a monoprotic acid. A disadvantage of their method is that it requires approximate values of all the parameters to be refined, *i.e.*, the concentration of the acid sample (in principle unknown), K_{HA} and E'_0.

The methods given below, however, do not require an approximate value of the concentration of the acid titrated, and one of the methods does not even require a value of K_{HA}. An approximate value of E'_0 must be known, but a very rough value is enough. This means that a crude calibration of the electrode couple is sufficient, and the value of E'_0 thus obtained can be used for months without recalibration. The methods include a non-linear regression procedure. In both cases a computer program can easily be written that performs the calculations according to the principles described below. The computation time required is short, generally only about 3–6 times that used for linear regression (for the same number of parameters).

The first method is intended for routine titrations of a particular acid, *e.g.*, in automatic analysis, and requires that K_{HA} is known, whereas this is not necessary in the second method. The methods are particularly useful for evaluating titrations of moderately strong acids ($1.5 \le \log K_{HA} \le 5$, $C_{HA} = 0.01M$) and very weak acids for which the results yielded by the Gran method are poor and the Hofstee method requires accurate determination of E'_0.

Method A, intended for use when the stability constant K_{HA} *is known*

If K_{HA} is known with sufficient accuracy it is possible to calculate V_e even without knowledge of E'_0, according to the following principle. An error (denoted by Δph) introduced into the ph values by an erroneous E'_0 will result in an incorrect [H], denoted by [H′]. Consequently,

$$\begin{aligned}[\mathrm{H}'] = 10^{-(\mathrm{ph}+\Delta\mathrm{ph})} &= [\mathrm{H}]\,10^{-\Delta\mathrm{ph}} \\ &= [\mathrm{H}]/f \text{ where } f = 10^{\Delta\mathrm{ph}} \qquad (4)\end{aligned}$$

Considering (4), equation (1) can be written in the form

$$y = -V_e + V + K_{HA}\left\{Vf[\mathrm{H}'] + \frac{V_0+V}{C}f^2[\mathrm{H}']^2 - \frac{V_0+V}{C}K_w\right\} + \frac{V_0+V}{C}\left\{f[\mathrm{H}'] - \frac{K_w}{f[\mathrm{H}']}\right\} \qquad (5)$$

The unknowns in the equation are V_e and f. In the first approximation f is put equal to 1. V_e is then obtained as the mean of the V_e values calculated from each titration point (V,[H′]) by using equation (5) (letting $y = 0$). If $f \neq 1$ (*i.e.*, the value of E'_0 is incorrect) and this mean value of V_e is inserted into equation (5), the equation will not give $y = 0$ for all V, [H′] pairs. Instead, y will have values denoted by Δy. Differentiation of equation (5) yields

$$\Delta y = -\Delta V_e + \Delta f\left\{K_{HA}V(\mathrm{H}') + \frac{V_0+V}{C}\left(K_{HA}\,2f[\mathrm{H}']^2 + [\mathrm{H}'] + \frac{K_w}{f^2[\mathrm{H}']}\right)\right\}$$

This equation is linear in ΔV_e and Δf. By use of calculated values of Δy from equation (5) and $f = 1$, these quantities may be calculated by linear regression. ΔV_e and Δf are used to correct V_e and f. The corrected values are in turn used to calculate new values of Δy by equation (5), and then new values of the differences ΔV_e and Δf are computed by equation (6) and so on. The iteration is repeated until two successive values of V_e differ by less than, for example, 0.01%.

The tolerable error in E'_0 which still gives convergence of the iteration to a correct result is at least ±60 mV (corresponding to an error in ph of ±1 unit). If desired, a corrected value of E'_0 may be obtained since $E'_0 = E'^{\text{guess}}_0 - 0.0592 \log f$ (at 25°C). In those cases where E'_j is not negligible when [H] is calculated, the following procedure is recommended: in the first approximation E'_j is neglected and a value of E'_0 is calculated according to the description above. This value of E'_0 is then used in calculating [H] values by using equation (2) and the calculations are repeated as described. Since E'_j in most cases is small, fast convergence may be expected.

When this method is used for titrations of many similar samples and the value of K_{HA} is unknown, an E'_0-titration is first performed. In the next titration, the first sample is titrated according to the Hofstee method, which gives the concentration of the sample and the value of K_{HA}. This value of K_{HA} is then used in the determination of the equivalence volumes of the other samples according to the proposed method.

Table 8. Titration error resulting from Method A, assuming an error of ±0.01 logarithmic units in log K_{HA} at different values of K_{HA} and C^0_{HA}. Ten titrant additions of equal volume are assumed

C^0_{HA}, M	log K_{HA}	Range of the titration parameter a used in calculating the equivalence volume	Titration error, %
0.01	1.0	0.10–1.00	<0.01
	2.0	0.10–1.00	0.06
	3.0	0.10–1.00	0.19
	4.0	0.10–1.00	0.14
	5.0	0.10–1.00	0.03
	6.0	0.10–1.00	<0.01
	7.0	0.10–1.00	<0.01
	8.0	0.10–1.00	0.01
	9.0	0.10–1.00	0.04
	10.0	0.10–1.00	0.20
	11.0	0.10–1.00	1.7
	7.0	0.20–2.00	0.22
	9.0	0.20–2.00	0.25
	10.0	0.20–2.00	0.40
	11.0	0.20–2.00	1.7
0.001	2.0	0.10–1.00	<0.01
	3.0	0.10–1.00	0.06
	4.0	0.10–1.00	0.19
	5.0	0.10–1.00	0.14
	6.0	0.10–1.00	0.03
	7.0	0.10–1.00	<0.01
	8.0	0.10–1.00	0.04
	9.0	0.10–1.00	0.20
	10.0	0.10–1.00	1.7

The results of a study of the effect of an error in log K_{HA} on the determination of V_e according to the proposed method are summarized in Table 8. For moderate titration errors (up to a few per cent), the titration error is approximately proportional to the error in log K_{HA}.

In the discussion above it has been assumed that the value of K_w is known, since a very approximate value is usually enough. When the titrations are performed in the acidic range the terms in equation (5) which contain K_w are small and a rough value of K_w may be used. It can be shown that an approximate value of K_w is sufficient even when the titrations are run in the alkaline range, provided that the electrode is calibrated for hydroxide-ion concentration when K_{HA} is determined.

If an erroneous value of K_w is used when K_{HA} is determined by the Hofstee method and an E'_0-titration in the alkaline range, an erroneous value of K_{HA} is obtained, as said before (log K^{obtained}_{HA} = log $K_{HA} + \Delta pK_w$, where ΔpK_w is the error in pK_w). If these incorrect values of K_w and K_{HA} are used in the calculations according to the proposed method, the errors in K_{HA} and K_w cancel each other so that *a correct value of the equivalence volume is obtained.* The condition for this is that the terms $K_{HA}(V_0 + V)[H]^2/C$ and $(V_0 + V)[H]/C$ in equation (1) are negligible.

If a titration is carried out in both fairly acidic and alkaline solution, K_w must be accurately known for this method to be used. This is the case when titration points are taken both before and after the equivalence point when moderately strong acids are titrated. However, when such acids are titrated it is recommended that only points taken before the equivalence point be used in order to avoid interfering equilibria. (This will be discussed in a subsequent part of this series.)

Method B, intended for use when the stability constant is unknown

Putting $K'_{HA} = fK_{HA}$ and $K'_w = K_w/f$, equation (5) may be written

$$y = -V_e + V + K'_{HA}\left\{V[H'] + \frac{V_0 + V}{C}f[H']^2 - \frac{V_0 + V}{C}K'_w\right\} + \frac{V_0 + V}{C}\left\{f[H'] - \frac{K'_w}{[H']}\right\} \quad (7)$$

In this case the unknowns are V_e, K'_{HA}, f and K'_w. Approximate values of E'_0 and K_w are required. First values are calculated for V_e and K'_{HA} by linear regression, letting $f = 1$ and $y = 0$. If $f \neq 1$ and/or the value of K_w is incorrect, and these values and the calculated values of V_e and K'_{HA} are inserted into equation (7), it will not give $y = 0$ for all V, $[H']$ pairs, but values denoted by Δy. Differentiation of equation (7) yields

$$\Delta y = -\Delta V_e + \Delta K'_{HA}\left\{V[H'] + \frac{V_0 + V}{C}f[H']^2 - \frac{V_0 + V}{C}K'_w\right\} + \Delta f\frac{V_0 + V}{C}\left\{K'_{HA}[H']^2 + [H']\right\} - \Delta K'_w\frac{V_0 + V}{C}\left\{K'_{HA} + \frac{1}{[H']}\right\} \quad (8)$$

Linear regression yields ΔV_e, $\Delta K'_{HA}$, Δf and $\Delta K'_w$. The differences so obtained are used to correct V_e, K'_{HA}, f and K'_w. The same iteration procedure as described above is then repeated until the value of V_e remains constant during two cycles of iteration.

When titrations of moderately strong acids and very weak acids are evaluated, the number of parameters may be reduced to three. These cases will be treated in more detail since the results yielded by the Gran method are poor and the Hofstee method requires a very accurate calibration of the electrode system.

When a titration of a *moderately strong acid* is evaluated it is recommended to use only titration points taken before the equivalence point, as mentioned before. The terms containing K_w in equation (7) may then be neglected and the number of parameters reduced to three. The calculations yield values for V_e, K'_{HA} and f. It is possible to calculate subsequently K_{HA} and E'_0 according to $K_{HA} = K'_{HA}/f$ and $E'_0 = E'^{\text{guess}}_0 - 0.0592 \log f$ (at 25°).

In the cases where $E'_j = j_H[H]$ cannot be neglected, it is possible to use the same iteration procedure as described above (see method A).

A greater positive than negative error in the ph-values may be tolerated without impairing the convergence of the iteration. The tolerable positive error may, for all K_{HA} values in the range $1.5 \leq \log K_{HA} \leq 5$ ($C_{HA} = 0.01M$), amount to 2 units of ph. The maximum negative error that still gives convergence varies with K_{HA}. In the most unfavourable case, $\log K_{HA} = 1.5$ ($C_{HA} = 0.01M$), the negative error may not exceed 0.1 ph-units. (Our investigation was made assuming ten equidistant titration points in the range $a = 0.1$–1.0.)

When titrations of *very weak acids* are evaluated, $K'_{HA}(V_0 + V)f[H']^2/C$ and $(V_0 + V)f[H']/C$ in equation (7) can be neglected if points taken at the very beginning of the titration curve are omitted. The results give the values of V_e, K'_{HA} $(= fK_{HA})$ and K'_w $(= K_w/f)$.

For $\log K_{HA} \leq 10$ ($C_{HA} = 0.01M$), 2 or 3 iteration cycles are sufficient even when the error in E'_0 amounts to ± 60 mV (*i.e.*, an error in ph amounting to ± 1 unit) and in pK_w to ± 1 unit. At $\log K_{HA} = 11$, four cycles are needed (assuming ten equidistant points in the range $a = 0.1$–1.0 or 0.2–2.0).

CONCLUSION

The results of this study may be summarized as follows.

When strong acids ($K_{HA}C_{HA} < 10^{-1}$) are titrated, there is no reason for using the complete equation (1), as perfectly satisfactory results may be obtained by using the Gran function $(V_0 + V)[H] = f(V)$. Titrations of weak acids with K_{HA} values in the range $5 < \log K_{HA} < 8.5$ ($C_{HA} = 0.01\,M$) may satisfactorily be evaluated by using the Gran function $V[H] = f((V)$.

The Hofstee method is non-approximative and can be used to evaluate titrations of acids of most strengths. However, for those acidic strengths for which the Gran functions yield poor results, the Hofstee method requires accurate knowledge of E'_0.

In automatic titrations it is desirable to be able to use all the titration points in the evaluation. This is in most cases impossible with Gran's functions. Furthermore, it is not desirable to be forced to make time-consuming determinations of E'_0 before almost every sample titration, as required by Hofstee's method for some values of $K_{HA}C_{HA}$. This disadvantage can be overcome by using one of the two other non-approximate methods presented in this paper. These methods require only very approximate E'_0-values.

It will be shown in forthcoming communications how similar methods can be applied to titrations of mixtures of acids and acids and weak bases, and how the same principles can be used in photometric titrations.

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ACID–BASE TITRATIONS BY STEPWISE ADDITION OF EQUAL VOLUMES OF TITRANT WITH SPECIAL REFERENCE TO AUTOMATIC TITRATIONS—II*

THEORY OF TITRATION OF MIXTURES OF ACIDS, POLYPROTIC ACIDS, ACIDS IN MIXTURE WITH WEAK BASES, AND AMPHOLYTES

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Summary—A general method for evaluating titration data for mixtures of acids and for acids in mixture with weak bases is presented. Procedures are given that do not require absolute [H]-data, *i.e.*, relative [H]-data may be used. In most cases a very rough calibration of the electrode system is enough. Further, for simple systems, very approximate values of the stability constants are sufficient. As examples, the titration of the following are treated in some detail: a mixture of two acids, a diprotic acid, an acid in presence of its conjugate base, and an ampholyte.

In the first paper in this series,[1] the applicability of the Gran functions[2] and the Hofstee method[3] to titration of monoprotic acids was discussed and two non-approximate methods were introduced that can use relative values of the hydrogen-ion concentration [H]. By using these methods, it is thus not necessary to measure absolute [H]-values and a very rough calibration of the electrode system is enough. One of the methods does not even require knowledge of the stability constants of the acids. In this paper, the same approach will be extended to mixtures of acids and to acids mixed with weak bases. First, a general procedure for the treatment of these types of titrations will be given. Then, four common types of titrations will be treated in more detail, *viz.* those of a mixture of two acids, a diprotic acid, an acid in the presence of its conjugate base and an ampholyte.

The titration of mixtures of acids is a problem that has been treated by numerous analytical chemists in the past. Two acids in admixture with each other can quite simply be titrated if the stability constants K_{HA} of the acids differ enough. How great this difference should be when traditional methods are used is dependent on the ratio between the concentrations of the acids and on the method that is used to detect the equivalence points of the titration. As a rule of thumb, a difference of 4 logarithmic units is usually considered satisfactory for instrumental detection of the end-point. For smaller values of the difference, the acids will apparently be titrated simultaneously and the evaluation of the titration will become increasingly difficult, yielding less reliable results. Some specific reactions of the anions may be utilized in order to apparently strengthen one of the acids.[4] If a specific reaction is difficult to find, a mathematical approach to the problem can be used. During the years a wide variety of solutions to the problem have been suggested.

Auerbach and Smolczyk[5] derived mathematical expressions for the evaluation of a titration of two acids in a mixture (the acids could be mono-, di- or triprotic). They also gave an error function to make possible the estimation of which titration points will give the most accurate results. The concentrations of the acids are taken as mean values of the results calculated from these points.

Frisque and Meloche[6] gave a mèthod for calculating the concentrations of two monoprotic acids in a mixture from one titration point and the total acid concentration. The pH of the titration point giving the minimum error is calculated from the stability constants of the acids.

Purdie *et al.*[7] devised a method to compare data obtained by titration of a mixture of two acids with theoretical titration data calculated for several ratios of the concentrations of the two acids. By graphical interpolation they determined the relative amounts of the two acids and knowledge of the sum of the concentrations of the acids permitted them to calculate the amounts of the individual acids.

All the methods[5–7] referred to above require knowledge of the sum of the concentrations of the acids. This is a drawback since other weak electrolytes that might be present in the sample, as impurities in the titrant (*e.g.*, carbonate ions) or in the neutral salt used to keep the ionic strength constant, often make the determination uncertain. Determination of the total concentration is also difficult if the acids are weak (refer to Part I). The methods also require exact knowledge of the stability constants of the acids.

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* Part I—*Talanta*, 1976, **23**, 769.

Methods for calculating the concentrations of two monoprotic acids in admixture with each other have been given by Komar,[8] Yui *et al.*[9,10] and Ivaska.[11,12] Ivaska[13] also gave a method for calculating the concentration of a diprotic acid. The methods require knowledge of the stability constants of the acids but not of the sum of the concentrations of the acids. Two titration points are enough for the calculations. If more points are used, better accuracy may be expected.

Kankare[14] devised a potentiostatic method for titrating mixtures of acids. This method has the advantage that the electrode system does not have to be calibrated. The sum of the concentrations of the acids must be known. Knowledge of the stability constants or of the "degree of deprotonation" of the acids is also required.

An error-minimization technique has been applied to the evaluation of mixtures of two acids by workers in this laboratory.[15] A similar technique has also been used by Meites *et al.*[16] for the titration of a weak acid contaminated by a small amount of a strong acid or base.

Midgley and McCallum gave a method for calculating the concentration of an acid in the presence of weak bases.[17] In the same paper they gave a method for the evaluation of a titration of a diprotic acid. The constants must be known. They also derived equations for the titration of a mixture of a weak acid (which may be polyprotic) and a strong acid.[18]

All the methods mentioned—Kankare's being the sole exception—require a very accurate calibration of the electrode system, *i.e.*, a very accurate determination of E'_0 (refer to Part I) should be made. This must be considered a drawback, especially in routine work, since it requires frequent and time-consuming E'_0-determinations. If the methods presented in this paper are used in calculating the equivalence volumes, approximate values of E'_0 and/or the stability constants are sufficient. The sum of the concentrations need not be known.

A GENERAL PROCEDURE FOR THE EVALUATION OF A TITRATION OF A MIXTURE OF ACIDS IN THE PRESENCE OF WEAK BASES

We assume that n acids having initial analytical concentrations $C^0_{HA_i}$ (*i.e.*, the total concentration irrespective of form) are titrated with V ml of a solution of strong base, *e.g.*, sodium hydroxide, of concentration C. There are also m weak bases present in the mixture, their initial analytical concentrations being $C^0_{B_j}$. The volume at the beginning of the titration is V_0 ml.

The stability constant (given in terms of concentrations of the different species and determined in a well-defined ionic medium) is given for the acid HA_i by

$$K_{HA_i} = \frac{[HA_i]}{[H][A_i]} \qquad (1)$$

if the charges are omitted for convenience. The stability constant of the conjugate acid HB_j of the base B_j is similarly given by

$$K_{HB_j} = \frac{[HB_j]}{[H][B_j]} \qquad (2)$$

and it is understood that $K_{HA_i} > K_{HB_j}$.

The total concentration of the acid HA_i when V ml of titrant have been added is

$$C_{HA_i} = [HA_i] + [A_i] = \frac{V_0 C^0_{HA_i}}{(V_0 + V)} \qquad (3)$$

Correspondingly, for the base B_j:

$$C_{B_j} = [HB_j] + [B_j] = \frac{V_0 C^0_{B_j}}{(V_0 + V)} \qquad (4)$$

The analytical concentration of added strong base, C_{OH}, in the solution is given by

$$C_{OH} = [OH] + \sum_i [A_i] - \sum_j [HB_j] - [H] \qquad (5)$$

Combination of equations (1) and (3) yields

$$[A_i] = \frac{V_0 C^0_{HA_i}}{(V_0 + V)(1 + [H]K_{HA_i})} \qquad (6)$$

and by combining equations (2) and (4) we obtain

$$[HB_j] = \frac{V_0 C^0_{B_j}}{(V_0 + V)}\left(1 - \frac{1}{1 + [H]K_{HB_j}}\right) \qquad (7)$$

The analytical concentration of added base is related to the concentration of the titrant by

$$C_{OH} = \frac{VC}{(V_0 + V)} \qquad (8)$$

By combining equations (5)–(8) we finally obtain

$$\sum_i \frac{V_0 C^0_{HA_i}}{1 + [H]K_{HA_i}} - \sum_j V_0 C^0_{B_j}\left(1 - \frac{1}{1 + [H]K_{HB_j}}\right) - (V_0 + V)\left([H] - \frac{K_w}{[H]}\right) - VC = 0 \qquad (9)$$

Equation (9) is valid for monoprotic acids and bases. Polyprotic acids and bases may under certain conditions be treated as mixtures of monoprotic species.[19,20] The constants for di- and polyprotic acids will then be titration constants and not true stability constants (*vide infra*).

In equation (9), V_0 and C are assumed to be known quantities. [H] is measured for different values of V. Furthermore, if K_{HA_i}, K_{HB_j} and K_w are known, then equation (9) is linear in $C^0_{HA_i}$ and $C^0_{B_j}$. In principle, $n + m$ corresponding values of V and [H] are sufficient to make possible the calculation of $C^0_{HA_i}$ and $C^0_{B_j}$. If there are more values of V and [H], equation (9) is solved for $C^0_{HA_i}$ and $C^0_{B_j}$ by linear regression analysis. Numerous manufacturers of computers have the necessary software ready for linear regression analysis. It should be noted that the accuracy of $C^0_{B_j}$ will be much less than the accuracy of $C^0_{HA_i}$.

Errors in the values of K_{HA_i}, K_{HB_j} and K_w (the constants may be known only approximately) give rise to errors in the resulting values of $C^0_{HA_i}$ and $C^0_{B_j}$. This is a problem that may often be solved by using a non-linear least squares method. Equation (9) may be written:

$$y = \sum_i \frac{V_0 C^0_{HA_i}}{1 + [H]K_{HA_i}} - \sum_j V_0 C^0_{B_j}\left(1 - \frac{1}{1 + [H]K_{HB_j}}\right) - (V_0 + V)\left([H] - \frac{K_w}{[H]}\right) - VC \qquad (10)$$

If incorrect values of K_{HA_i}, K_{HB_j} and K_w are used, equation (10) will not give $y = 0$ for all (V, [H])-pairs. Instead, y will have values denoted by Δy. Differentiation of equation (10) yields:

$$\Delta y = \sum_i r_{1i}\Delta C^0_{HA_i} + \sum_i r_{2i}\Delta K_{HA_i} + \sum_j r_{3j}\Delta C^0_{B_j} + \sum_j r_{4j}\Delta K_{HB_j} + r_5\Delta K_w \qquad (11)$$

where

$$r_{1i} = \frac{V_0}{1 + [H]K_{HA_i}}$$

$$r_{2i} = -\frac{V_0 C^0_{HA_i}[H]}{(1 + [H]K_{HA_i})^2}$$

$$r_{3j} = \frac{V_0}{1 + [H]K_{HB_j}} - V_0$$

$$r_{4j} = -\frac{V_0 C^0_{B_j}[H]}{(1 + [H]K_{HB_j})^2}$$

$$r_5 = (V_0 + V)/[H]$$

Equation (11) is linear in $\Delta C^0_{HA_i}$, $\Delta C^0_{B_j}$, ΔK_{HA_i}, ΔK_{HB_j} and ΔK_w. These quantities can be calculated by linear regression if the approximate values for K_{HA_i}, K_{HB_j} and K_w and the calculated values for $C^0_{HA_i}$ and $C^0_{B_j}$ are used. This requires at least $2(n + m) + 1$ corresponding values of V and [H]. The values of the difference so obtained are then used to correct the values of $C^0_{HA_i}$, $C^0_{B_j}$, K_{HA_i}, K_{HB_j} and K_w. New values of the differences are then obtained by using equations (10) and (11), and so on. The iteration is repeated until the value of $C^0_{HA_i}$ does not change by more than, for example, 0.01%.

Use of relative [H]*-values*

In the foregoing, absolute measurement of [H] has been presupposed. This implies that E'_0 (see Part I) for the electrode system in use is determined as accurately as possible. In the following, the possibility of calculating $C^0_{HA_i}$, though E'_0 is only approximately known, will be demonstrated. An error in the ph-values, denoted by Δph (ph = $-\log[H]$), introduced by an erroneous value of E'_0 will result in an incorrect [H] denoted by [H′]. Consequently,

$$[H'] = 10^{-(\mathrm{ph}+\Delta\mathrm{ph})} = [H]10^{-\Delta\mathrm{ph}} = [H]/f$$

where $f = 10^{\Delta\mathrm{ph}}$. Putting $K'_{HA_i} = fK_{HA_i}$, $K'_{HB_j} = fK_{HB_j}$ and $K'_w = K_w/f$, equation (10) may be written:

$$y = \sum_i \frac{V_0 C^0_{HA_i}}{1 + [H']K'_{HA_i}} - \sum_j V_0 C^0_{B_j}\left(1 - \frac{1}{1 + [H']K'_{HB_j}}\right) - (V_0 + V)\left(f[H'] - \frac{K'_w}{[H']}\right) - VC \qquad (12)$$

Differentiation of equation (12) yields:

$$\Delta y = \sum_i r'_{1i}\Delta C^0_{HA_i} + \sum_i r'_{2i}\Delta K'_{HA_i} + \sum_j r'_{3j}\Delta C^0_{B_j} + \sum_j r'_{4j}\Delta K'_{HB_j} + r'_5\Delta K'_w + r'_6\Delta f \qquad (13)$$

Here, $r'_{1i} - r'_5$ are defined as $r_{1i} - r_5$ above, except that K_{HA_i}, K_{HB_j}, K_w and [H] are replaced by K'_{HA_i}, K'_{HB_j}, K'_w and [H′], respectively; r'_6 is defined by

$$r'_6 = -(V_0 + V)[H'] \qquad (14)$$

Equation (12) is solved for $C^0_{HA_i}$ and $C^0_{B_j}$ by using approximate values of K'_{HA_i}, K'_{HB_j} and K'_w, and $f = 1$ (letting $y = 0$). Values of $\Delta C^0_{HA_i}$, $\Delta K'_{HA_i}$, $\Delta C^0_{B_j}$, $\Delta K'_{HB_j}$, $\Delta K'_w$ and Δf are then obtained from equation (13) by linear regression. The same iteration procedure as described is then repeated until the value of $C^0_{HA_i}$ remains constant during two cycles of iteration.

The number of parameters may in practice often be reduced by one. In *the acidic range* it is possible to neglect the term $(V_0 + V)K'_w/[H']$ in equation (12), and in *the alkaline range* $(V_0 + V)f[H']$ can be neglected. In the latter case K'_w $(=K_w/f)$ and not f appears as a parameter.

It is only for titration of rather simple systems that all parameters can be determined from a moderate number of titration points. This means calculation of the concentrations, and refinement of the constants and f. Examples are: most diprotic acids, an acid in the presence of its conjugate base and a mixture of two acids in about equal concentrations and having log K_{HA}-values that differ by 2 logarithmic units or more. For more complicated systems the iteration procedure will converge either not at all or only very slowly and with possibly poor accuracy of the results.

Further, the approximate values assigned to K_{HA_i}, K_{HB_j}, f and K_w must not differ too much from the correct values in order to give convergence. The more complicated the system is, the closer must the approximate values be to the correct ones.

The number of parameters can be reduced by measuring E'_0 as exactly as possible and/or determining some or all of the stability constants.

For routine work where many similar samples are to be titrated, a method that does not need an accurate value of E'_0 is desirable. Otherwise, too frequent E'_0-determinations with consequent low analysis rate would be required. A determination of the stability constants will often prove worthwhile even in cases when it is not essential in order to obtain convergence, as this will result in faster convergence and reduced computing times. The stability constants of monoprotic species are easily determined by the Hofstee method as described in Part I. (It should be noted that this method does not demand that the acid or base is completely pure; however, the impurities must not be interfering protolytes.) A method for determining the stability constants of a diprotic acid will be given below.

Convergence, precision and accuracy will be treated in more detail for a special case: titration of a mixture of two acids. Subsequently, some common titration problems will be treated that cannot be evaluated by the Gran method or by any of the methods presented in Part I that use points taken before the equivalence point (the drawbacks of using points taken after the equivalence point have already been discussed above). These problems include titration of (*i*) a diprotic acid, (*ii*) an acid in presence of its conjugate base (*e.g.*, acetic acid in presence of acetate ions) and (*iii*) an ampholyte (*e.g.*, potassium hydrogen phthalate).

TITRATION OF A MIXTURE OF TWO MONOPROTIC ACIDS

The stability constants of the acids are denoted by K_{HA_1} and K_{HA_2} and their initial total concentrations by $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$. The titration is assumed to be carried out in the acidic range so that the term $(V_0 + V)K_w/[\mathrm{H}]$ can be neglected. For calculation of $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$ from the titration points (V, [H]), four different cases may be distinguished, depending on how many of the parameters K_{HA_1}, K_{HA_2} and f are to be refined.

1. *Refinement of* K_{HA_1}, K_{HA_2} *and* f. The calculation of $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$ is based on equations (12) and (13). In this special case, equation (12) gives:

$$y = \frac{V_0C^0_{\mathrm{HA}_1}}{1 + [\mathrm{H}']K'_{\mathrm{HA}_1}} + \frac{V_0C^0_{\mathrm{HA}_2}}{1 + [\mathrm{H}']K'_{\mathrm{HA}_2}} - (V_0 + V)f[\mathrm{H}'] - VC$$

where $[\mathrm{H}'] = [\mathrm{H}]/f$, $K'_{\mathrm{HA}_1} = fK_{\mathrm{HA}_1}$ and $K'_{\mathrm{HA}_2} = fK_{\mathrm{HA}_2}$. Equation (13) gives:

$$\Delta y = r'_{11}\Delta C^0_{\mathrm{HA}_1} + r'_{12}\Delta C^0_{\mathrm{HA}_2} + r'_{21}\Delta K'_{\mathrm{HA}_1} + r'_{22}\Delta K'_{\mathrm{HA}_2} + r'_6\Delta f$$

where

$$r'_{11} = \frac{V_0}{1 + [\mathrm{H}']K'_{\mathrm{HA}_1}}$$

$$r'_{12} = \frac{V_0}{1 + [\mathrm{H}']K'_{\mathrm{HA}_2}}$$

$$r'_{21} = -\frac{V_0C^0_{\mathrm{HA}_1}[\mathrm{H}']}{(1 + [\mathrm{H}']K'_{\mathrm{HA}_1})^2}$$

$$r'_{22} = -\frac{V_0C^0_{\mathrm{HA}_2}[\mathrm{H}']}{(1 + [\mathrm{H}']K'_{\mathrm{HA}_2})^2}$$

$$r'_6 = -(V_0 + V)[\mathrm{H}']$$

$C^0_{\mathrm{HA}_1}$, $C^0_{\mathrm{HA}_2}$, K_{HA_1} $(=K'_{\mathrm{HA}_1}/f)$, K_{HA_2} $(=K'_{\mathrm{HA}_2}/f)$ and f are then calculated by the same procedure as described above.

2. *Refinement of* K_{HA_1} *and* K_{HA_2} *when* E'_0 *is known.* The calculation of $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$ is based on equations (10) and (11). In this case, equation (10) gives:

$$y = \frac{V_0C^0_{\mathrm{HA}_1}}{1 + [\mathrm{H}]K_{\mathrm{HA}_1}} + \frac{V_0C^0_{\mathrm{HA}_2}}{1 + [\mathrm{H}]K_{\mathrm{HA}_2}} - (V_0 + V)[\mathrm{H}] - VC$$

Equation (11) gives:

$$\Delta y = r_{11}\Delta C^0_{\mathrm{HA}_1} + r_{12}\Delta C^0_{\mathrm{HA}_2} + r_{21}\Delta K_{\mathrm{HA}_1} + r_{22}\Delta K_{\mathrm{HA}_2}$$

where

$$r_{11} = \frac{V_0}{1 + [\mathrm{H}]K_{\mathrm{HA}_1}}$$

$$r_{12} = \frac{V_0}{1 + [\mathrm{H}]K_{\mathrm{HA}_2}}$$

$$r_{21} = -\frac{V_0C^0_{\mathrm{HA}_1}[\mathrm{H}]}{(1 + [\mathrm{H}]K_{\mathrm{HA}_1})^2}$$

$$r_{22} = -\frac{V_0C^0_{\mathrm{HA}_2}[\mathrm{H}]}{(1 + [\mathrm{H}]K_{\mathrm{HA}_2})^2}$$

3. *Refinement of* f *with known* K_{HA_1} *and* K_{HA_2}. With $[\mathrm{H}] = f[\mathrm{H}']$, equation (10) gives:

$$y = \frac{V_0C^0_{\mathrm{HA}_1}}{1 + f[\mathrm{H}']K_{\mathrm{HA}_1}} + \frac{V_0C^0_{\mathrm{HA}_2}}{1 + f[\mathrm{H}']K_{\mathrm{HA}_2}} - (V_0 + V)f[\mathrm{H}'] - VC \quad (15)$$

Differentiation of equation (15) gives:

$$\Delta y = r'_{11}\Delta C^0_{\mathrm{HA}_1} + r'_{12}\Delta C^0_{\mathrm{HA}_2} + r'_7\Delta f \quad (16)$$

where

$$r'_{11} = \frac{V_0}{1 + f[\mathrm{H}']K_{\mathrm{HA}_1}}$$

$$r'_{12} = \frac{V_0}{1 + f[\mathrm{H}']K_{\mathrm{HA}_2}}$$

$$r'_7 = -\frac{V_0C^0_{\mathrm{HA}_1}[\mathrm{H}']K_{\mathrm{HA}_1}}{(1 + f[\mathrm{H}']K_{\mathrm{HA}_1})^2} - \frac{V_0C^0_{\mathrm{HA}_2}[\mathrm{H}']K_{\mathrm{HA}_2}}{(1 + f[\mathrm{H}']K_{\mathrm{HA}_2})^2} - (V_0 + V)[\mathrm{H}']$$

Approximate values of $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$ are calculated by equation (15), using linear regression and putting $f = 1$ and $y = 0$. Then corrections for $C^0_{\mathrm{HA}_1}$, $C^0_{\mathrm{HA}_2}$ and f are calculated by equation (16), and so on.

4. K_{HA_1}, K_{HA_2} *and* E'_0 *are known.* In this case the problem of calculating $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$ is simply solved by linear regression with two parameters. It is also possible to solve it graphically, in which case one of the parameters is obtained from the intercept of a straight line with the *y*-axis and the other is calculated from the slope of the line.

Before deciding on a method, one should check whether the calculations give accurate results and how well the parameters that are to be refined must be known so that convergence of the iteration procedure is obtained. Table 1 shows the accuracy obtained by the four different methods described above for evaluating the results when mixtures of two acids are titrated with 0.1*M* sodium hydroxide. The stability constants and the concentrations of the acids are given in the table. Nine equal additions of titrant in the range $a = 0.1$–0.9 ($\Delta a = 0.1$) were assumed, a being the titration parameter defined by $a = VC/(V_0C^0_{\mathrm{HA}_1} + V_0C^0_{\mathrm{HA}_2})$. The results in the table were obtained by

Table 1. Random titration errors obtained with synthetic titration data of a mixture of two acids with properties shown in the first column when the parameters shown in the second column are refined. Exactly correct V-values and ph-values that were correct to the third decimal place were used in the calculation

Strengths and concentrations, M, of the acids	Parameters	|Error|%, in $C^0_{\mathrm{HA}_1}$	$C^0_{\mathrm{HA}_2}$	$C^0_{\mathrm{HA}_1} + C^0_{\mathrm{HA}_2}$
$\log K_{\mathrm{HA}_1} = 2$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	<0.1	<0.1	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	<0.1	<0.1	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$	<0.1	<0.1	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}$	<0.1	<0.1	<0.1
$\log K_{\mathrm{HA}_1} = 3$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 7.5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 2.5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	1	3	0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	0.3	0.6	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$	<0.1	0.3	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}$	<0.1	0.2	<0.1
$\log K_{\mathrm{HA}_1} = 3.5$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	11	11	0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	7	7	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$	0.2	0.2	<0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}$	<0.1	<0.1	<0.1

using theoretically calculated values of ph, correct to three decimal places. The values of V were exact. This way of testing the evaluation methods gives an idea of their relative precisions. The data in the table give a representative selection from many calculations based on different values of the stability constants and the concentrations of the acids. The results may therefore be used to compare the different methods. As is seen from the table, it is possible to use approximate values of K_{HA_1}, K_{HA_2} and f but still calculate accurate values of $C^0_{\mathrm{HA}_1}$ and $C^0_{\mathrm{HA}_2}$ if there is a sufficient difference between the stability constants. When the difference between the stability constants decreases and/or the disproportion between the concentrations of the acids increases, the value of f—or better—the values of K_{HA_1} and K_{HA_2} must be known. Another way of improving the results in such a situation is by increasing the number of titration points. As seen from the table, determination of K_{HA_1} and K_{HA_2} in separate experiments and refinement of f gives accurate results even when the difference between the constants is small. This is also an attractive way of working for automatic titrations of many similar samples. As already mentioned, the Hofstee method can be used to determine the stability constant of a monoprotic acid. Experiments with formic acid

Table 2. Maximum errors in log K_{HA} and ph (E'_0) that give convergence of the calculations in evaluating titrations of a mixture of two acids. The first two subcolumns in the third column give the tolerable errors in K_{HA_i} for small errors in ph, and the tolerable errors in ph for small errors in K_{HA_i}. The third subcolumn illustrates the situation when both errors are of the same magnitude

Strengths and concentrations, M, of the acids	Parameters	Max. deviation from the correct value for convergence $\lvert\Delta \log K_{\mathrm{HA}_i}\rvert$	$\lvert\Delta \mathrm{ph}\rvert$	$\lvert\Delta \log K_{\mathrm{HA}_i}\rvert + \lvert\Delta \mathrm{ph}\rvert$
$\log K_{\mathrm{HA}_1} = 2$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	0.3	0.15	0.15
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	0.3		
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$		0.5	
$\log K_{\mathrm{HA}_1} = 2$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 2.5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 7.5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	0.15	0.15	0.15
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	0.3		
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$		0.5	
$\log K_{\mathrm{HA}_1} = 9$, $\log K_{\mathrm{HA}_2} = 11$ $C^0_{\mathrm{HA}_1} = 5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\; K_w/f$*	0.1	0.1	0.1
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	0.15		
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$		0.3	
$\log K_{\mathrm{HA}_1} = 3$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	0.15	0.15	0.15
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	0.15		
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$		0.3	
$\log K_{\mathrm{HA}_1} = 3$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 7.5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 2.5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}\, f$	0.08	0.07	0.07
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, K_{\mathrm{HA}_1}\, K_{\mathrm{HA}_2}$	0.08		
	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$		0.3	
$\log K_{\mathrm{HA}_1} = 3.5$, $\log K_{\mathrm{HA}_2} = 4$ $C^0_{\mathrm{HA}_1} = 5 \times 10^{-3}$, $C^0_{\mathrm{HA}_2} = 5 \times 10^{-3}$	$C^0_{\mathrm{HA}_1}\, C^0_{\mathrm{HA}_2}\, f$		0.2	

* $\Delta \mathrm{p}K_w$ may in this case amount to ±1 [see equation (14)].

and propionic acid show that the values obtained by the Hofstee method are also valid for mixtures. Our method gives rather accurate values of f in addition to $C^0_{HA_1}$ and $C^0_{HA_2}$. Therefore, it is possible to calculate E'_0 by

$$E'_0 = E'^{\text{guess}}_0 - 0.0592 \log f \qquad (17)$$

and this E'_0-value can be used as a good starting value for E'_0 in the next titration, which is an advantage.

Table 2 gives the maximum errors that can be tolerated in the initial values of E'_0 (expressed as Δph) and K_{HA_1} and K_{HA_2} for some values of the stability constants and the concentrations. If the errors are greater, the iteration procedures either do not converge or converge to a completely wrong result. The values in Table 2 were calculated assuming titration with $0.1M$ sodium hydroxide and nine titration points with $\Delta a = 0.1$. The number of cycles required to give convergence to the correct result (the criterion here being less than 0.01% difference in $C^0_{HA_1}$ between two subsequent cycles) for the extreme values of $|\Delta \log K_{HA}|$ and $|\Delta ph|$ lies within the range 3–10. Greater errors can be tolerated if damping factors are employed. [The equations for Δy were derived assuming that the correction terms $\Delta C^0_{HA_1}$ *etc.* are very small. For greater values of the correction terms the equations do not hold exactly.] The use of damping factors implies computation of Σy^2 from the first calculated values of $C^0_{HA_1}$ and $C^0_{HA_2}$ and the approximately known values of K_{HA_1}, K_{HA_2} and f, then adjustment of these values by adding the correction terms $\Delta C^0_{HA_1}$, $\Delta C^0_{HA_2}$, ΔK_{HA_1}, ΔK_{HA_2} and Δf. The corrected values are then used to compute a new value of Σy^2. If this new value is less than the previous one the iteration procedure is continued. If the new value is greater than the first the correction terms are divided by a damping factor R which is first given the value 2. A new value of Σy^2 is computed and compared with the first. If it is still greater than this, the value of R is put equal to 4 (8, 16, 32 and so on) until the new value of Σy^2 is less than the first value. The iteration is then continued.

Examples. A mixture of two acids having $\log K_{HA_1} = 2$ and $\log K_{HA_2} = 4$ and $C^0_{HA_1} = C^0_{HA_2} = 0.005M$ is titrated. K_{HA_1}, K_{HA_2} and f are refined. Nine titration points with $\Delta a = 0.1$ are assumed. Without using damping factors the maximum tolerable errors are: $|\Delta \log K_{HA_i}| \leq 0.3$, $|\Delta ph| \leq 0.15$. With damping factors the tolerable errors are increased to $|\Delta \log K_{HA_i}| \leq 0.7$, $|\Delta ph| \leq 0.3$. In a similar case with $\log K_{HA_1} = 3$, $\log K_{HA_2} = 4$, $C^0_{HA_1} = 0.0075M$ and $C^0_{HA_2} = 0.0025M$, the maximum tolerable errors without the use of damping factors are $|\Delta \log K_{HA_i}| \leq 0.08$, $|\Delta ph| \leq 0.07$. With damping factors the corresponding values are $|\Delta \log K_{HA_i}| \leq 0.2$, $|\Delta ph| \leq 0.15$. It should be noted that the convergence will be slow in the cases when damping factors must be used.

Table 3 gives the errors in the calculated values of $C^0_{HA_1}$ and $C^0_{HA_2}$ that are introduced by an erroneous value of E'_0 if f is not refined. A value of $\Delta ph = \pm 0.002$ has been assumed. The table was calculated assuming titration with $0.1M$ sodium hydroxide, nine additions and $\Delta a = 0.1$. Moderate titration errors (up to a few per cent) are approximately proportional to the Δph-values.

Table 4, based on the same assumptions regarding titrant, number of titration points and distance between the points as Table 3, lists the errors in the calculated values of $C^0_{HA_1}$ and $C^0_{HA_2}$ that are introduced by using erroneous values of K_{HA_1} and K_{HA_2} if these are not refined. The error in the values of the logarithmic constants, $\Delta \log K_{HA_i}$, was assumed to be ± 0.002. The concentration errors were calculated for the most unfavourable case, *i.e.*, a positive error in K_{HA_1} and a negative error in K_{HA_2} (or the other way round). For positive (or negative) errors in both constants, the titration errors will be smaller, smallest when the titration points are obtained in the ph-range around ph = 7.

From the preceding tables it may be concluded that

Table 3. The effect of a systematic error in ph on the determination of the concentrations of two acids in a mixture, depending on the strengths and concentrations of the two acids when f is not refined. $\Delta ph = \pm 0.002$

Strengths and concentrations, M, of the acids	|Error|, %, in the determination of		
	$C^0_{HA_1}$	$C^0_{HA_2}$	$C^0_{HA_1} + C^0_{HA_2}$
$\log K_{HA_1} = 2, \log K_{HA_2} = 4$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.08	0.06	0.01
$\log K_{HA_1} = 2, \log K_{HA_2} = 4$ $C^0_{HA_1} = 2.5 \times 10^{-3}, C^0_{HA_2} = 7.5 \times 10^{-3}$	0.15	0.04	0.01
$\log K_{HA_1} = 6, \log K_{HA_2} = 8$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	<0.01	<0.01	<0.01
$\log K_{HA_1} = 9, \log K_{HA_2} = 11$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.02	0.5	0.2
$\log K_{HA_1} = 3, \log K_{HA_2} = 4$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.6	0.6	0.03
$\log K_{HA_1} = 3, \log K_{HA_2} = 4$ $C^0_{HA_1} = 7.5 \times 10^{-3}, C^0_{HA_2} = 2.5 \times 10^{-3}$	0.7	1.6	0.1

Table 4. The effect of a systematic error in the stability constants of two acids on the calculation of their concentrations, depending on the strengths and concentrations of the two acids when the constants are not refined. $\Delta \log K_{HA_1} = \pm 0.002$

Strengths and concentrations, M, of the acids	|Error| %, in the determination of		
	$C^0_{HA_1}$	$C^0_{HA_2}$	$C^0_{HA_1} + C^0_{HA_2}$
$\log K_{HA_1} = 2, \log K_{HA_2} = 4$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.10	0.06	0.08
$\log K_{HA_1} = 2, \log K_{HA_2} = 4$ $C^0_{HA_1} = 2.5 \times 10^{-3}, C^0_{HA_2} = 7.5 \times 10^{-3}$	0.16	0.11	0.07
$\log K_{HA_1} = 6, \log K_{HA_2} = 8$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.10	0.24	0.17
$\log K_{HA_1} = 9, \log K_{HA_2} = 11$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.04	0.7	0.4
$\log K_{HA_1} = 3, \log K_{HA_2} = 4$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.4	0.4	<0.1
$\log K_{HA_1} = 3, \log K_{HA_2} = 4$ $C^0_{HA_1} = 7.5 \times 10^{-3}, C^0_{HA_2} = 2.5 \times 10^{-3}$	0.2	0.7	<0.1
$\log K_{HA_1} = 3.5 \log K_{HA_2} = 4$ $C^0_{HA_1} = C^0_{HA_2} = 5 \times 10^{-3}$	0.9	0.9	<0.1

when the difference between the stability constants of the acids is small, it will be advantageous to determine K_{HA_1} and K_{HA_2} in separate experiments. *When these quantities are known there is rarely much to be gained by an accurate determination of* E'_0. This is because the error in E'_0 is then added to the errors in the log K_{HA_i}-values and the resulting systematic error will often be greater than the random error introduced by the additional refinement of f (refer to Tables 1 and 3). When there is sufficient difference between the stability constants, all parameters can be refined, but faster convergence and less computational work can be expected if even in this case the constants are determined in separate experiments.

Titration of *a strong and a weak acid* is a special case of titration of two acids since, by definition, one of the acids is completely dissociated. Thus, the same value may always be assigned to the stability constant of the strong acid, *e.g.*, 10^{-10}. There is nothing to be gained by refining the value of this constant during the calculation and the number of parameters to be refined is therefore reduced by one.

TITRATION OF DIPROTIC ACIDS

If the difference between the successive stability constants of the diprotic acid is not less than about 0.6 logarithmic units,[19] the evaluation of the titration of a diprotic acid is the same as that of two monoprotic acids having $C^0_{HA_1} = C^0_{HA_2}$.

The number of parameters is consequently reduced by one, owing to the condition that $C^0_{HA} = C^0_{HA_1} = C^0_{HA_2}$. However, the "titration constants" that result by refining initially given approximate values of K_{HA_1} and K_{HA_2} are not identical with the true stability constants of the diprotic acid. The stability constants can be obtained from the titration constants or *vice versa*, according to Simms[20] or Klas.[21] If, for a certain titration problem, refinement of the constants is not desired, titration constants and not true stability constants should be used in the calculations. In the example below, the titration constants are denoted by K_1 and K_2 (generally K_n).

As an example, a titration of a 0.005M solution of an acid having $\log K_1 = 3$ and $\log K_2 = 4$, with 0.1M sodium hydroxide, will be considered. Nine titration points are used and $\Delta a = 0.1$. The parameters are C^0_{HA}, K'_1, K'_2 and f. The conditions for convergence are $|\Delta \log K_n| \leq 0.2$, $|\Delta \mathrm{ph}| \leq 0.5$, $|\Delta \log K_n| + |\Delta \mathrm{ph}| \leq 0.2$ (see text to Table 2). In addition to the concentration of the acid the results will thus comprise values of K_1, K_2 and f. It is thereby possible to calculate a good, approximate value of E'_0 by equation (17). As said before, this is an advantage in automatic titrations. The values of the titration constants can be obtained from $K_1 = K'_1/f$ and $K_2 = K'_2/f$. The values of the constants that are obtained when both f and K_1, K_2 are refined will not be highly accurate. If the intention is *to determine the constants*, E'_0 should be determined by an E'_0-titration before the sample is titrated and f should not be refined.

TITRATION OF AN ACID IN THE PRESENCE OF ITS CONJUGATE BASE

The parameters are C^0_{HA}, $C^0_A (= C^0_B)$, K_{HA} and f. This is a special case of a titration of a mixture of an acid and a weak base, having $K_{HA} = K_{HB}$. As an example, a titration of a 0.01M solution of an acid having $\log K_{HA} = 3.5$, with 0.1M sodium hydroxide, in the presence of 0.01M concentration of the conjugate base has been studied. Nine titration points with $\Delta a = 0.1$ were assumed. The conditions for convergence for calculation of C^0_{HA} and C^0_A with refinement of K_{HA} and f are

$$|\Delta \log K_{HA}| \leq 0.7, |\Delta \mathrm{ph}| \leq 1$$

$$|\Delta \log K_{HA}| + |\Delta \mathrm{ph}| \leq 0.7.$$

It should be noted, however, that when this method is used, an accurate value will be obtained for C_{HA}^0 only, whereas the values of C_A^0, K_{HA} and f will be approximate.

When determining the concentrations of many similar samples by automated analysis it may be worthwhile to determine the value of K_{HA} by the Hofstee method. This will reduce the computations appreciably. If this is done, values of C_{HA}^0 and C_A^0 are calculated and the value of f (initially put = 1) is refined. Use of this method will yield an accurate value of f which may be used to calculate an accurate value of E_0' by equation (17). This value of E_0' is subsequently used in the next titration, resulting in fast convergence and saving of computation time. For the example above, an error as large as ± 0.1 in $\log K_{HA}$ gives an error $<0.1\%$ in C_{HA}^0.

TITRATION OF AN AMPHOLYTE

This, too, is a special case of titration of a mixture of an acid and a weak base, but here $C_{HA}^0 = C_B^0$. The parameters are C_{HA}^0, f, K_{HA} and K_{HB}.

The example given is a titration of a $0.01M$ solution of an ampholyte having $\log K_{HA} = 5$ and $\log K_{HB} = 3$. Nine titration points having $\Delta a = 0.1$ are assumed. Refinement of all parameters gives slow convergence and not very accurate results. However, even if f is not refined, a large error in E_0' can be tolerated without impairing the result. A systematic error in ph corresponding to $|\Delta \text{ph}| = 0.3$ gives a titration error of less than 0.1%. Fast convergence and accurate results are obtained. The condition for convergence is $|\Delta \log K_{HA}| \leq 0.3$. The value of $\log K_{HB}$ may be set = 0.

Here, it would be appropriate to use "titration constants". However, for the sake of clearness, the notations K_{HA} and K_{HB} have been retained.

CONCLUSION

What distinguishes the proposed methods presented in this paper and in Part I from most other mathematical approaches to evaluation of titrations is that it is sufficient to use approximate E_0'-values, *i.e.*, often a very rough calibration of the electrode system is sufficient. Further, for titrations of monoprotic acids it is not necessary to know the stability constants of the acids. For other titrations, *e.g.*, mixtures of acids having stability constants that differ by more than 2 logarithmic units, and of most diprotic acids, it is mostly sufficient to know approximate values for the constants. When the values of the constants are unknown they may be guessed and, if necessary, the guessing is repeated until the calculations converge. For more complicated titrations, such as titrations of mixtures of acids with a small difference between their stability constants, knowledge of the constants is required for accurate results. For monoprotic and diprotic acids these constants are easy to determine, as described. An advantage of the proposed methods when mixtures of acids are titrated is that it is not necessary to determine separately the sum of the concentrations of the acids.

The method of stepwise addition of titrant, combined with the proposed evaluation methods, has the following advantages in comparison with conventional titration methods: it makes possible the titration of very weak acids (*e.g.*, $\log K_{HA} = 10$–11, $C_{HA} = 0.01M$) that cannot be determined by conventional methods in aqueous medium and also titration of a mixture of two acids with a small difference between the stability constants. Further, the results can be evaluated statistically and systematic errors traced.

Another advantage is that the method is very suitable for automation and experimental results supporting the theories presented in Parts I and II have been achieved by using an automatic apparatus. These results and the apparatus will be presented in Part III.

There are, of course, titration problems that can be solved equally well by conventional methods as by the methods presented in these papers. Part of the aim of these papers has, however, been to devise methods that make possible the solution of most titration problems by using similar or closely related techniques.

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ACCURACY OF ANALYSIS OF STEELS BY USE OF A SPARK-SOURCE MASS SPECTROMETER WITH ELECTRICAL DETECTION

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Summary—The precision and accuracy of spark-source mass spectrometry with electrical detection has been studied, with five steel standard reference materials (NBS-SRM 661–665). Two different modes of analysis have been evaluated, magnetic scanning with electrical detection of the individual ions in sequence, using the total ion-current as reference, and magnetic switching between masses, with current integration. Measurements of isotope abundances have been used to evaluate the precision. The relative sensitivity coefficients of Ti, V, Cr, Mn, Co, Ni, Cu, As, Zr, Nb, Mo, Sb, La, Ta and W have been determined *vs.* iron as an internal standard. The accuracy of analyses based on these experimentally measured relative sensitivity coefficients was confirmed by comparing the results for a pure iron sample with those obtained by neutron-activation analysis.

In spark-source mass spectrometry two different modes of operation are possible with electrical detection, scanning of the mass spectrum with simultaneous detection of the total ion-current and switching to specifically chosen masses before a measurement until a preset total ion-current signal is reached. Several workers[1–4] have determined the precision of the peak-switching mode to be 2–5% relative standard deviation for several metals. This contrasts with a precision of 10–20% obtainable with photographic ion-detection.[5,6]

Standard reference materials are required for the experimental determination of the relative sensitivity coefficients (S_R). In this paper the coefficient for element x is defined as $S_R(x/y)_z$ and is equal to the ratio of the concentrations of elements x and y in the matrix material z as determined from the singly-charged ions, divided by the true concentration ratio:

$$S_R(x/y)_z = [(C_x/C_y)_{ms}/(C_x/C_y)_{true}]_z.$$

For steel standards, iron can conveniently be used as the reference element. Experimentally determined coefficients obtained by electrical detection with NBS steel standards have been published by Capellen, Conzemius and Svec,[7] Hull [8] and Blanchard.[9]

In this paper we report the precision and accuracy obtained for the analysis of steel by use of electrical detection in the magnetic scanning and peak-switching modes. In a previous paper[6] a similar study was described for the same samples and photographic ion-detection.

EXPERIMENTAL

Apparatus

The experiments were performed with a double-focusing mass spectrometer with Mattauch–Herzog geometry (JMS-01 BM-2, JEOL, Tokyo), incorporating an automatic spark-control system (MS-AS-01, JEOL) which allows continuous sparking between the electrodes by vibration of one electrode and control of the spark gap by shifting the other electrode by means of a servo-motor. The total ion-current is kept constant with an ion-beam control unit. When a preset value is reached, an electrostatic field is applied between two beam-suppressing plates to deflect the ions, preventing them from entering the analyser.

The electrical detection system (MS-ED-01, JEOL) has two modes of operation, as follows.

Magnetic scanning. While the sample is sparking, the magnetic field is increased linearly or decreased exponen-

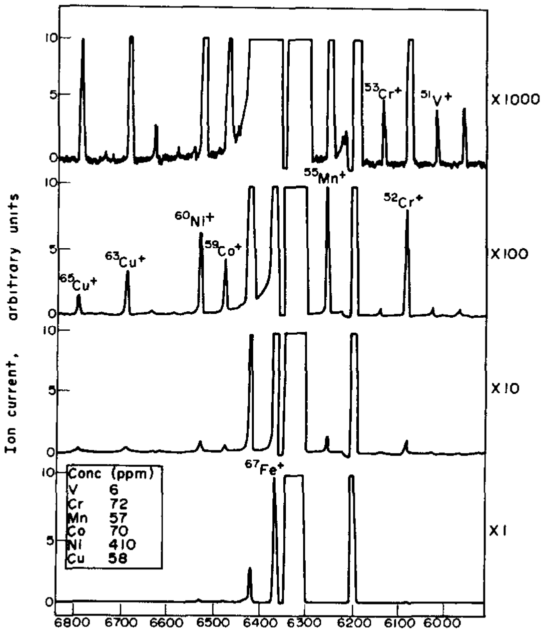

Fig. 1. Part of a mass spectrum with linear ratio scan output. Sample, NBS-SRM 665 steel standard.

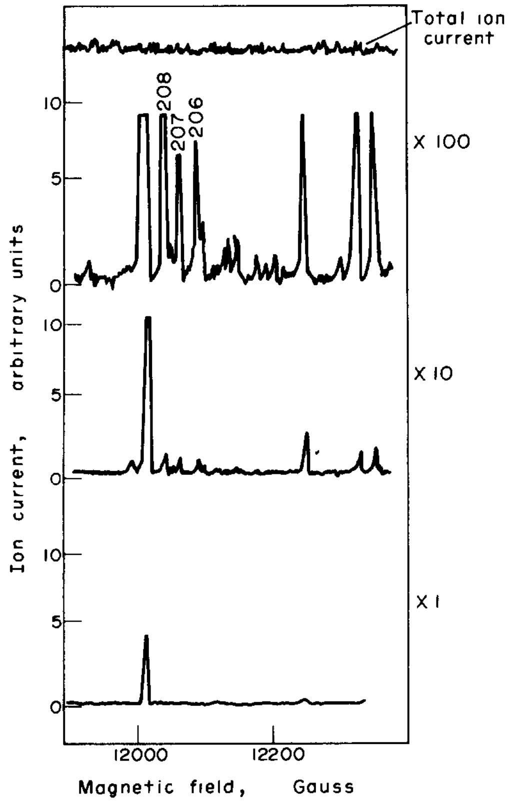

Fig. 2. Part of a mass spectrum with linear ratio scan output. Sample, NBS-SRM 661 steel standard (concentration Pb: 0.25 ppm).

tially, so that the ions of the individual isotopic species are swept sequentially across the first Cu–Be dynode of a 20-stage electron multiplier. The ratio of the instantaneous collector current to the total ion-current of the unresolved ion-beam is recorded with a 4-channel strip-chart recorder. The sensitivity of adjacent traces varies by a factor of 10, so that a dynamic concentration range of more than 10^5 is covered in a single scan. The magnetic field strength is also indicated at every 100 gauss. An example of part of a mass spectrum is shown in Fig. 1. The sensitivity of the technique is about 0.1 ppm. Figure 2 shows a mass spectrum of the isotopes of lead in the NBS-SRM 661 steel standard, the lead being present at a concentration of 0.25 ppm. One channel is used here to indicate the total ion-current, the others the mass spectrum.

Magnetic peak-switching. In this mode, 6 channels are available. The magnetic field can be switched to preset values at which the ion-beams of the isotopes of interest are detected by the electron multiplier. For each mass selected the collector current is integrated until a predetermined charge has been collected at the total ion-beam monitor. The ion-beam is then automatically switched off and the magnetic field is changed to a value corresponding to the next mass selected for measurement. The results are displayed on a digital voltmeter and are also printed. The sensitivity obtainable in this mode is more than 3 times better than that with the scanning mode.

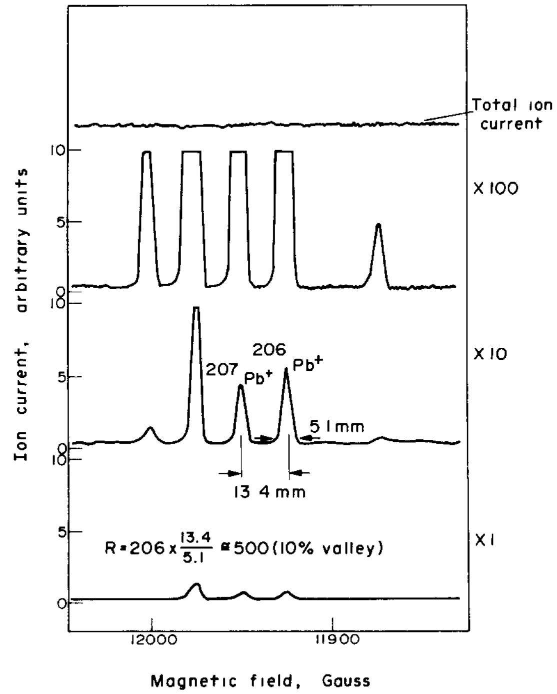

Fig. 4. Part of a mass spectrum showing the resolution for the magnetic scanning mode. Sample, NBS-SRM 664 steel standard.

Samples

The standard reference materials NBS-SRM 661–665 were used. They have been described elsewhere.[6] A high-purity iron sample, prepared for the "Verein Deutscher Eisenhüttenleute" was also analysed. It has already been studied by neutron-activation analysis.[10] The samples were prepared as described earlier,[6] but in order to improve the location of the spark, a portion of the top of both electrodes was cut away, leaving only a quarter of the original surface (Fig. 3).

Mass-spectrometry procedure

The width of the slits was adjusted as follows: object slit 100 μm, α-slit (in front of the electrostatic field) 2.0 mm,

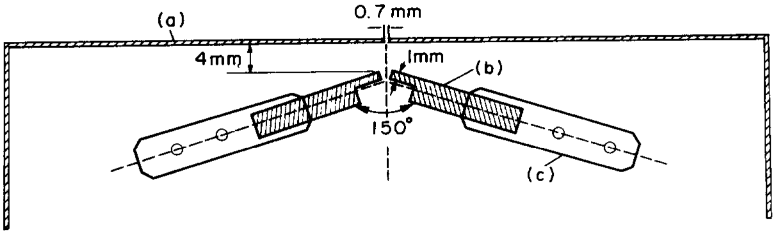

Fig. 3. Electrode geometry. (a) accelerating slit (tantalum), (b) sample electrode, (c) sample-holder (tantalum).

Table 1. Measurements of isotopic abundance by magnetic scanning (sample NBS-SRM 661 steel standard, Mo 0.19% w/w)

	Peak height, *arbitrary units*						
Scan No.	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
1	485	395	555	575	325	950	315
2	530	370	590	770	230	1200	330
3	730	350	630	550	270	1100	350
20	750	370	830	840	480	1400	470
Mean	645	440	638	644	378	1089	403
Standard deviation, %	14.6	19.0	13.9	16.3	21.4	19.1	20.2
Standard error of mean, %	3.3	4.3	3.1	3.6	4.8	4.3	4.5
Calculated abundance, %	15.22	10.39	15.06	15.20	8.92	25.70	9.51
Natural abundance, %	15.84	9.04	15.72	16.53	9.46	23.78	9.63
Relative deviation, %	−3.9	+14.9	−4.2	−8.0	−5.7	+7.5	−1.2

β-slit (energy-defining slit—behind the electrostatic field) 2.0 mm and collector slit 250 μm.

The following spark conditions, which ensured a stable continuous spark, were chosen: spark-source voltage 65 kV, pulse length 20 μsec, repetition frequency 3000 sec^{-1} and ion-accelerating voltage 29.5 kV.

The scan-speed was 40 min/full range (m/e 1–250) and the recorder speed was 1 mm/sec. For peak-switching, an integrated monitor charge of 0.9 nC was chosen; the analysis time per element was about 15 sec.

The mass resolution in the magnetic scanning mode under the conditions described above was about 500 (10% valley) as appears from Fig. 4. All samples were presparked for at least 5 min.

RESULTS AND DISCUSSION

Evaluation of the precision by measurements of isotopic ratios

The abundances of the molybdenum isotopes in the steel standard NBS-SRM 661 were determined in order to evaluate the precision of the analysis. Molybdenum is present at a concentration of 0.19% by weight and the precision may be influenced by a heterogeneous distribution. The measurements were therefore repeated for the isotopes of iron. In addition, the precision was evaluated for impurities at lower concentration levels, namely tungsten (150 ppm) and silver (4 ppm).

Magnetic scanning. The mass intervals around the multi-isotopic elements iron, molybdenum, silver and tungsten were scanned, 20 scans being recorded in sequence. The precision of the measurements is shown in Tables 1 and 2. In order to calculate the isotopic abundances, the average intensity of the ion-current for an isotope was compared with the sum of the intensities for all isotopes of the element. The isotopes ^{58}Fe and ^{180}W were not considered because they are subject to interference from ^{58}Ni and ^{180}Hf respectively. The precision of the determination of the isotopic abundance appears to be considerably higher for iron than for the other elements, namely 11.6% relative standard deviation (r.s.d.) against 17.8% for molybdenum, 17.6% for silver and 13.4% for tungsten.

The average deviation between the calculated and true abundance for all isotopes is about 5%. The systematic positive deviation for ^{94}Mo is due to a small interference from ^{94}Zr which was also revealed by photographic detection. The systematic positive deviations for ^{54}Fe and ^{57}Fe are due to the large difference in the abundance of the iron isotopes, so their peaks have to be measured on 2 different recorder traces. Exact calibration of these 2 recorder channels showed a 13% deviation between them. After this correction the calculated abundance for the iron isotopes became 6.19% for ^{54}Fe, 91.29% for ^{56}Fe and 2.20% for ^{57}Fe.

Magnetic peak-switching. Similar experiments were performed by peak-switching. For iron, molybdenum, silver and tungsten, the isotopes were examined in sequence. For each measurement the magnetic field was manually optimized and the collector current was integrated until a preset exposure of 0.9 nC was recorded at the total ion-beam monitor. A total of 20 measurements was carried out for each isotope. The results are listed in Tables 3 and 4. Peak-switch-

Table 2. Isotopic abundance measured by magnetic scanning (sample NBS-SRM 661, Fe 95.6% w/w, Ag 4 ppm, W 150 ppm)

	^{54}Fe	^{56}Fe	^{57}Fe	^{107}Ag	^{109}Ag	^{182}W	^{183}W	^{184}W	^{186}W
Mean peak height (20 measurements)	579	7436	206	469	439	385	206	460	410
Standard deviation, %	13.3	10.2	11.4	17.6	17.5	13.2	15.7	9.4	15.1
Standard error of mean, %	3.0	2.3	2.6	3.9	3.9	3.0	3.5	2.1	3.4
Calculated abundance, %	7.02	90.15	2.50	51.65	48.35	26.32	14.08	31.44	28.02
Natural abundance, %	5.82	91.66	2.19	51.35	48.65	26.41	14.40	30.64	28.41
Relative deviation, %	+20.6	−1.7	+14.2	+0.6	−0.6	−0.3	−2.2	+2.6	−1.4

Table 3. Isotopic abundance measured by magnetic peak-switching (sample NBS-SRM 661, Mo 0.19% w/w)

	Collected ion-charge, *arbitrary units*						
Measurement No.	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
1	11072	6610	11402	11070	6868	16902	6611
2	11592	6743	11489	11358	6854	16713	6586
3	10703	6695	11579	11262	6813	16566	6642
20	12378	6618	11655	13152	7545	18051	7934
Mean	11782	7242	11569	12399	7062	18134	7067
Standard deviation, %	5.0	7.4	3.0	5.6	3.1	5.6	7.1
Standard error of mean, %	1.1	1.7	0.7	1.3	0.7	1.3	1.6
Calculated abundance, %	15.73	9.67	15.44	16.55	9.43	24.21	9.43
Natural abundance, %	15.84	9.04	15.72	16.53	9.46	23.78	9.63
Relative deviation, %	−0.7	+7.0	−1.8	+0.1	−0.3	+1.8	−2.1

Table 4. Isotopic abundance measured by magnetic peak-switching (sample NBS-SRM 661, Fe 95.6% w/w, Ag 4 ppm, W 150 ppm)

	^{54}Fe	^{56}Fe	^{57}Fe	^{107}Ag	^{109}Ag	^{192}W	^{183}W	^{184}W	^{186}W
Mean of 20 D.V.M.* readings	34223	480083	12073	5959	5985	3188	1690	3467	3462
Standard deviation, %	3.5	3.0	3.5	4.6	6.2	4.2	5.2	5.3	3.7
Standard error of mean, %	0.8	0.7	0.8	1.0	1.4	0.9	1.2	1.2	0.8
Calculated abundance, %	6.48	90.90	2.29	49.89	50.11	26.96	14.29	29.32	29.28
Natural abundance, %	5.82	91.66	2.19	51.35	48.65	26.41	14.40	30.64	28.41
Relative deviation, %	+11.3	−0.8	+4.6	−2.8	+3.0	+2.1	−0.8	−4.3	+3.1

* Digital voltmeter.

Table 5. Effect of homogeneity on precision

	Scanning		Peak switching	
	r.s.d., %	r.s.d. due to heterogeneity,* %	r.s.d., %	r.s.d. due to heterogeneity,* %
Fe	11.6	—	3.3	—
Mo	17.8	13.5	5.3	4.2
Ag	17.6	13.2	5.4	4.3
W	13.4	6.7	4.6	3.2

* $s_{het} = \sqrt{s^2_{total} - s^2_{Fe}}$.

Table 6. Influence of lower electron multiplier voltage and wider collector-slit on the measured isotopic ratios for iron

	Collector-slit 250 μm, electron multiplier voltage 0.5 kV			Collector-slit 1 mm, electron multiplier voltage 1 kV		
	^{54}Fe	^{56}Fe	^{57}Fe	^{54}Fe	^{56}Fe	^{57}Fe
Calculated abundance, %	6.53	90.84	2.30	6.18	91.29	2.19
Natural abundance, %	5.82	91.66	2.19	5.82	91.66	2.19
Relative deviation, %	+12.2	−0.9	+5.0	+6.2	−0.4	0.0

Table 7. Magnetic peak-switching: reproducibility within a series of 8 successive integrations
(sample NBS-SRM 661 steel standard)

Element	Isotope	Relative standard deviation, %			Average r.s.d., %
		Series 1	Series 2	Series 3	
Fe	54	2.5	2.0	1.6	2.0
	56	2.0	1.2	1.4	
	57	1.2	2.6	3.4	
Mo	92	3.8	1.5	4.2	2.8
	94	2.5	2.7	2.5	
	95	1.0	1.6	4.7	
	96	2.9	3.3	2.0	
	97	4.6	2.5	3.1	
	98	1.5	1.8	4.0	
	100	3.9	2.2	2.8	
Ag	107	4.5	5.3	3.5	4.9
	109	5.4	7.6	3.1	
W	182	2.9	4.1	2.4	4.5
	183	2.7	5.0	6.7	
	184	3.2	4.3	8.9	
	186	5.1	4.8	3.8	

ing appears to be capable of producing a more precise determination than does scanning, namely 3.3% r.s.d. for iron and about 5% for the impurities. The lower precision for the impurities suggests a contribution of the heterogeneous distribution of the impurities at the micro-level. It was found by weighing the electrodes before and after a controlled sparking that about 4 μg of material was consumed for each individual reading. For scanning, the amount of material consumed is about a tenth of this. This results in a larger contribution of the heterogeneous distribution of the impurities as is apparent from Table 5.

The average deviation between the calculated and true abundance of all the measured isotopes is about 3%. The systematic positive deviation which remains for ^{54}Fe and ^{57}Fe could be due to two causes: saturation of the electron multiplier for the intense ^{56}Fe ion-beam, or widening of this ion-beam by the space-charge effect, so that a different fraction of the isotopic ion-beam enters through the collector-slit for this isotope than for the others. Therefore the experiments were repeated for a lower multiplier voltage (0.5 kV instead of 1 kV) and for a wider collector slit-width (1 mm instead of 250 μm). The results summarized in Table 6 show that the systematic deviations remain at a lower electron multiplier voltage, but decrease considerably with a wider collector-slit.

With the electrical detection system used, it is possible to carry out repetitive measurements automatically, 1, 2, 4 or 8 integrations being made before the field is switched to the next mass. Within such a series of measurements, the reproducibility is expected to be better because in the previous experiments there is an uncertainty in the reproducibility of the magnetic field. Three series of eight integrations were performed for each isotope and the relative standard deviations within each series are listed in Table 7. For the iron isotopes the precision is 2% r.s.d. This represents the limit of the precision of the electrical detection system under the conditions used.

Table 8. Effect of changes in duty cycle on precision

Pulse repetition rate, sec^{-1}	Pulse length, μsec	Relative standard deviation, %						
		^{51}V	^{52}Cr	^{55}Mn	^{57}Fe	^{59}Co	^{60}Ni	Average
Scanning								
3000	20	16.0	12.2	11.6	10.6	7.1	12.1	11.6
1000	80	17.8	10.6	8.2	8.2	9.2	9.9	10.7
1000	40	12.7	8.9	9.3	11.8	11.0	8.5	10.4
1000	20	13.5	14.6	8.3	9.6	7.9	8.6	10.4
Peak-switching								
3000	20	2.1	1.7	1.8	2.0	3.0	2.8	2.2
1000	80	2.4	2.0	1.8	1.8	3.1	1.7	2.1
1000	40	1.6	4.2	3.1	2.0	1.0	0.9	2.1
1000	20	3.0	1.9	2.4	3.7	2.0	1.9	2.5

Table 9. Magnetic scanning: reproducibility of experimental sensitivity coefficients for standard NBS-SRM 662

Element	Isotope	Concentration, % w/w	r.s.d., %	Relative sensitivity coefficient
Ti	48	0.23	16	2.8
V	51	0.07	15	1.8
Cr	52, 53	0.54	10	1.8
Mn	55	2.7	14	2.6
Fe	57	95.3	—	1.0
Co	59	0.28	13	0.9
Ni	60	0.53	15	0.9
Cu	63, 65	0.9	17	1.8
As	75	0.31	26	3.4
Zr	90, 91	0.42	23	2.2
Nb	93	0.50	12	1.7
Mo	95, 97, 98, 100	0.09	18	1.3
Sb	121, 123	0.05	25	3.8
La	139	0.0023	31	5.4
Ta	181	0.21	14	1.1
W	182, 183, 184, 186	0.16	26	0.8

Table 10. Magnetic scanning: reproducibility of experimental sensitivity coefficients

NBS-SRM standard	Average standard deviation %
661	18
662	18
663	18
664	16
665	21

Instrumental parameters

To examine the influence of the spark conditions on the precision of the analysis, the mass range 51–60 a.m.u. was repeatedly measured in the scanning and in the peak-switching modes for the reference material SRM 661. All previous experiments were carried out with a pulse length of 20 μsec and a pulse repetition rate of 3000 sec^{-1}. When using a duty cycle higher than 6% (*e.g.*, 80 μsec × 3000 sec^{-1} or 40 μsec × 3000 sec^{-1}) it was difficult to obtain stable sparking conditions long enough to carry out the experiment. The sample electrodes burned up so quickly and irregularly that they soon made contact and fused together. The variation in precision with pulse length and repetition rate is summarized in Table 8. The r.s.d. for scanning is for 20 scans in sequence; for peak-switching it refers to 5 switching cycles in which 8 integrations are performed in sequence of increasing mass. It can be concluded that the pulse repetition rate and the pulse length have only a negligible influence on the precision. The standard deviations

Table 11. Magnetic peak-switching: reproducibility of experimental sensitivity coefficients for standard NBS-SRM 662

Element	Isotope	Magnetic field, *gauss*	Concentration, % w/w	Standard deviation %	S_R
Ti	48	5850	0.23	13	2.7
V	51	6031	0.067	8	1.6
Cr	52	6090	0.53	7	1.8
Mn	55	6261	2.5	8	2.4
Fe	57	6370	95.3	—	1.0
Co	59	6481	0.27	7	0.89
Ni	60	6534	0.49	7	0.83
Cu	63	6689	0.81	4	1.6
As	75	7289	0.33	13	3.6
Zr	90	7973	0.47	11	2.5
Nb	93	8102	0.58	11	2.0
Mo	98	8315	0.096	10	1.4
Sb	121	9219	0.053	11	4.4
La	139	9866	0.0024	14	6.0
Ta	181	11213	0.018	16	0.9
W	184	11300	0.014	8	0.65

Average r.s.d. 10%.

shown in Table 8 correspond to the values found for the iron isotopes in Tables 2 and 7. Other experiments showed that the accelerating voltage has no detectable influence on the precision. The maximum accelerating voltage of 29.5 kV can thus be used to obtain the highest sensitivity.

Morrison and Colby[11] reported that the spark-gap voltage has an influence on the precision of the measurements. An accurate measurement of this parameter was not possible with our equipment since

Table 12. Magnetic peak-switching: reproducibility of experimental sensitivity coefficients

NBS-SRM standard	Average r.s.d. %
661	11
662	10
663	12
664	9
665	10

Overall average r.s.d. 10%.

Table 13. Magnetic scanning: experimental S_R values for 5 steel standards

Element	Relative sensitivity coefficient					Weighted average S_R for all standards	r.s.d., %
	661	662	663	664	665		
Ti	2.6 ± 0.7	2.8 ± 0.4	2.1 ± 0.3	2.2 ± 0.2	2.0 ± 0.5	2.2	14
V	1.7 ± 0.2	1.8 ± 0.3	1.6 ± 0.1	1.6 ± 0.2	1.8 ± 0.5	1.6	11
Cr	1.7 ± 0.1	1.8 ± 0.2	1.6 ± 0.2	1.7 ± 0.3	1.9 ± 0.4	1.7	12
Mn	2.6 ± 0.2	2.6 ± 0.4	2.4 ± 0.4	2.8 ± 0.5	2.7 ± 0.8	2.6	12
Fe	1	1	1	1	1	1	
Co	0.94 ± 0.04	0.9 ± 0.1	*	1.0 ± 0.1	0.9 ± 0.2	0.95	8
Ni	0.88 ± 0.09	0.9 ± 0.1	†	0.9 ± 0.1	0.9 ± 0.1	0.89	15
Cu	1.8 ± 0.2	1.8 ± 0.3	1.7 ± 0.2	1.9 ± 0.3	1.6 ± 0.3	1.8	14
As	4.2 ± 0.6	3.4 ± 0.9	3.0 ± 0.8	3.5 ± 0.9		3.7	20
Zr	2.3 ± 0.8	2.2 ± 0.5	2.0 ± 0.4	1.8 ± 0.4		2.0	25
Nb	2.2 ± 0.3	1.7 ± 0.2	1.9 ± 0.4	1.6 ± 0.2		1.8	12
Mo	1.8 ± 0.5	1.3 ± 0.3	1.3 ± 0.3	1.4 ± 0.2		1.4	18
Sb	5.6 ± 0.9	3.8 ± 0.9	4 ± 1	4.2 ± 0.6		4.5	18
La	4 ± 1	5 ± 2	5 ± 1	6 ± 2		4.8	32
Ta	1.0 ± 0.3	1.1 ± 0.2	0.8 ± 0.2	1.0 ± 0.1		1.0	17
W	0.6 ± 0.2	0.8 ± 0.2	0.6 ± 0.1	0.63 ± 0.09		0.6	18
Average r.s.d., %	18	19	19	17	21		16

* Interference by $^{118}Sn^{2+}$.
† Interference by $^{120}Sn^{2+}$.

Table 14. Magnetic peak-switching: experimentally determined S_R values for 5 steel standards

Element	Relative sensitivity coefficients in sample					Weighted average S_R for all standards	r.s.d., %
	661	662	663	664	665		
Ti	2.4 ± 0.3	2.7 ± 0.4	2.2 ± 0.1	2.1 ± 0.1	2.1 ± 0.3	2.2	8
V	1.7 ± 0.2	1.6 ± 0.2	1.6 ± 0.1	1.6 ± 0.1	1.7 ± 0.3	1.6	9
Cr	1.7 ± 0.2	1.8 ± 0.1	1.67 ± 0.08	1.6 ± 0.1	1.8 ± 0.3	1.7	7
Mn	2.7 ± 0.2	2.4 ± 0.2	2.6 ± 0.2	2.8 ± 0.1	2.9 ± 0.3	2.7	6
Fe	1	1	1	1	1	1	
Co	0.94 ± 0.06	0.89 ± 0.06	*	0.90 ± 0.05	0.89 ± 0.04	0.89	6
Ni	0.90 ± 0.09	0.83 ± 0.06	†	0.81 ± 0.05	0.82 ± 0.04	0.82	6
Cu	1.7 ± 0.2	1.62 ± 0.07	1.6 ± 0.3	1.82 ± 0.09	1.9 ± 0.1	1.7	6
As	4.2 ± 0.9	3.6 ± 0.5	3.6 ± 0.6	1.9 ± 0.2		3.2	10
Zr	2.4 ± 0.5	2.5 ± 0.3	2.1 ± 0.2	1.9 ± 0.2		2.1	11
Nb	2.2 ± 0.2	2.0 ± 0.2	1.6 ± 0.1	1.5 ± 0.1		1.8	8
Mo	1.56 ± 0.05	1.4 ± 0.1	1.2 ± 0.1	1.39 ± 0.03	1.2 ± 0.1	1.42	4
Sb	4.1 ± 0.5	4.4 ± 0.5	4.2 ± 0.9	5.3 ± 0.9		4.3	14
La	5.4 ± 0.8	6 ± 1	6 ± 1	7 ± 1		5.9	18
Ta	1.0 ± 0.1	0.9 ± 0.1	0.9 ± 0.1	1.1 ± 0.2		0.9	16
W	0.7 ± 0.2	0.65 ± 0.06	0.7 ± 0.1	0.8 ± 0.2		0.68	13
Average r.s.d. %	12	10	13	9	11		10

* Interference by $^{118}Sn^{2+}$.
† Interference by $^{120}Sn^{2+}$.

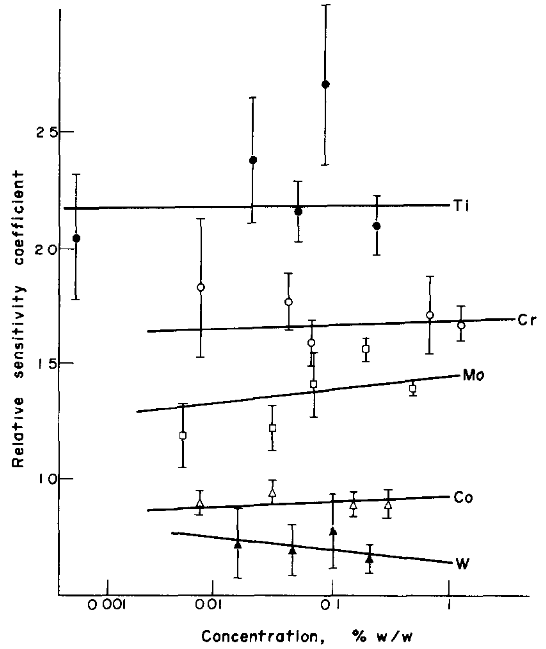

Fig. 5. Effect of concentration on the relative sensitivity coefficients of some elements in steel standards. ● Ti, ○ Cr, △ Co, □ Mo, ▲ W.

it appeared impossible to control the spark gap precisely. A spark-source voltage of 65 kV was chosen as previous experiments showed this to be suitable for the steel samples.[6]

Reproducibility of experimental sensitivity coefficients

To perform quantitative analyses with an electrical detection system, the mass-analysed signal, which is in fact the ratio of the collector signal to the monitor signal, is compared with a signal corresponding to a known concentration. In this work, "matrix referencing"[12] is used: all signals are referred to ^{57}Fe.

A total of 20 scans ranging from 48 to 186 a.m.u. was recorded, each taking 15 min. The average concentrations and the standard deviations are listed in Table 9 for standard NBS-SRM 662. When more than one isotope was used, the weighted average concentration and the corresponding standard deviation were calculated from

Table 15. Magnetic peak-switching: relative sensitivity coefficients as a function of concentration for steel standards (slopes of the straight lines obtained by the least squares method)

Element	Slope*	Concentration interval, % *w/w*
Ti	0.0052 ± 0.11	0.0006–0.24
V	−0.083 ± 0.099	0.0006–0.31
Cr	0.020 ± 0.085	0.0007–1.31
Mn	−0.16 ± 0.13	0.0057–1.50
Co	0.026 ± 0.038	0.007–0.30
Ni	0.034 ± 0.047	0.041–1.99
Cu	−0.14 ± 0.077	0.0058–0.50
As	−0.51 ± 0.72	0.010–0.09
Zr	0.15 ± 0.39	0.009–0.19
Nb	−0.35 ± 0.19	0.022–0.29
Mo	0.065 ± 0.054	0.0050–0.49
Sb	0.75 ± 0.81	0.002–0.035
La	−1.3 ± 1.6	0.00007–0.0006
Ta	−0.067 ± 0.19	0.020–0.20
W	−0.065 ± 0.12	0.01–0.21

* ΔS_R per unit change in logarithm of concentration.

$$\bar{c} = \frac{\Sigma(c_i/s_i^2)}{\Sigma(1/s_i^2)} \quad \text{and} \quad s = \frac{100}{\bar{c}}\,\frac{\sqrt{N}}{\Sigma(1/s_i^2)}\,\%$$

where N is the number of isotopes. An average relative standard deviation of 18% was obtained. The results of similar experiments for the other steel standards are summarized in Table 10 and it may be concluded that the precision is about 18%.

For magnetic peak-switching, 8 successive measurements were carried out for each isotope before switching to the next. This sequence was repeated 10 times. The average of the 80 concentrations calculated for each isotope, the standard deviation and the S_R-values are shown in Table 11 for standard reference sample 662. An average standard deviation of 10% was obtained. Table 12 lists the average precision resulting

Table 16. Determination of trace impurities in iron: comparison of results obtained by neutron-activation analysis (NAA) and spark-source mass spectrometry (SSMS)

	Concentration, *ppm*				Deviation from NAA values, %	
		SSMS				
Element	NAA	Photoplate	Scanning	Peak-switching	Scanning	Peak-switching
V	2.52 ± 0.15	2.5 ± 0.1	2.0 ± 12%	2.9 ± 9%	−21	+14
Cr	6.2 ± 1.0	6.4 ± 0.5	6.9 ± 8%	7.5 ± 8%	+11	+21
Mn	10.7 ± 0.3	10 ± 2	13 ± 20%	12 ± 8%	+21	+12
Co	80.4 ± 1.1	64 ± 3	97 ± 9%	78 ± 7%	+20	−3
Ni	864 ± 5	800 ± 100	1000 ± 15%	820 ± 7%	+16	−5
Cu	41.0 ± 1.0	39 ± 5	44 ± 20%	42 ± 7%	+8	+3
As	8.55 ± 0.35	11 ± 2	7 ± 43%	7.4 ± 15%	−14	−14
Mo	64.2 ± 1.0	70 ± 10	60 ± 25%	74 ± 9%	−6	+15
					Average	
		average r.s.d.	19%	9%	15	11

Table 17. Relative sensitivity coefficients* determined in steel standards by using peak-switching

Element	Capellen *et al.*[7]	Hull[8]	Blanchard[9]	This study
Ti	6.6 ± 73%	2.4 ± 25%		2.2 ± 8%
V	1.7 ± 22%	1.6 ± 16%	1.99	1.6 ± 9%
Cr	1.5 ± 13%	1.5 ± 9.1%	2.06	1.7 ± 7%
Mn	2.4 ± 33%	2.6 ± 19%	3.13	2.7 ± 6%
Fe	1		1	1
Co	0.90 ± 8.9%	1.0 ± 26%	0.81	0.89 ± 6%
Ni	0.79 ± 11%	0.96 ± 19%	0.73	0.82 ± 6%
Cu	1.6 ± 37%	2.1 ± 17%	1.48	1.7 ± 6%
As	4.6 ± 70%	6.2 ± 22%		3.2 ± 10%
Zr	2.8 ± 7.1%	2.6 ± 8.3%		2.1 ± 11%
Nb	2.0 ± 20%	1.8 ± 7.2%		1.8 ± 8%
Mo	1.9 ± 26%	1.3 ± 7.8%		1.42 ± 4%
Ta		0.80 ± 21%		0.9 ± 16%
W		0.56 ± 17%		0.68 ± 13%

* Shown as coefficient ± relative standard deviation.

from similar experiments with the other standards. They confirm the 10% precision found for NBS 662. The experiments for scanning and peak-switching were carried out in 2 groups over a one-month period.

Sensitivity coefficients as a function of concentration—accuracy of analysis

The concentrations of the impurities in the steel standards NBS-SRM 661–665 cover one or more orders of magnitude. Hence, analysis of these standards shows whether the S_R-values vary with the concentration. The results are listed in Table 13 for the scanning mode and in Table 14 for the peak-switching mode.

The specified uncertainty of the certificate values differs widely for the different elements and was interpreted as being twice the standard deviation. The standard deviation of each S_R-value was obtained from

$$s = \frac{100}{S_R} \cdot \frac{a}{b} \sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2}\ \%$$

where a refers to value found by mass spectrometry and b to the certified concentration. The last columns of Tables 13 and 14 list the weighted averages of the relative sensitivity coefficients and the standard deviation

$$\bar{S}_R = \frac{\Sigma(S_{R,i}/s_i^2)}{\Sigma(1/s_i^2)}; \quad s = \frac{100}{\bar{S}_R} \frac{\sqrt{N}}{\Sigma(1/s_i^2)}\ \%.$$

The overall mean relative standard deviation obtained was 16% for scanning and 10% for peak-switching. Since there is no significant increase compared with the standard deviation for the individual standard samples, it can be concluded that S_R is not a function of the elemental concentration in steel at the level of precision allowed by spark-source mass spectrometry. By way of example, Fig. 5 shows the S_R-values measured by peak-switching for Ti, Cr, Co, Mo and W, plotted as a function of the concentration of these elements in the samples. The slope of the most probable straight line drawn through the data points does not significantly differ from zero in all cases. The results of regression analysis on the data are shown in Table 15 for all elements considered.

Tables 13 and 14 show that the precision of the experimental determination of S_R-values is of the order of 10% for magnetic peak switching and 16–18% for magnetic scanning. This gives an idea of the accuracy with which steels can be analysed by using the experimentally determined S_R-values. This was confirmed by comparing the results for the analysis of a high-purity iron sample with those obtained by neutron-activation[10] (Table 16); the results found by photoplate detection are shown for comparison.

CONCLUSIONS

Comparing Tables 13 and 14 it is apparent that there is fair agreement between the relative sensitivity coefficients for all the elements considered, obtained through magnetic scanning and magnetic peak-switching. Switching is the more precise method, with a 10% r.s.d., the corresponding precision of scanning being 16–18%. However, a quick survey by scanning provides quite acceptable results. A previous study showed that the precision with photographic detection was 15%. The accuracy was of the same order as the precision for the three modes of operation, as illustrated by the comparison of the results with those obtained by neutron-activation analysis.

Other workers have reported sensitivity coefficients for spark-source mass spectrometric analysis of steel standard samples by peak-switching. Their results are summarized in Table 17 and are in agreement with the values reported here. The S_R-value of iron was taken as unity by all authors with the exception of Hull, who used internal referencing to vanadium; these values have been converted for the comparison, setting the S_R-value of vanadium at 1.6.

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RADIOTRACER STUDIES ON CALCIUM ION-SELECTIVE ELECTRODE MEMBRANES BASED ON POLY(VINYL CHLORIDE) MATRICES

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Summary—Radiotracer studies with ^{45}Ca and ^{36}Cl demonstrate that PVC matrix membranes containing Orion 92-20-02 liquid calcium ion-exchanger are permselective to counter-cations. Diffusion coefficients are quoted for the migration of ^{45}Ca between pairs of calcium solutions and are discussed in terms of solution concentration, membrane thickness and concentration level of sensor in the membrane. Migration of calcium ions from calcium chloride solution to a Group (II) metal chloride solution through a PVC membrane containing calcium liquid ion-exchanger is discussed in terms of solvent extraction and electrode selectivity coefficient parameters. Thus, magnesium, strontium and barium ions appear to inhibit migration through the membrane by their low affinity for the membrane liquid ion-exchanger sites, while the inhibition by beryllium ions is attributed to site blockage by the strong affinity of dialkylphosphate sites for beryllium.

The high quality of ion-exchange membranes as selectively permeable devices is well established[1] but liquid ion-exchangers have greater selectivity for counter-ions than the resinous materials and it is for this reason that liquid ion-exchanger membranes have utility as selective ion-sensors in ion-selective electrodes.[2,3] The ideal in principle is a membrane of perfect selectivity for one counter-ion relative to all others, because the selectivity coefficient, $k^{\text{pot}}_{\text{AB}}$ would then approach zero and thus nullify the contribution of $k^{\text{pot}}_{\text{AB}}(a_{\text{B}})^{z_{\text{A}}/z_{\text{B}}}$ in equation (1) to give a simple linear relation between ion-selective electrode response, E, with respect to a suitable reference electrode, and the logarithm of the activity, a_{A}, of the principal counter-ion A:

$$E = \text{constant} \pm \frac{2.303RT}{z_{\text{A}}F}\log(a_{\text{A}} + k^{\text{pot}}_{\text{AB}}(a_{\text{B}})^{z_{\text{A}}/z_{\text{B}}}) \qquad (1)$$

In equation (1) the positive sign holds for cations and the negative for anions, a_B is the activity of the interfering counter-ion B, and the z terms refer to the number of charges on the counter-ions.

Perfect selectivity is unknown and the selectivity coefficient must always be borne in mind when using ion-selective electrodes. It is therefore desirable to have a better understanding of selectivity. As a step in this direction, the present paper reports a radiotracer study on the calcium ion permeability of PVC matrix membranes containing Orion 92-20-02 liquid-ion exchanger, and the membranes are also shown to be impermeable to chloride ions.

EXPERIMENTAL

Experiments using membranes prepared in the manner previously described[4–6] involved radioactive tracer exchange between two solutions separated by a membrane, studied either by continuous recording or by intermittent sampling and monitoring. The detailed procedures are described below.

Procedure I

A 7-mm diameter disc of PVC–liquid ion-exchanger ion-selective electrode membrane cut from a master membrane prepared from 0.17 g of PVC (Breon 111) + 0.40 g of Orion 92-20-02 calcium ion-exchanger, was sealed (with a cement made of PVC in tetrahydrofuran) to a PVC tube fitted to the end of a drawn-out B10 socket. A solution containing 0.1 ml of calcium chloride solution (*ca.* 1 mCi of ^{45}Ca per ml), diluted to 2 ml with water to give a 0.005*M* calcium solution, was placed inside the tube, which was then closed with a B10 stopper to prevent evaporation. This assembly was suspended inside a tube 14 cm long and 2.3 cm in internal diameter, sealed at one end with a mica window (5 mg/cm^2) by "Araldite". The outer tube contained 10 ml of $10^{-4}M$ calcium chloride or magnesium chloride, as appropriate. The entire assembly was positioned in a mica end-window Geiger-Müller counter system as depicted in Fig. 1. The increase in activity of the external solution was thus monitored continuously by the pen recorder as the β-emitting ^{45}Ca ions migrated through the membrane.

The design of this experiment is such that the results are only qualitative, but the preliminary results obtained led to the design of procedure II. Co-ion diffusion studies were made with calcium chloride labelled with chlorine-36.

Procedure II

Apparatus assemblies like that depicted in Fig. 2 were kept in an air thermostat at 35 ± 0.5°, a temperature higher than ambient being chosen in order to overcome problems of dissipating the heat generated by the magnetic stirrers. A 22-mm diameter disc of PVC–liquid ion-exchanger ion-selective electrode membrane cut from an appropriate master membrane prepared as in procedure I was cemented to a PVC tube of 16 mm internal diameter. The other end of the tube was connected to a glass tube (A) fitted with a side-arm and having a Teflon-covered magnetic-stirrer bar hanging from a fishing swivel by a nylon fishing line. The membrane end of (A) was immersed in a solution contained in a 25-ml beaker (B) provided

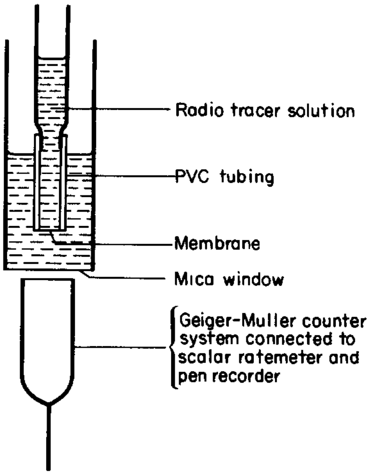

Fig. 1. Apparatus assembly for continuously monitoring the permeation of radiotracer ions through PVC matrix membranes.

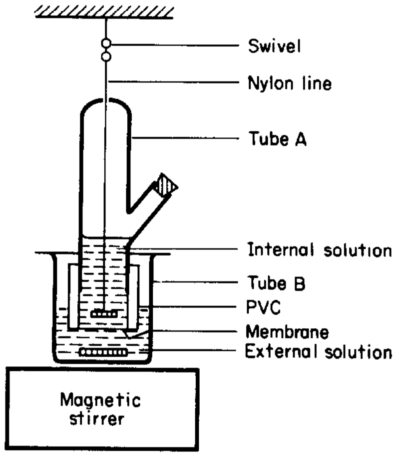

Fig. 2. Apparatus aassembly for studying the permeation of radiotracer ions through PVC matrix membranes by intermittent sampling.

with a Teflon-covered magnetic-stirrer bar. Both (A) and (B) were charged with appropriate solutions (10 ml) which were stirred with the magnetic stirrers during experimentation. The solutions were monitored for radioactivity by withdrawing 10-μl samples at appropriate times through the side-arm of (A). A Lang–Levy auto-zero micropipette was used to spot the samples onto 5.5-cm diameter discs of Whatman No. 1 filter paper and the ^{45}Ca activity was counted with a Geiger-Müller mica end-window tube.

Discs of PVC alone, and of PVC containing only dioctyl phenylphosphonate mediator were similarly examined. Additionally, permeation selectivity was examined with ^{36}Cl.

Calcium content of the liquid ion-exchanger

The calcium content of the liquid ion-exchanger was determined by Crump's EDTA procedure[7] and the results used for evaluating the calcium content of the various membranes.

Selectivity coefficient determinations

Selectivity coefficients, $k^{\text{pot}}_{\text{AB}}$, were determined by a mixed-solution method,[8,9] with a fixed level of interferent B.

RESULTS

Selectivity coefficients are summarized in Table 1 along with certain solvent extraction data.

The main results relate to the migration of calcium ions between solutions of calcium chloride or between solutions of calcium chloride and another Group (II) metal chloride separated by a PVC matrix membrane containing Orion 92-20-02 liquid calcium ion-exchanger based on a dialkylphosphate sensor plus phosphonate mediator. The selective permeability of the membrane to cations is shown by the non-diffu-

Table 1. Extraction coefficients of alkaline earth cations from 4*M* sodium nitrate into di(2-ethylhexyl)phosphoric acid in benzene, and selectivity coefficients, $k^{\text{pot}}_{\text{CaB}}$, of PVC matrix membrane ion-selective electrodes with dialkylphosphate sensors

Counter-ion, B	Log of extraction coefficient*		$k^{\text{pot}}_{\text{CaB}}$†		
			Ca di(2-ethylhexyl)-phosphate sensor with decanol	Orion 92-20-02 liquid ion-exchanger	
	pH = 7.0	pH = 5.2	25°C	25°C	35°C
Be^{2+}	4.3	4.3	2.6§	7.2§	11.2§
			2.6	12.0	14.0
			(5 × 10^{-5})	(5 × 10^{-5})	(5 × 10^{-5})
Mg^{2+}	1.2	1.4	1.0	0.01	0.055§
					0.052
				(4 × 10^{-4})	(4 × 10^{-4})
Ca^{2+}	0.9	2.2	1.0	1.0	1.0
Sr^{2+}	−0.2	0.1	0.5	0.05	0.09
			(4 × 10^{-4})	(4 × 10^{-4})	(4 × 10^{-4})
Ba^{2+}	−0.6	−0.5	0.5	0.002	0.01
			(4 × 10^{-4})	(4 × 10^{-4})	(4 × 10^{-4})
Zn^{2+}	—	—	—	—	0.13§
					0.12
					(4 × 10^{-4})

* Based on data from Ref. 10

† This work. Number in parentheses are the molarity of the interfering counter-ion B.

§ These $k^{\text{pot}}_{\text{AB}}$ values were determined with the sulphate of the interferent ion; all others refer to the chloride systems.

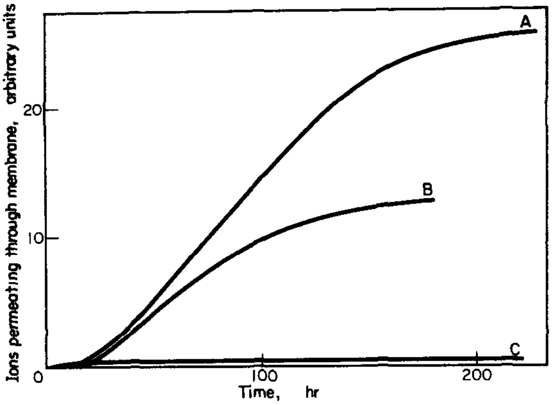

Fig. 3. Traces showing the permeation of $^{45}Ca^{2+}$ through a PVC matrix membrane with trapped Orion 92-20-02 liquid ion-exchanger, into calcium chloride (curve A) and magnesium chloride (curve B) solutions. Curve C confirms membrane permselectivity to counter-cations by the near-zero diffusion of $^{36}Cl^-$ under similar conditions to those prevailing for curve A.

sion of chloride ions through it (Fig. 3 and Table 2). Results obtained by both procedures I and II also confirm the impermeability of the PVC matrix to calcium ions, which gave no diffusion through a PVC membrane alone or containing dioctyl phenylphosphonate[11,12] mediator but no dialkylphosphate.

Both procedures approximate the way liquid ion-exchanger membranes are used in ion-selective electrodes, but procedure I serves only to demonstrate the migration or otherwise of radioactive species through the membrane (Fig. 3).

The quantitative migration data were obtained by procedure II. Thus, diffusion coefficients for calcium, $\bar{D}$, were calculated from steady-state ^{45}Ca diffusion across the membrane (with calcium solutions on each side) by means of the equation[13]

$$\bar{D} = \frac{d(C''/C')}{dt}\,\frac{V''Ch}{\bar{C}q} \qquad (2)$$

where h is the membrane thickness [0.050 cm except for membranes 9 and 10 (0.030 cm) and membrane 11 (0.025 cm)], measured with a micrometer gauge, q is the cross-sectional area of the membrane (2.01 cm^2), C' and C'' are the tracer concentrations (proportional to radioactivity) in the initially active and inactive solutions respectively, C is the total calcium ion concentration (that is, tracer + non-tracer) in the solutions on each side of the membrane (Table 2) and $\bar{C}$ that in the membrane ($4.34 \times 10^{-2}M$ except for membranes 9 and 10 where $\bar{C}$ is $3.35 \times 10^{-2}M$), and V'' is the volume (10 ml) of the initially inactive solution.

Table 2. Diffusion coefficients, $\bar{D}$, and time-independent $d(C''/C')/dt$ data for solution/membrane systems, obtained by procedure II

Series	Membrane constituents	Solution A (internal), $[CaCl_2]$, M	Solution B (external), $[CaCl_2]$, M	$\bar{D}$, 10^9 cm^2/sec	$\frac{d(C''/C')}{dt}$, 10^7 sec^{-1}
1	PVC (0.17 g) matrix only	10^{-3}*	10^{-3}	—	Zero over > 10 days
2	PVC (0.17 g) + dioctyl phenylphosphonate (0.36 g)	10^{-3}*	10^{-3}	—	Zero over > 7 days
3	As for procedure I	10^{-3} and 10^{-1} labelled with ^{36}Cl	10^{-3} and 10^{-1}	—	Zero over > 9 days
4	As for procedure I	10^{-3}*	10^{-3}	10.6	18
5	As for procedure I	10^{-3}	10^{-3}*	11.1	19
6	As for procedure I	10^{-2}*	10^{-2}	14.3	2.5
7	As for procedure I	10^{-2}	10^{-2}*	14.9	2.6
8	As for procedure I	10^{-1}*	10^{-1}	23–32†	0.40–0.56†
9	As for procedure I but with 0.20 g of ion-exchanger	10^{-3}*	10^{-3}	1.0	2.2
10	As for procedure I but with 0.20 g of ion-exchanger	10^{-2}*	10^{-2}	2.8	0.63
11	As for procedure I but with 0.20 g of ion-exchanger and 0.085 g of PVC	10^{-3}*	10^{-3}	5.1	18.0

* These solutions are labelled with ^{45}Ca.

† Difficulty in guaranteeing time-independence of tracer flux at such high concentration.

Equation (2) was used under steady-state conditions when the tracer flux through the membrane was time-independent, that is, when the tracer concentration ratio between the initially inactive and active solutions increased linearly with time. The calcium diffusion coefficients between calcium solutions are summarized in Table 2.

Equation (2) is restricted to the measurement of self-diffusion coefficients, but the C''/C' *vs.* time profiles for the migration of ^{45}Ca from calcium solutions to other Group (II) metal solutions are similar to those for migration between calcium solutions. Hence, in order to compare the migration of labelled calcium between solutions of similar concentration and initially composed of calcium chloride and Group (II) metal salts respectively, $d(C''/C')/dt$ data for the time-independent regions are summarized in Tables 2 and 3.

Except for experiment 8 where there was extreme difficulty in locating the time-independent region of the tracer flux, the results in Tables 2 and 3 are means of replicate determinations with individual values within $\pm 8\%$ of the mean, except for experiment 4 where the mean is that of five determinations with a coefficient of variation of 4.7%. The results are discussed in the context of these error ranges.

DISCUSSION

The permeation of the counter-cations but not of the chloride co-ions (Fig. 3 and Tables 2 and 3) confirms that these membranes possess the permeation selectivity characteristic of ion-exchanger membranes. Thus, migration of counter-ions through the membrane placed between two solutions is not "one-way traffic", because in order to preserve electrical balance, counter-ion migration in one direction must be accompanied by an equivalent migration in the reverse direction. This is demonstrated by the results of experiments 4–7 (Table 2), 13–26 (Table 3), 28 and 29 (Table 3) based on migrations from internal to external solutions and *vice versa.*

Table 3. Time-independent $d(C''/C')dt$ data for solution/membrane systems, obtained by procedure II (membrane composition as described in procedure I)

Series	Solution A (internal)	Solution B (external)	$\frac{d(C''/C')}{dt}$ 10^7 *sec*$^{-1}$
12	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $BeSO_4$	5.6
13	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $BeCl_2$	2.5
14	$10^{-3}M$ $BeCl_2$	$10^{-3}M$ *$CaCl_2$	2.2
15	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $MgCl_2$	8.0
16	$10^{-3}M$ $MgCl_2$	$10^{-3}M$ *$CaCl_2$	8.4
17	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $SrCl_2$	8.5
18	$10^{-3}M$ $SrCl_2$	$10^{-3}M$ *$CaCl_2$	9.1
19	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $BaCl_2$	8.4
20	$10^{-3}M$ $BaCl_2$	$10^{-3}M$ *$CaCl_2$	7.5
21	$10^{-2}M$ *$CaCl_2$	$10^{-2}M$ $MgCl_2$	1.66
22	$10^{-2}M$ $MgCl_2$	$10^{-2}M$ *$CaCl_2$	1.68
23	$10^{-2}M$ *$CaCl_2$	$10^{-2}M$ $SrCl_2$	1.08
24	$10^{-2}M$ $SrCl_2$	$10^{-2}M$ *$CaCl_2$	1.17
25	$10^{-2}M$ *$CaCl_2$	$10^{-2}M$ $BaCl_2$	0.91
26	$10^{-2}M$ $BaCl_2$	$10^{-2}M$ *$CaCl_2$	0.82
27	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $ZnSO_4$	3.7
28	$10^{-3}M$ *$CaCl_2$	$10^{-3}M$ $ZnCl_2$	3.7
29	$10^{-3}M$ $ZnCl_2$	$10^{-3}M$ *$CaCl_2$	3.8

* These solutions are labelled with ^{45}Ca.

Of course, diffusion behaviour may not be exclusively determined by the processes within the membrane, owing to the influence of such factors as concentration profiles within the bulk solutions. These are kept uniform by stirring in procedure II, but such agitation does not affect the Nernst diffusion layers or "films" which adhere to the membrane surfaces. However, film control of diffusion of counter-ions is less significant in the present systems for, compared with conventional ion-exchanger membranes with typical self-diffusion coefficients of $\sim 2 \times 10^{-6}$ cm^2/sec for counter-ions,[14] the coefficients here are smaller by 2–3 orders of magnitude (Table 2). This implies that the self-diffusion of counter-ions is more likely to be diffusion controlled.

In the present case, the diffusion coefficient is directly proportional to membrane thickness rather than being independent of it. This is a consequence of the observed permeation of calcium ions through the membrane (experiments 4 and 11) being independent of membrane thickness, a feature that may be attributed to the diffusing species experiencing the same resistances such as may occur from having a viscous interface at the membrane surface, arising from some loss of plasticizing mediator.

The observed values of *ca.* 10^{-8}–10^{-9} cm^2/sec for $\bar{D}$ (Table 2) are similar in magnitude to those found by Bailey and Dalziel[15,16] for the diffusion of calcium ions from solution to a small membrane disc; the low order of magnitude is considered as characteristic of diffusion through a very viscous medium.

The data in Table 2 indicate the effects of solution concentration and the amount of sensor in the membrane as well as the effect of membrane thickness. Experiments 4–10 (Table 2) show that increase in solution concentration leads to an increase in the diffusion coefficient. A similar dependence has been observed for ion-exchange resins[17–20] and attributed to an apparent increase of co-ion concentration in the pores to provide pathways of high mobility for the migration of counter-ions.[19,21] However, here it has been shown that there is no co-ion migration (Fig. 3 and Table 2) through the PVC membrane containing liquid ion-exchanger. Hence, the migrations suggest a lesser role for co-ion mobility pathways for counter-ions and a greater role for the solvent mediator and osmotic and other forces in the utilization of liquid ion-exchanger sites as pathways.

From the purely theoretical standpoint, the effect of a lower amount of exchanger in the membrane (Table 2, experiments 9 and 10) should, because of decreasing electrostatic retardation, increase the diffusion coefficient. The reverse is the case and $\bar{D}$ is even lower than expected from the reduced membrane thickness (from 0.05 to 0.03 cm). These low values arise from the low slope of the time-independent region of the C''/C' *vs.* time plot and are a direct consequence of a lower flux arising from having fewer liquid ion-exchanger site pathways in a more viscous PVC membrane (Table 2, experiments 9 and 10) than in the corresponding controls (Table 2, experiments 4–7).

Equation (2) cannot be applied to permeation between calcium chloride and Group (II) metal salt solutions, and suitable radiotracers in neutral solution are not conveniently available for a wider study of steady-state diffusion of alkaline earth metal cations. Nevertheless, interesting patterns emerge for the mobility of labelled calcium between calcium chloride and Group (II) metal salt solutions. These are based on the rate of attainment of tracer equilibrium, namely $\mathrm{d}(C''/C')/\mathrm{d}t$ data for the time-independent regions of C''/C' *vs.* time plots (Tables 2 and 3).

The low $\mathrm{d}(C''/C')/\mathrm{d}t$ values for calcium migration through the membrane into the chlorides (Table 3) of magnesium (experiments 15, 16, 21 and 22), strontium (experiments 17, 18, 23 and 24), and barium (experiments 19, 20, 25 and 26) relative to values for migration between calcium solutions at similar concentration levels (Table 2, experiments 4–7) match the low electrode selectivity coefficients ($k^{\mathrm{pot}}_{\mathrm{CaB}}$) for these ions (Table 1). This pattern may arise from the relative reluctance of the interferent ions even to enter the membrane, as illustrated by their tendency to have lower solvent extraction coefficients (Table 1). This reluctance decreases the migration of calcium ions in the reverse direction.

The low $\mathrm{d}(C''/C')/\mathrm{d}t$ values for the migration of calcium into beryllium solutions at $10^{-3}M$ level (Table 3, experiments 12 and 13) is rather surprising in view of this explanation for magnesium, strontium and barium. However, it is suggested that beryllium ions block the liquid ion-exchanger sites because of the high affinity of the exchanger for beryllium, as shown by the data for solvent extraction and electrode selectivity coefficients (Table 1). Kinetic forces may also be at work as in the exchange of solvent water with hydrated metal ions, which in the case of beryllium has a rate constant over six orders of magnitude less than that for calcium.[22]

Ion-selective electrodes having selectivity coefficients much greater than unity frequently need considerable recovery treatment after exposure to interferents. Also, ion-selective electrodes can suffer shocks on exposure to certain other ions, for example, the calcium ion-selective electrode with Orion 92-20-02 liquid ion-exchanger trapped in the PVC matrix membrane requires prolonged contact with calcium ions in order to recover from contact with zinc ions. That the sites may be blocked by zinc ions is suggested by $\mathrm{d}(C''/C')/\mathrm{d}t$ data for $10^{-3}M$ calcium and zinc solutions (Table 3, experiments 27–29) and those for the corresponding calcium and beryllium system.

The difference between beryllium chloride and beryllium sulphate (Table 3–experiments 12–14) appears to be due to the anion. A similar effect was observed for the selectivity coefficient, $k^{\mathrm{pot}}_{\mathrm{CaBe}}$, of the calcium ion-selective electrode in the presence of the two beryllium salts as interferents (Table 1). No such differences were observed for zinc.

CONCLUSION

The radiotracer studies have confirmed the selective permeability to counter-ions, of membranes made with calcium liquid ion-exchanger contained in PVC. The migration of calcium ions through such membranes under various conditions of concentration, interference and membrane thickness can be explained in terms of the availability of membrane pathways (which, of course, provide ways for ionic conduction as opposed to the electronic conduction of glass membranes).

The mobility of calcium ions between calcium chloride solutions and Group (II) metal salt solutions through the PVC matrix membranes is consistent with solvent extraction and ion-selective electrode parameters (possibly tempered by kinetic factors), but it has not been possible to distinguish between the separate roles of equilibrium ion-exchange and mobility in the membrane, which seem to be inter-related in electrode selectivity. Nevertheless, the consensus on ion-transport in untrapped liquid ion–ion exchange membranes is that the actual mobilities of the associated (ion *plus* site) pairs for the usual long-chain liquid ion-exchangers are approximately the same for all counter-ion species[23,24] so that electrode selectivities (and overall transfers of ions in the present study) are related simply to equilibrium ion-exchange.[23–26]

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GAS CHROMATOGRAPHY OF TERNARY COMPLEXES OF MANGANESE(II), IRON(II), COBALT(II) AND NICKEL(II) WITH HEXAFLUOROACETYLACETONE AND DI-n-BUTYLSULPHOXIDE

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Summary—The gas chromatographic behaviour of the ternary complexes of selected bivalent first-row transition metal ions with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione H(HFA), and di-n-butylsulphoxide, DBSO, was studied. Calibration plots of peak area *vs.* amount of metal injected were linear over a range of 60–900 ng for manganese(II), iron(II), cobalt(II) and nickel(II). The average relative standard deviation was less than 3·0% for all the metals studied. Detection limits of 60, 109, 112 and 115 ng for cobalt(II), nickel(II), iron(II) and manganese(II), respectively, were obtained with flame-ionization detection. Various liquid phases, including OV-1, SE-30, and Dexsil 300 were used. The best results were obtained on columns of 5% Dexsil 300. No appreciable thermal decomposition was observed on stainless-steel or glass columns, but the best formed peaks were obtained on all-glass columns. The elution of the metallic species was confirmed by venting the exit gases from the gas chromatograph directly into an atomic-absorption spectrophotometer.

The volatility of certain metal chelates, particularly those of chromium and beryllium with fluorinated β-diketones, has permitted their determination by gas chromatography.[1,2] With the use of the electron-capture detector, detection limits as low as 10^{-14} g have been reported for chromium.[3] A problem encountered with many cations is that the co-ordination number is more than twice the number of charges on the cation and the resulting chelates with bidentate β-diketones are hydrated or polymeric.[4–6] This problem can be surmounted by deliberate introduction of neutral donors such as tri-n-butyl phosphate, TBP, or di-n-butylsulphoxide, DBSO, to form anhydrous adducts of these chelates. The authors[7] have previously shown that the zinc adduct, $Zn(HFA)_2 \cdot 2DBSO$, was sufficiently volatile to be eluted from a gas chromatograph without apparent decomposition. The preparation of similar adducts and the gas chromatography of the DBSO adducts of the hexafluoroacetylacetonates of the lanthanides, thorium, and uranium have been reported.[8–13] Little work has been reported on this approach for the bivalent transition metal ions, although the gas chromatography of bivalent transition metal chelates has been reported by Sievers, Ross and co-workers,[14–17] where β-diketones with bulky terminal groups which gave anhydrous chelates were employed. Belcher, Uden and co-workers[4,18,19] also successfully chromatographed several bivalent metals as their monothio-β-diketonates and as chelates with bidentate and quadridentate β-ketoamines.

The synergic extraction and gas chromatography of iron(II) and iron(III) adducts with hexafluoroacetylacetone, H(HFA), and TBP was reported by Tomažič and O'Laughlin.[20] Burgett[21,22] reported that copper(II), iron(II), cobalt(II), nickel(II) and lead(II) were quantitatively extracted when 0.01*M* solutions of these metals were equilibrated with 0.03*M* H(FHD) (1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione) and 0.03*M* DBSO. Burgett reported that all the adducts, except for those of lead and copper, could be eluted from a gas chromatographic column. The lead adduct decomposed and copper was reported not to form an adduct. The synergic extraction and gas chromatographic behaviour of zinc(II), cadmium(II) and lead(II) with H(HFA) and DBSO have been previously reported.[7] Although all three were quantitatively extracted, only the zinc adduct could be eluted; the cadmium and lead adducts apparently decomposed on the column.

Several reviews on the determination of metals by gas chromatography have been published. These include books by Moshier and Sievers,[1] Guiochon and Pommier[23] and reviews by Belcher[24] and Kutal.[25]

The present paper reports on the gas chromatography of manganese(II), iron(II), cobalt(II) and nickel(II) as ternary complexes prepared by synergic extraction of the cations with H(HFA) and DBSO into cyclohexane. The gas chromatographic behaviour of these adducts was studied as a function of the metal concentration, neutral donor concentration and nature of the stationary phase in both glass and stainless-steel columns.

EXPERIMENTAL

Apparatus

The gas chromatographic studies were performed on a Bendix Model 2500-Life Sciences Gas Chromatograph equipped with on-column injection and a flame-ionization detector. A Loenco Model 15C-X Gas Chromatograph equipped with a thermal-conductivity detector was used in the atomic-absorption studies. The chromatograms were recorded on a Honeywell Model 194 Electronik strip-chart recorder.

Both the Perkin-Elmer Model 290B and Model 403 Atomic Absorption Spectrophotometers were used in the atomic-absorption studies. Each was used with an air–acetylene flame and a Perkin-Elmer Model 56 strip-chart recorder. A Perkin-Elmer Deuterium Arc Background Corrector was used on the Model 403.

A Cary Model 15 Spectrophotometer, a Perkin-Elmer Model 180 Infrared Spectrophotometer, and a Varian Model A-60 Nuclear Magnetic Resonance Spectrophotometer were employed to check the purity of the reagents, chelates, and adducts.

Reagents and materials

Reagent grade nitrate, chloride, or acetate salts were used to prepare stock metal solutions. H(HFA), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, was obtained from Pierce Chemical Company and its purity was checked by ultraviolet, NMR, and infrared spectroscopy as well as by gas chromatography. All solvents were reagent grade.

The H(HFA) complexes of Co(II), Fe(II), Mn(II), and Ni(II) were obtained from PCR, Inc. Tri-n-butyl phosphate, TBP, and di-n-butylsulphoxide, DBSO, were used without purification.

Chromosorb W-HP 100/120 mesh was obtained from Analabs, Inc., Dexsil 300 was obtained from Regis Chemical Company through the Bendix Corporation, and SE-30 and OV-1 were obtained from the Bendix Corporation.

Columns were constructed of borosilicate glass tubing or type 304 stainless-steel tubing.

Bendix "Col-Treet" and "Glass-Treet" were obtained from the Bendix Corporation. Dimethylchlorosilane and dimethyldichlorosilane were obtained from Pierce Chemical Company.

Column pretreatment

Before coating the Chromosorb W-HP was pretreated by a method described previously.[7,26]

The glass columns were rinsed with Bendix "Glass-Treet", and absolute methanol, then flushed with air and dried in an oven for several hr at 110°. The stainless-steel columns were treated as suggested by Analabs, Inc.[27] The columns were rinsed successively with absolute methanol, isopropyl alcohol, chloroform, isopropyl alcohol, dilute nitric acid (1.0*M*), and then thoroughly rinsed with demineralized water and finally with absolute methanol. The empty columns were then flushed with air and dried in an oven for several hr at 110°.

Preparation of column packing

The silated Chromosorb W-HP was coated with Dexsil 300, SE-30, or OV-1 by slurrying with a chloroform solution of the coating. Excess of solvent was removed in a rotary evaporator and the product dried at 110° with occasional stirring. The resulting product was dried for 24 hr in a vacuum desiccator, then placed in a large sintered-glass filtering funnel; a gentle stream of dry nitrogen was passed upwards through the funnel to remove any fines.

Packing and conditioning of the columns

Dry column packing was poured into the tube and compacted with gentle tapping. Use of a vibrator gives more fines and poorer performance. The ends of the columns were plugged with glass wool that had been soaked in a solution of 5% dimethyldichlorosilane and 5% dimethylchlorosilane in toluene, followed by an absolute methanol rinse and drying for several hr, at 110°. The columns were brought to conditioning temperature and 20 μl of Bendix "Col-Treet" were injected to silate any active sites. The Dexsil 300 columns were conditioned at 350° for 24 hr and the SE-30 and OV-1 columns at 300° for 24 hr with a low flow of nitrogen.

Preparation of organic solutions of mixed-ligand complexes

Solutions of the metal–H(HFA)–neutral donor complexes were prepared by solvent extraction utilizing the methods previously described[7] or by placing a weighed amount of the hydrated chelates in a volumetric flask and diluting to standard volume with a solution of DBSO or TBP in cyclohexane to yield a stoichoimetric adduct with a minimum excess of neutral donor present.

Solutions of mixtures of several metal complexes were prepared by solvent extraction or by mixing appropriate volumes of the solutions above to form mixtures. All solvent extraction mixtures were sampled directly from the organic layer in the extraction tubes or from the volumetric flasks by syringe.

RESULTS AND DISCUSSION

Metal–HFA–neutral donor adducts

Three different stationary phases were investigated for the best gas chromatographic response characteristics. Recent work[12,13,21,22,28] has shown the excellent gas chromatographic behaviour and thermal stability of the carborane-cage compound, Dexsil 300, which was the stationary phase used for the majority of the gas chromatographic studies. SE-30, a methylsilicone gum rubber phase which has also shown good utility for application to volatile metal chelates, and OV-1, also a methylsilicone gum rubber phase, were used for comparative purposes. McReynold's constants indicate that Dexsil 300 is more polar than SE-30 and OV-1 which have about the same polarity.

The metal–HFA–neutral donor complexes of Ni(II), Fe(II), Co(II), and Mn(II) were chromatographed. Several attempts were made to elute the TBP adducts but these proved unsuccessful, owing to the inability to separate the adduct peak from that of TBP. Only the DBSO adducts were studied further.

Initial studies were performed on glass columns packed with 5% OV-1 on 100/120 mesh Chromosorb W-HP. The peak representing the adduct was broad and not well resolved from that of DBSO. Somewhat sharper peaks were obtained by using SE-30; however, all the retention times on an 18 × 1/4 in. column packed with 5% SE-30 on Chromosorb W were less than 3 min and resolution was poor. The best formed peaks were obtained on short columns of 5% Dexsil 300 on Chromosorb W. The elution behaviour of the bivalent metal chelates was studied on both glass and stainless-steel columns of varying lengths from 18 in. to 6 ft, all of 1/4 in. o.d.

The chromatographic behaviour of $Co(HFA)_2 \cdot 2DBSO$ on both stainless-steel and glass columns packed with 5% Dexsil 300 and 5% SE-30 on 100/120 mesh Chromosorb W-HP was studied. The results were similar to those found for the zinc adduct $Zn(HFA)_2 \cdot 2DBSO$[7] with response decreasing in the order: 5% Dexsil 300-glass, 5% Dexsil 300-stainless steel, 5% SE-30-glass, 5% SE-30-stainless

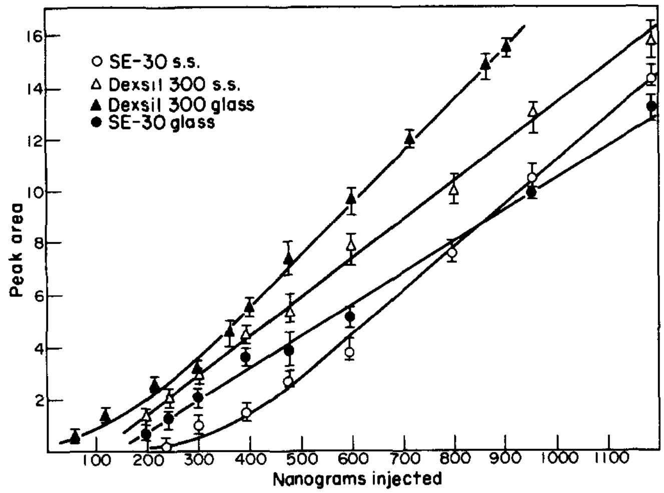

Fig. 1. Dependence of peak area on weight of $Co(HFA)_2 \cdot 2DBSO$ injected on glass and stainless steel columns packed with SE-30 and Dexsil 300 on Chromosorb W.

steel as shown in Fig. 1. Glass columns (10 × 1/4 in.) packed with 5% Dexsil 300 were used for all subsequent work. All calibration curves were obtained from 3–5 replicate injections for each concentration.

The areas of all peaks were determined by triangulation. The substantial difference in the response on stainless-steel and glass columns may be due in part to some decomposition on the hot steel column walls, but this could not be verified. The best formed peaks were consistently obtained on glass columns packed with Dexsil 300 on Chromosorb W.

The methods by which the columns were cleaned and packed obviously have some bearing on the different response curves obtained. The retention times were less for SE-30 than for Dexsil 300, making it more difficult to resolve the DBSO peak from that of the metal complex.

Determination of the H(HFA)–DBSO adducts

The DBSO adducts of Zn(II), Ni(II), Mn(II), Co(II), and Fe(II) were examined as shown in Fig. 2. A flame-ionization detector was used. The chelates were prepared by extracting various concentrations of the metals at the optimum conditions for extraction: pH 5.0–5.5, 0.01*M* K(HFA) and 0.05*M* DBSO in cyclohexane. Solutions of the various metals were also prepared by weighing appropriate amounts of the metal–HFA chelates (to give the same metal concentrations as when prepared by extraction) into a 100-ml volumetric flask and diluting to volume with 0.04*M* DBSO. The chromatographic peaks obtained from both types of solution were the same and subsequent studies were carried out with complexes prepared by the latter method.

The stoichiometry of the ternary complexes was inferred from the slopes of the log *D* *vs.* log [DBSO] plots. The formation of a di-adduct was indicated. Furthermore, solutions prepared by mixing the chelates of the metals with sufficient DBSO in cyclohexane to give a di-adduct gave chromatographic peaks identical with those for the metal complexes prepared by solvent extraction.

The detection limits for the 5 metal–HFA–DBSO complexes are shown in Table 1, the zinc chelate having the lowest detection limit. Electron-capture detectors cannot be used because they are swamped by the excess of H(HFA).

Retention time vs *metal concentration*

Studies of retention time as a function of metal concentration were performed (*a*) at constant DBSO concentration (0.04*M*) and (*b*) at constant ratio of DBSO to metal ion concentration. In both studies the retention times decreased with decreasing metal concentration.

The retention times in (*a*) decreased from 2.10 min for 952 ng to 1.43 min for 59.6 ng of cobalt, and from

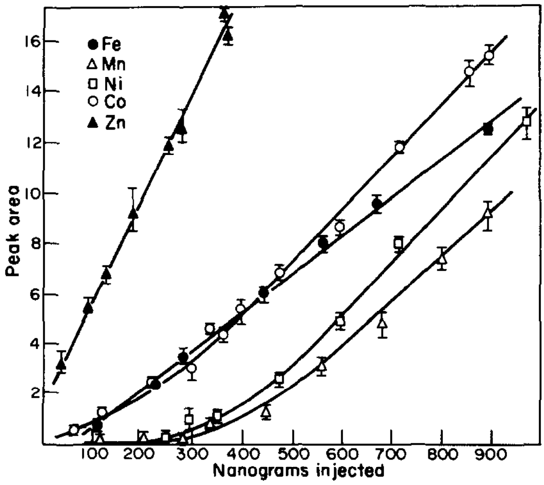

Fig. 2. Dependence of peak area on weight of the H(HFA)–DBSO complexes of Fe(II), Mn(II), Ni(II) and Co(II). Data on Zn(II) are included for comparison.[7]

Table 1. Gas chromatographic detection limits for some selected bivalent metal complexes

	Detection limit, *ng*
$Zn(HFA)_2 \cdot 2DBSO$	45.5
$Co(HFA)_2 \cdot 2DBSO$	59.6
$Ni(HFA)_2 \cdot 2DBSO$	109.0
$Fe(HFA)_2 \cdot 2DBSO$	112.0
$Mn(HFA)_2 \cdot 2DBSO$	115.0

2.53 min for 890 ng to 1.59 min for 115 ng of manganese. Nickel and iron gave similar results. In (*b*), retention times for 1112–222 ng of manganese varied from 2.39 to 1.54 min, and for 1172–234 ng of nickel from 3.15 to 1.93 min. Cobalt and iron gave similar results. Variations in retention times between the two studies at the same metal concentration are possibly due to changes in carrier-gas flow-rate and temperature during analysis.

Studies of the variation in peak area with DBSO concentration at a constant metal ion concentration of 0.008*M* are shown in Fig. 3. The initial DBSO concentration was 0.016*M* which is the minimum concentration required to form the di-adduct; 3–5 replicate 2-μl injections at each DBSO concentration were made. Some variations may be explained by the fact that as the excess of DBSO increases, the tail of the DBSO peak extends under the peak for the metal complex. Except possibly in the case of manganese, this study does not indicate the decomposition of the adduct at lower DBSO concentrations.

The response of the flame ionization detector is greater for zinc than for the other metals (Fig. 2). Because the areas under the peaks were determined by triangulation and some difficulty was caused by the tail due to excess of DBSO, the only real significance of the data in Fig. 3 may be that the excess of DBSO has no apparent effect on the stability of the complexes.

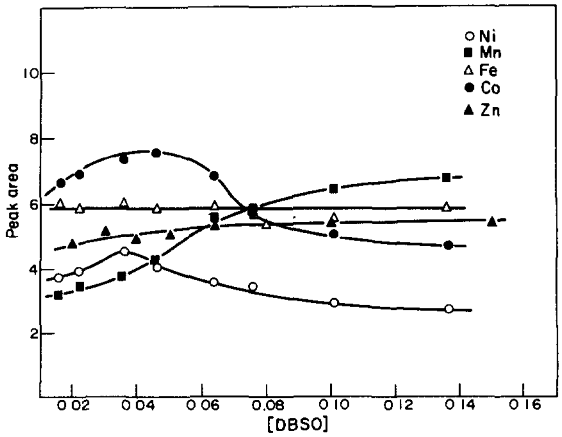

Fig. 3. Dependence of peak area on the concentration of DBSO for the H(HFA)-DBSO adducts of Fe(II), Mn(II), Ni(II) and Co(II). Data on Zn(II) are included for comparison.[7]

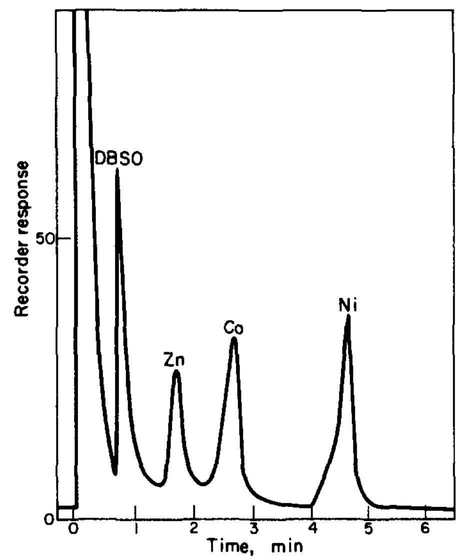

Fig. 4. Chromatogram of a mixture of the Zn(II), Co(II) and Ni(II) adducts of H(HFA) and DBSO at 170°.

Separation of mixtures of mixed-ligand complexes

Mixtures of the complexes were chromatographed and possible separations studied. The separation of a mixture of the zinc, nickel, and cobalt adducts isothermally or with temperature programming is shown in Figs. 4 and 5. Retention times for the individual complexes at uniform temperature indicated the elution order to be zinc, iron(II), cobalt, nickel, and manganese. As seen from the retention times in Table 2, possible separations include Zn–Co–Ni, Zn–Co–Mn, Zn–Fe–Ni, Zn–Fe–Mn mixtures. These

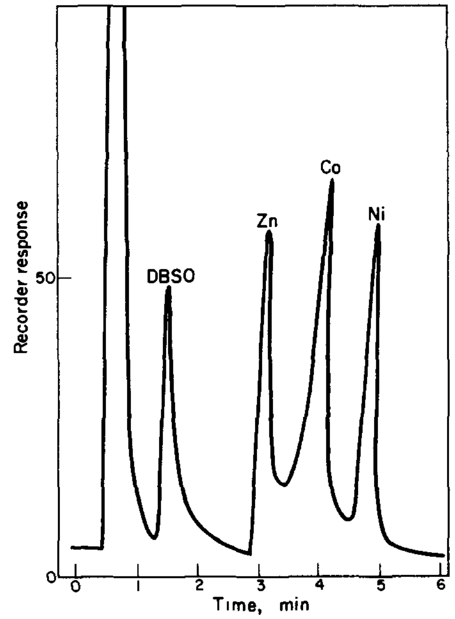

Fig. 5. Chromatogram of a mixture of the Zn(II), Co(II) and Ni(II) adducts of H(HFA) and DBSO temperature programmed from 150–185° at 8°/min.

Table 2. Retention times of metal–H(HFA)-DBSO adducts on an 18 × 1/4 in. glass column packed with 5% Dexsil 300 on Chromosorb W

Conditions	Metal	Retention time, *min* Leading edge	Centre of peak
170°,	Zn(II)	1.69	2.06
flow-rate	Fe(II)	1.85	2.18
38.26 ml/min	Co(II)	2.07	2.46
	Ni(II)	2.26	3.44
	Mn(II)	2.40	3.52
180°,	Zn(II)	1.38	1.58
flow-rate	Fe(II)	1.42	1.61
38.26 ml/min	Co(II)	1.58	1.74
	Ni(II)	1.65	1.84
	Mn(II)	2.01	2.60
150°–200°	Zn(II)	2.66	3.09
10°/min	Co(II)	3.00	3.16
flow-rate	Fe(II)	3.23	3.41
38.26 ml/min	Ni(II)	4.06	4.53
	Mn(II)	4.23	4.63

separations were performed isothermally at temperatures of 170°, 175°, 180° and 185° and by temperature programming from 150 to 200° at several programming rates from 2°/min to 15°/min, the results being essentially the same.

Loading effect in gas chromatographic analysis

The gas chromatographic work showed that multiple injections were necessary before reproducible peak areas could be obtained. This "loading effect" of the columns was found for all metals studied. It was observed that broad peaks or two separate peaks were obtained when one metal complex was chromatographed immediately after a different metal complex under isothermal conditions. This appeared to be caused by a peak with a retention time corresponding to the metal previously chromatographed, appearing along with that for the complex injected. After several injections this peak disappeared and the peak area for the complex injected became reproducible.

A possible explanation for this behaviour would be the retention of some of the first metal complex on the front end of the column and its displacement by the injection of the second metal complex. It is also possible that the first metal complex is partially decomposed in the injection area and reformed upon the injection of the second metal complex, by reaction with excess of H(HFA) and DBSO. The fact that this phenomenon was not observed when the column was left at temperature for several hours before the second metal complex was chromatographed favours the first explanation. Even then, it was still necessary to make several injections before the peak areas became reproducible. These phenomena would cause serious problems in the quantitative analysis of mixtures of metals.

Mass spectroscopy of the metal complexes

Mass spectra were obtained for the $Zn(HFA)_2 \cdot 2DBSO$ and the $Ni(HFA)_2 \cdot 2DBSO$ adducts, using GC-MS. The results obtained yielded little useful information. No molecular-ion peak and few fragments containing the metal ion could be unambiguously identified. The mass spectra for similar chelates reported in the literature also gave complex fragmentation patterns[21,29–32] which were only indicative of the nature of the species actually eluted.

Elemental analysis

Attempts to obtain the crystalline forms of the adducts for elemental analysis were unsuccessful. Evaporation at 100° of 5 ml of 0.01*M* solution of adduct in cyclohexane yielded a thick colourless oil for the zinc adduct and highly coloured oils for the others. These oils were dissolved in cyclohexane and injected into a gas chromatograph. The resulting chromatogram showed a peak for the adduct and a peak due to excess of DBSO. The oils could not be distilled without decomposition.

In order to verify the presence of the metal in the various adducts the exit gases from the thermal conductivity cell were vented directly into the nebulizer assembly of an atomic-absorption spectrophotometer *via* a short length of heated stainless-steel tubing. The

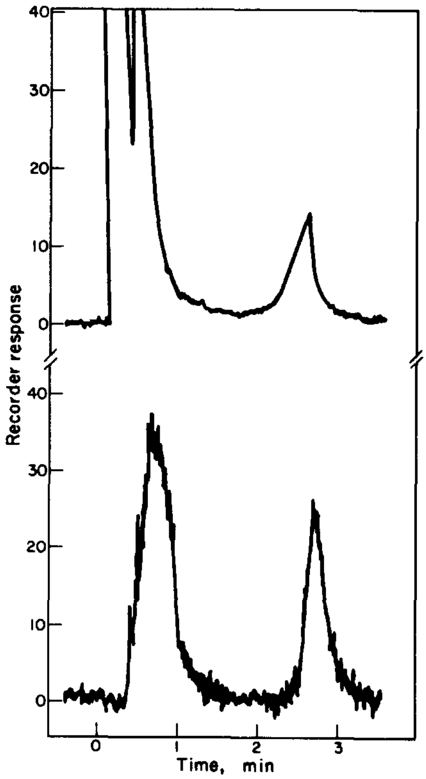

Fig. 6. Gas chromatographic (upper trace) and atomic absorption (lower trace) responses for $Co(HFA)_2 \cdot 2DBSO$. GLC parameters: 180°, 20 in × 1/4 in s.s. column, 5% Dexsil 300 on Chromosorb W. Atomic absorption parameters: Perkin-Elmer 403, 240.72 nm.

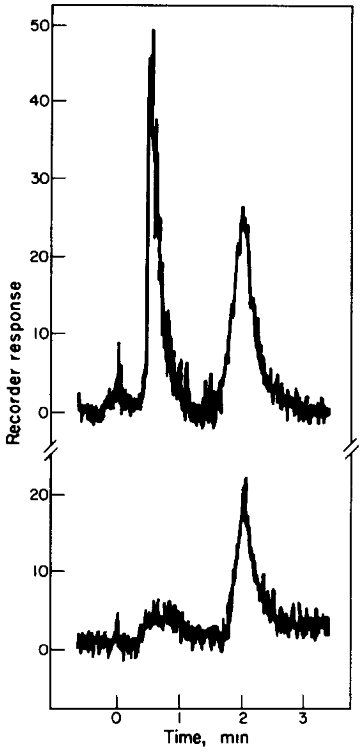

Fig. 7. Atomic-absorption responses for Fe(HFA)$_2$·2DBSO after gas chromatography at 180° with (lower trace) and without (upper trace) background correction on a Perkin-Elmer 403 at 248.32 nm.

spectrophotometer was set at the optimum wavelength for the metal concerned. The output of the spectrophotometer was recorded on a strip-chart recorder. Figure 6 shows the trace for the response from both the thermal conductivity detector and the Perkin-Elmer 403 unit for the elution of cobalt. The initial large peak was a non-specific absorption due to the elution of DBSO and could be largely eliminated by using the background corrector as shown in Fig. 7 for the iron complex. Similar results were seen for the other metals.

These results and similar studies on zinc, nickel, manganese, copper, and chromium complexes confirm that these metal complexes are eluted.

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A NEW ELECTROCHEMICAL ANALYSER FOR NITRIC OXIDE AND NITROGEN DIOXIDE

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Summary—Individual sensors employing Teflon-bonded diffusion electrodes have been developed to measure nitric oxide and nitrogen dioxide separately, simultaneously, and continuously at part-per-million levels. The NO sensor was biased at 1.5 V and that for NO_2 at 0.8 V, both relative to the hydrogen electrode. The crucial factor in the virtual elimination of response from carbon monoxide, a relatively abundant air-pollutant, was the use of gold electrodes for both detectors. At 0.8 V NO does not react on gold. Although NO_2 does oxidize at 1.5 V it was removed quantitatively from NO/NO_2 mixtures by triethanolamine on firebrick. The NO_2 reduction signal and the NO oxidation signal were stable and reproducible.

Knowledge of the nitric oxide and nitrogen dioxide concentrations in ambient air,[1] working environments[2] and stack gases[3] is frequently required. Many approaches have been suggested for their quantitative measurement, including spectroscopy, gas chromatography, chemiluminescence, ion-specific electrodes, coulometry and wet chemistry.[4,5] Most of these methods, however, measure only one of these oxides, and complete analysis requires conversion of one gas into the other or a third species, with the introduction of additional uncertainties.[5] Moreover, currently available techniques for NO and NO_2 measurement are not well adapted for use in portable instruments.[2]

We have previously reported techniques for measurement of carbon monoxide in ambient air,[6,7] of breath alcohol,[8] and of hydrogen sulphide,[9] based on the electrochemical oxidation of these gases at constant-potential Teflon-bonded diffusion electrodes. We now report the extension of this general technique to the separate and direct measurement of NO and NO_2, with particular reference to the characteristics of this technique which make it a useful addition to air-pollution monitoring instrumentation. An experimental monitoring system with separate sensing elements for both NO and NO_2 was constructed to demonstrate the feasibility of this electrochemical detection method. The selected operating conditions resulted in establishment of rapid response times, linearity of response, minimum interference by other common air constituents and pollutants, and signal stability.

EXPERIMENTAL

The instrument consisted of two independent gas-measuring systems, each comprising a pump, flowmeter, electrochemical sensor and electronic circuits. The sensor was similar to that reported previously[9] and contained a potentiostat, thermistors for signal-temperature compensation, and provision for battery recharge. The low power requirements of the pumping system (0.3 W) and of the electronic components (0.025 W) permitted continuous operation for at least 8 hr on batteries.

The physical dimensions of the NO and NO_2 sensors were identical to those of the sensors previously described.[6,7] In both sensors, the sensing and counter-electrodes were "Teflon"-bonded gold diffusion electrodes, while the reference electrode was a Pt-catalysed diffusion electrode. Although the latter is not a reversible electrode, its potential remained essentially constant (± 0.01 V) within the range 1.00 ± 0.03 V. The NO_2 and NO sensing electrodes were kept at a constant potential (0.8 V and 1.5 V, respectively, with respect to the hydrogen electrode). In a recent fundamental study of the reactivity of gold electrodes we found that both CO and NO gave negligible responses at 0.8 V but that NO_2 yielded a substantial reduction current.[10] Between 1.0 and 1.3 V, CO was oxidized at a small but significant rate, but at 1.5 V its reactivity virtually disappeared again. At 1.5 V NO and NO_2 were both oxidized (the signal for the former being 2–3 times that for the latter, for equal concentrations). However, a filter containing 4 g of triethanolamine-impregnated firebrick can be used to remove NO_2 quantitatively from NO/NO_2 mixtures.[11] To guard against SO_2 interference in NO_2 determination, any of several mercuric salts can be used in a small filter.

The electrolyte, 25% w/w sulphuric acid (3.4 molal) was chosen on the basis of experience, to maintain water balance in the sensor during operation in ambient air with variable humidity.

The NO_2 and NO instruments were zeroed with "Zero Grade 1.0 Air" from Airco Industrial Gases (<1.0 ppm CO, <0.1 ppm NO) which was first passed through activated carbon and alumina to remove traces of NO. All measurements were made at a constant gas flow-rate through the sensor, usually 700 ml/min. The signals (currents) were read on panel meters calibrated directly in ppm NO or ppm NO_2 and also displayed on a Hewlett-Packard Model 680 recorder. The actual currents were measured at the electrochemical sensor (*i.e.*, before amplification) by determining the potential drop across a precision resistor.

The relationship between sensor signal and concentration was checked in two ways. Reference gases of NO in nitrogen and NO_2 in air were obtained from Airco Industrial Gases. These gases and various dilutions with ultra high-purity nitrogen and "zero grade" air, respectively, were drawn into the instrument from 12-l. bags made of polyester-coated aluminium (3M Corporation). Nitrogen was used as the diluent for NO to preclude reaction with oxygen in the sample bag. Secondly, NO or NO_2 samples were drawn into the instrument after passage through an exponential-dilution flask[11] approximately 1.2-l. in volume, at constant flow-rate. In these experiments the NO_2 samples were generated in an air-stream by a permeation tube (at thermostatically controlled temperature) from Metronics Associates.

The response of the NO_2 instrument to NO and of the NO instrument to NO_2 was investigated, as were responses of both systems to SO_2, CO, *n*-propyl nitrate, nitromethane, aniline, nitrobenzene and ammonia. SO_2 and CO/air mixtures were obtained from Airco Industrial Gases and Matheson Gas Products Co., respectively. Samples of the organic compounds were conveniently prepared by collection of the vapour above several ml of pure liquid placed in a large flask, and the ammonia sample was collected from above an aqueous ammonia solution.

RESULTS AND DISCUSSION

Instrument signals

When nitric oxide was introduced into the instrument it was rapidly oxidized according to the equation

$$NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e \qquad (1)$$

which was substantiated[10] by the observation that NO, NO_2^-, and NO_2 are all readily oxidized at 1.5 V. The current generated by the reaction reached a steady-state value, i_l, of approximately 11 μA/ppm NO.

When nitrogen dioxide was introduced into the appropriate intake port it was reduced:

$$NO_2 + 2H^+ + 2e \rightarrow NO + H_2O \qquad (2)$$

as evidenced[10] by the rapid reduction of NO_2^- and the unreactivity of NO. The current due to the electro-reduction process reached a steady-state value which was approximately equal to $-12\,\mu$A/ppm NO_2.

Instrument signals for both gases were reproducible to within $\pm 1\%$ in successive trials.

Signal/time behaviour

A sensing system with a first-order response can be described by the following equation

$$\frac{di}{dt} = k(i_l - i) \qquad (3)$$

where i is the instantaneous instrument signal at time t, k is the first-order response coefficient, and i_l corresponds to the signal which would obtain at steady state for the instantaneous concentration, n, of reactive gas in the sensor. For the systems described in this paper,

$$i_l = \alpha n \qquad (4)$$

where α is a constant of proportionality and is usually given in μA/ppm.

In the simplest case the sensor is suddenly subjected to a constant concentration of reactive gas, n_0, for which $i = 0$ at $t = 0$. In this instance

$$\ln\left(1 - \frac{i}{\alpha n_0}\right) = \ln\left(1 - \frac{i}{i_l}\right) = -kt \qquad (5)$$

Similarly, if at $t = 0$ the sensor is at steady state with concentration n_0 passing and then the active gas source is removed (*i.e.*, $t = 0$, $i = i_l = \alpha n_0$)

$$\ln\left(\frac{i}{i_l}\right) = \ln\left(\frac{i}{\alpha n_0}\right) = -kt \qquad (6)$$

The response/time curves for 5.8 ppm NO on signal rise and fall followed equations (5) and (6), respectively. The plots had nearly identical slopes from which the first-order response coefficient $k = 0.51\ \text{sec}^{-1}$ was derived. Approximately 6.6 sec was required for attainment of $0.95i_l$ (rise) and for relaxation to $0.05i_l$ (fall). Neither line extrapolated precisely back to the origin because there was a small lag time (< 1 sec) required at 700 ml/min flow-rate to flush the 5–10-ml volume of the tubing in the system before the sensor.

On the corresponding first-order plots for 4.2 ppm NO_2, both the rise to $0.95i_l$ and the decay back to $0.05i_l$ on admission and removal of the sample gas occurred in 48 sec, which amounts to $k = 0.062\ \text{sec}^{-1}$.

First-order rise and decay had been observed for electro-oxidation of CO,[7] whereas H_2S oxidation signals rose and decayed according to second-order kinetics.[9]

Instrument signal as a function of concentration

Eight concentrations of NO_2 in air in the range 0–4.2 ppm were passed into the NO_2 detector. Seven samples were prepared by dilution of a 4.2-ppm reference gas with "zero" air. The other sample, 3.1-ppm, was obtained from the permeation tube. Least-squares analysis of reduction current *vs.* ppm NO_2 yielded a straight line with a slope of -12.5 μA/ppm NO_2. The standard deviation of the data points from the line was 0.072 ppm NO_2, a portion of which reflects the uncertainty of gas mixing.

The signal/concentration relationship was also linear as determined from eleven gas mixtures from 0 to 39 ppm NO. The slope of the least-squares line was 11.5 μA/ppm and the standard deviation of the points from the line was 0.51 ppm NO. It is important to note that the value of the standard deviation is dependent on the highest concentration tested. In addition, the instrument panel meter was set at 70% full scale for 1410 ppm NO. Two gas samples containing 466 and 39 ppm of NO then gave readings of 22.5 and ~2% of full scale respectively.

Another method available for characterization of the signal/concentration relationship involves the use of an exponential-dilution flask.[12] After establishment of a constant concentration, n_0, of the reactive gas in the flask of volume V, dilution is begun at time zero with air or nitrogen at flow-rate G. With perfect differential mixing the concentration of NO or NO_2 leaving the flask and entering the instrument is given by

$$n = n_0 \exp(-\beta t) \qquad (7)$$

where $\beta = G/V$.

The exponential flask, in conjunction with a gas analyser, is useful for measurement of response to a continuously varying gas concentration. However, certain precautions need to be taken regarding interpretation of the results. The shape of the detector-response/time curve when sampling the dilution-flask effluent is influenced both by the rate of dilution (β) and by the instrument response constant (k). To demonstrate this point consider a system which (*a*) at $t = 0$ is sampling a constant NO or NO_2 concentration, (*b*) has a first-order instrument-response, and (*c*) has i_t and n related by equation (4). Substitution of equations (4) and (7) into (3) gives

$$\frac{di}{dt} + ki = k\alpha n_0 e^{-\beta t} \qquad (8)$$

With initial conditions $t = 0$, $i = \alpha n_0$, the solution of equation (8) is

$$i = \frac{\alpha n_0}{(k - \beta)} [k \exp(-\beta t) - \beta \exp(-kt)] \qquad (9)$$

The two limiting cases for equation (9) are:

$$(1)\ k \gg \beta : i = \alpha n_0 e^{-\beta t} \qquad (10)$$

$$(2)\ k \ll \beta : i = \alpha n_0 e^{-kt} \qquad (11)$$

In case (1), the instrument response is so rapid that the slope of the ln i *vs.* t plot equals β. In case (2), gas dilution is rapid compared with the instrument response, and therefore, the experimental slope corresponds to an assessment of the instrument response constant, k.

For cases in which $k \sim 10\beta$, for example, at times not too near zero, equation (9) can be approximated to

$$i = \frac{\alpha n_0 k \exp(-\beta t)}{(k - \beta)} \qquad (12)$$

Comparison of equations (10) and (12) reveals that the measured signal for the dilution-flask effluent will read higher by a factor of $k/(k - \beta)$ than is predicted by exponential-dilution theory *per se*. Nonetheless, the slope of the ln i *vs.* t plot will eventually equal β at some $t \gg 0$, provided that $k > \beta$.

Dilution tests were carried out for initial NO_2 concentrations of 3.08 and 0.77 ppm. The gas concentrations at the end of the runs were 45 and 11 ppM (parts per milliard), respectively. Background signal fluctuations with no NO_2 passing were equivalent to only ±2–3 ppM (peak to peak). The flask volume V was ~1200 ml and the gas flow-rate G was 650 ml/min which gave a theoretical β of 0.0090 sec^{-1}. Uncertainties were about ±25 ml/min for flow-rate and about ±50 ml for the effective flask volume. As predicted by equation (9), there was curvature of the plots for $t < 30$ sec ($k \sim 7\beta$). At longer times the plots became linear with slopes of 0.0087 sec^{-1} and 0.0083 sec^{-1}, respectively.

Dilution-flask measurements for two starting concentrations (466 and 5.8 ppm NO) were made at $G = 700$ ml/min. Background current fluctuations contributed an uncertainty of ±3 ppM NO. In this instance the slopes of the plots (0.010 and 0.0098 sec^{-1}) were in better agreement with $\beta = 0.0097$ sec^{-1}, probably because $k \sim 53\beta$ for NO.

The present results demonstrate, within experimental uncertainty, a linear relationship between signal and concentration for NO_2 and NO.

Specificity of instrument response

The extent of interference from common air pollutants with typical NO and NO_2 detection systems is indicated in Table 1. It was shown recently that commercial chemiluminescence NO_2-analysers respond nearly quantitatively to certain other nitrogen compounds.[13] By way of comparison, ammonia, n-propyl nitrate, nitromethane, nitrobenzene and aniline were essentially inert in the present electrochemical NO and NO_2 instruments, even at levels many orders of magnitude greater than ever exist in ambient air (Table 1). Moreover, carbon dioxide and water vapour, which cause significant negative interferences in chemiluminescence detection of NO,[14] do not alter the NO or NO_2 signals obtained with the electrochemical analyser.

Table 1. Response of NO and NO_2 measuring systems to various substances

	NO system		NO_2 system	
Interferent gas	Concentration tested, *ppm*	Concentration required to give signal equivalent to 1.0 *ppm* NO, *ppm*	Concentration tested, *ppm*	Concentration required to give signal equivalent to 1.0 *ppm* NO_2, *ppm*
SO_2	2150	No signal	20	No signal
NO	—	—	466	No signal
NO_2	25	No signal	—	—
CO	900	3000	900	1000
n-propylnitrate	2.6×10^4	$>2 \times 10^5$	2.6×10^4	$>2 \times 10^5$
nitromethane	4.0×10^4	$>2 \times 10^5$	4.0×10^4	$>2 \times 10^5$
aniline	520	30,000	520	No signal
ammonia	7300	No signal	7300	No signal
nitrobenzene	290	No signal	290	No signal

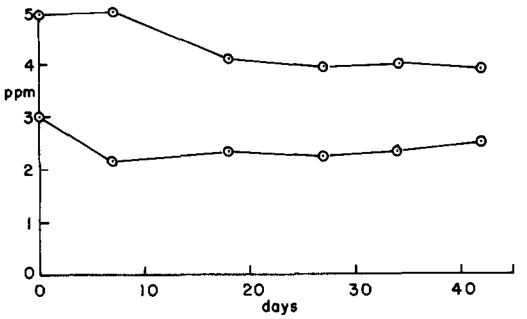

Fig 1. Long-term signal stability. Upper: ppm NO indicated on meter *vs.* time (days) since last calibration. Lower: ppm NO_2 indicated on meter *vs.* time (days) since last calibration.

Twelve-hour zero drift

This parameter has been defined[15] as the difference, expressed in ppm, between the maximum and minimum instrument signal during twelve consecutive hours, with "zero" air passing through the analyser. It is a mandatory test in the certification of automated analysers for certain pollutant gases.[15] Recorder traces showed twelve-hour zero drifts of 0.008 ppm for NO_2 and 0.06 ppm for NO.

Long-term signal stability

An NO/NO_2 instrument was calibrated and then permitted to run continuously on laboratory air for six weeks without recalibration. At weekly intervals meter readings were taken with 5-ppm NO and 3-ppm NO_2 samples. The variation of meter reading with time is shown in Fig. 1. These results, together with the zero drift data, demonstrate that the instrument gives reliable quantitative responses to NO and NO_2 after lengthy periods of non-exposure to these gases, without the need for frequent calibration.

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ANALYSIS OF TUNGSTEN CARBIDES BY X-RAY FLUORESCENCE SPECTROMETRY

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Summary—Five sample presentation techniques were examined for the X-ray fluorescence spectrometric analysis of tungsten carbide alloys in powder and cemented forms. Powder samples may be oxidized by air at 600° before fusion (I), or preferably by lithium nitrate during fusion (II); the fusion is effected with lithium–lanthanum tetraborate followed by briquetting with graphite. Powder samples may also be blended with wax and briquetted (III). Cemented carbides are surface-prepared with silicon carbide before analysis (V). Briquettes prepared by blending carbide powder, lithium–lanthanum tetraborate and graphite (IV), give poor reproducibility, however, owing to micro-absorption effects the technique is not recommended. The determination of eight common elements in tungsten carbide is discussed and the relative standard deviations are 0.002–0.004 for major and 0.008–0.01 for minor elements.

The analysis of tungsten carbides (WC) by optical emission spectrometry (OES), the manufacturing process, the cost benefits of composition control, the preparation of standard samples and a literature survey have been discussed previously.[1]

X-Ray fluorescence spectrometry (XRF) of cemented hard metals or briquetted pre-sintered products affords a convenient method for the precise determination of tungsten, tantalum and niobium and is also suitable for titanium and cobalt, the other major alloying elements. Accordingly, tungsten carbides have been analysed by XRF, using the following sample preparation techniques: solutions,[2] prior oxidation and fusion with borates, incorporation of barium as a heavy element absorber,[3,4] pressure-compacted powders[5] and cemented hard metals.[6,7]

The objectives of the present work were: to develop flexible multi-element XRF methods which could be applied to unknown samples; to achieve the standardization of a suite of powdered and cemented reference standard samples for the direct analyses of intermediate and final products; to evaluate sample preparation and presentation methods compatible with point-to-plane OES techniques.[1] Five sample preparation/surface treatment techniques were examined: prior (I) or *in situ* (II) fusion conversion, of carbides into oxides, fusion with lithium–lanthanum tetraborate, blending with graphite and compaction to a briquette; blending of powdered carbides with wax (III) or powdered lithium–lanthanum tetraborate and graphite (IV) and compaction to a briquette; and sintered solids (V) with diamond or silicon carbide grit polishing.

EXPERIMENTAL

Apparatus

Spectrometer, Siemens automatic vacuum path SRS-1; generator, 4 kW Kristallflex IV; X-ray tubes, Cr 2.6 kW or Mo 3 kW; sample holders, sintered carbon, rotated during irradiation; crystals, LiF_{220} and Ge_{111}; collimator, 0.15°; detectors, gas flow proportional 90% Ar–10% CH_4 (Dz) or scintillation, Tl–NaI (Sz).

Table 1. X-ray fluorescence spectrometric measurement conditions

Element	Method	Line	Crystal	X-Ray tube	Detector
Nb	all (I–V)	K_α	LiF_{220}	Mo	Sz
Ta	all (I–V)	L_{α_1}	LiF_{220}	Mo	Sz
Ni	all (I–V)	K_α	LiF_{220}	Mo	Dz
Co	all (I–V)	K_α	LiF_{220}	Mo	Dz
Fe	all (I–V)	K_α	LiF_{220}	Mo	Dz
V	all (I–V)	K_α	LiF_{220}	Mo	Dz
W	fusion (I & II)	L_{α_1}	LiF_{220}	Mo	Sz
Ti	fusion (I & II)	K_α	Ge_{111}	Cr	Dz
W	unfused (III & IV) &	L_{β_2}	LiF_{220}	Mo	Sz
Ti	cemented (V)	K_{β_1}	LiF_{220}	Mo	Dz

Measurement conditions

Measurements terminated at a time (40–200 sec) adequate to accumulate counts sufficient for the required precision, using the conditions set out in Table 1.

Reagents

Graphite powder, briquetting grade; lithium nitrate, anhydrous; fusion mixture ($<500\ \mu$m) (64% lithium tetraborate–36% lanthanum tetraborate); cold-bonding paraffin wax powder; Johnson Matthey spectrographically pure oxides heated at 600–900° immediately before use.

Recommended procedures

Fusion briquettes. Hand-crush solid or chip carbides to 500 μm in a tungsten carbide mortar and further crush to $<125\ \mu$m in a 10-cm^3 tungsten carbide grinding barrel on a "Siebetechnik" vibratory disc mill.

Grind tungstic oxides to $<63\ \mu$m in a tungsten carbide grinding barrel and dry at 110°; prior oxidation of carbides can be achieved if desired by heating in air at 600° for 30 min. Weigh 100 mg (I) ($<63\ \mu$m oxide) or 85 mg (II) ($<125\ \mu$m carbide) into a 95/5% Pt/Au crucible containing 2 g of fusion mixture and 500 mg of lithium nitrate and mix with a platinum wire; also prepare calibration standards from appropriate pure oxides. Oxidize carbide samples *in situ* by heating from 400° to 800° (7°/min). Fuse all samples at 980° for 10 min. Cool, recover the fused bead, weigh and add graphite powder (1.5 × recovered bead weight). Mill the fusion bead and graphite powder for 3 min in a 100-cm^3 tungsten carbide grinding barrel. Press the milled powder to a 25 mm diam. briquette at 900 kg/cm^2 for 20 sec. Prepare a fresh surface for irradiation by rubbing on P600 grit SiC abrasive paper by hand.

Wax-bonded carbides (III). Weigh 5 g of carbide powder samples ($<10\ \mu$m) or analysed calibration standards into a phial containing 50 mg of cold-bonding paraffin powder and place on a high-speed mixer for 1 min. Add 5 g of boric acid to a press (25 mm ram) to form a backing, add the carbide–wax mixture and press at 5000 kg/cm^2 for 20 sec.

Cemented hard metals (V). Machine-brush on 60 grit silicon carbide abrasive discs. Use a fresh disc for each re-preparation.

Assays are referred to appropriate fused, wax-bonded or cemented solid calibration standards, using synthetic oxide, or powdered and cemented carbide primary standards as described previously.[1]

RESULTS AND DISCUSSION

The preparation, testing and standardization of a suite of powdered and cemented carbides has been discussed by the authors.[1] Other matters discussed were the possibility of elemental inhomogeneity, surface preparation techniques for cemented solid carbides and oxidation and fusion techniques for powdered oxides and carbides.

Klyachko and Yakovleva[8] state that tungsten losses are significant when tungstic oxide is heated at 900°, whereas 3-hr ignition tests at 750° (Gabler and Peterson[9]) showed that losses are confined to volatile elements, notably molybdenum, lead and tin. Blaas *et al.*[3] have advocated oxidation of carbide samples at 450° and this low temperature has particular application to the analysis of samples containing molybdenum. A study has been made of potential losses due to high-temperature oxidation; the oxidation of WC powders was necessary so that standardization analyses could be done against synthetic oxide standards.

Isothermal weight-change studies as a function of time were carried out by heating in air a 1-g ($<125\ \mu$m) sample (60% W, 11% Ti, 8% Ta, 1% Nb as carbides + 13% Co). Maximum weight increase was achieved in 15 min at temperatures in the range 600°–900° (100° intervals) and was in accordance with stoichiometric oxide formation and elimination of carbon; the stoichiometry of the conversion was not of great significance in view of the known uncertainty in the state of oxidation of ignited cobalt oxide. At 450° oxidation was only 50% complete in 45 min, and after 3.5 hr the sample still contained 0.8% residual carbon. Accordingly a 30-min oxidation at 600° was incorporated in the recommended procedure.

The fused oxide/briquette techniques described in the recommended procedure derive from the work of Hasler[10] and subsequent developments.[1,11–13] The present work required an assessment of the potentialities of the fusion/briquette techniques and the standardization of the prepared samples. Accordingly, 6 calibration mixtures were prepared from pure materials and fused and briquetted to cover the ranges: WO_3, 20–95%; TiO_2, 0–20%; Co_3O_4, Ta_2O_5, 0–15%; MoO_3, Fe_2O_3, SiO_2, Al_2O_3, 0–5%; Nb_2O_5, Mn_3O_4, 0–2%, and 20 other oxides, including V_2O_5, $<1\%$. For major elements, the incremental additions were randomized between the various mixtures and bore no relationship to the carbide compositions being analysed. The concentration ranges of Fe_2O_3, SiO_2, Al_2O_3, Mn_3O_4 are not relevant to the analysis of hard metals but were added because a variety of oxide products and residues are analysed by the same technique and it was desired to use a flexible, wide-ranging system to reveal interelement effects. A further 6 calibration standard briquettes were prepared to approximate to the composition of the 6 standard carbide samples after oxidation.

With flux/sample ratio of 21/1 and lanthanum oxide/sample ratio of 3.15/1, matrix effects were found to be negligible. The fusion briquette composition represents both increased dilution and lanthanum concentration as compared with the concentrations recommended by Norrish and Hutton.[11] However the freedom from interference effects is considered to justify the lower X-ray intensities, because results are obtained without the use of extensive computations. The further availability of the briquettes for optical emission measurements is of great benefit.[1]

Calibration graphs were linear for the elements measured and correlation coefficients and lower limits of detection are given in Table 2. The lower limits of detection, calculated as the equivalent of three standard deviations of the background, are adequate for present purposes. With this system a notable spectral interference is TiK_α with VK_α; however, measurement of the apparent VK_α/TiK_α ratio in vanadium-free standards provided a correction factor which was applied successfully to the VK_α count-rate for calib-

Table 2. Calibration data for the fusion briquette procedures (I and II)

Element	Range % (nominal)	Sensitivity *cps/1% element*	Background *equivalent* *% element*	Lower limit of detection* %	Correlation coefficient
W	20–80	32	0.91	0.04	0.9999
Ta	0–15	35	0.81	0.03	0.9990
Ti	0–15	740	0.07	0.002	0.9990
Co	0–15	52	0.60	0.02	0.9999
Fe	0–5	36	1.28	0.03	0.9986
Nb	0–2	200	1.02	0.01	0.9992
V	0–1	90	0.26	0.01	0.9979
Ni	0–1	52	0.60	0.02	0.9999

* Calculated as 3 standard deviations of background

ration standards and assays. With the measurement conditions used, 1% TiO_2 produced an interference equivalent to 0.024% V_2O_5 and a standard deviation of 0.008% was obtained at the 0.2% V_2O_5 level.

The 6 standard carbide powders were analysed by the proposed fusion techniques (I, II), supported by atomic-absorption spectrophotometry for trace elements, gravimetric techniques for carbon, absorbed water and oxygen, and by optical emission spectrometry for a range of trace elements. Summation of the results obtained (complete analyses) on the 6 powdered samples had a mean value of 99.8%, which is considered satisfactory.

Previous OES studies had been made of *in situ* oxidation–fusion of tungsten carbide powders as compared to air-oxidation followed by fusion.[1] However, the greater precision of measurement available with XRF necessitated an extensive study. The *in situ* oxidation–fusion technique involves a preheating and fusion cycle as compared to a simple fusion; however, a double weighing procedure and potential loss of volatile elements is avoided and calculations are reduced. A comparative set of results is presented in Table 3 and an oxidation temperature of 800° was used to accentuate possible losses.

Inspection of the data and application of statistical tests indicate that losses of tungsten oxide must be insignificant at temperatures below 800° and that the techniques give equivalent results. The temperature recommended for air-oxidation however is a conservative 600° and the *in situ* oxidation is in general the preferred technique and allows better precision for tungsten assays.

The standardized analytical data on the powdered carbide materials together with the subsidiary determinations indicated previously, allow the ready calculation of the compositions of the derived cemented products. Both the pre-sintered powders (III) and the cemented products (V) were examined directly by XRF, and calibration graphs were obtained for all major and trace elements.

Predictable interelement absorption effects were noted for pre-sintered and cemented carbides; however for practical analysis the usual matrix matching of calibration standard samples to assays, or correction techniques, would be appropriate. Absorption in-

Table 3. Comparison of prior and *in situ* oxidation procedures (Sample No. SW9)

Element		Nb	W	Ta	Co	Ti
prior	$\bar{x}$, %	0.64	72.08	5.19	6.46	7.44
oxidation (I)	1 s ($n = 4$), %	0.005	0.17	0.01	0.01	0.03
in situ	$\bar{x}$, %	0.64	71.98	5.16	6.45	7.46
oxidation (II)	1 s ($n = 4$), %	0.008	0.11	0.02	0.02	0.03

(s = standard deviation).

Table 4. Reproducibility data (1 s, $n = 4$) for direct carbide analysis methods [sample No. SW5 (powder)/SW6 (cemented)]

Method	Nb	W	Ta	Ni	Co	Fe	Ti
Carbide powder briquetted with graphite and flux (unfused) (IV) %	0.016	0.11	0.03	0.036	0.04	0.064	0.07
Carbide powder, wax-bonded (III) %	0.004	0.08	0.02	0.001	0.02	0.002	0.03
Cemented carbide, SiC-polished (V) %	0.004	0.10	0.02	0.001	0.05	0.002	0.02
Cemented carbide, diamond-polished (V) %	0.003	0.08	0.01	0.001	0.03	0.003	0.04
Calibration result, %	1.22	55.4	10.8	0.07	10.3	0.33	15.1

* Not recommended for use.

terferences particularly noted were Co with Ta/W, and Ti with Co; spectral interferences were much less extensive than those observed in OES with the same system.[1] Calibration curves were of the same form for sets of wax-bonded pre-sintered carbides, and SiC- or diamond-polished cemented carbides; no advantage is derived from diamond-polishing.

An attempt was made to reduce absorption effects with the direct analysis of pre-sintered carbide powders; the powdered carbides were diluted with lanthanum–lithium tetraborate and graphite (IV) which is analogous to the dilution-buffer process in the oxidation–fusion work. However, matrix effects were not eliminated, as evidenced by deviations from calibration graphs. The associated poorer precision experienced can be attributed to the non-intimate mixing of the lanthanum and carbide particles and accordingly the simple wax-bonded procedure is to be preferred.

Reproducibility data for these different techniques are presented in Table 4.

The work presented demonstrates that accurate results for major element determinations in tungsten carbides can be obtained by XRF with briquettes which have been prepared by fusion. The direct XRF analysis of pre-sintered carbide powders or cemented products was demonstrated by at least one satisfactory technique; however, interelement absorption effects of the type common in XRF militate against simple calibration procedures and in situations where the precision of measurement is acceptable, OES may be a preferred technique.[1] The proposed methods are suitable for the complete composition control of a tungsten carbide manufacturing plant and similar standard deviations are observed for all the recommended techniques.

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USE OF SULPHIDE PRECIPITATION IN SEPARATION AND DETERMINATION OF MOLYBDENUM(V)

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Summary—Molybdenum(V) is quantitatively precipitated as sulphide ($\geq 99.7\%$) from $0.1M$ hydrochloric acid without formation of molybdenum blue and without need for a long digestion. Precipitation is more complete and co-precipitation less than with Mo(VI) sulphide. The precipitate can also be used directly for gravimetric estimation. In the presence of EDTA, molybdenum(V) sulphide is not precipitated from $0.1M$ hydrochloric acid and can be separated from copper, bismuth, antimony and tin sulphides and determined cerimetrically in presence of the EDTA.

Molybdenum is often precipitated as sulphide to separate it from elements[1a] forming acid-soluble sulphides. Complete precipitation is difficult from hydrochloric acid medium,[1a] and there is partial reduction to molybdenum blue,[2a] a milligram of molybdenum or more escaping the first precipitation. The precipitate, filterable only after long digestion, is contaminated by elemental sulphur[3a] and appreciable amounts of other elements, especially tungsten, vanadium and iron, present in the solution.[1a,2b,4a] Separation from other elements forming acid-insoluble sulphides is not possible. Other sulphide reagents have not found wide acceptance because of similar disadvantages or cost. Molybdenum in lower oxidation states is reported to give incomplete precipitation.[2a]

The precipitate cannot be used directly for gravimetric determination.[2c] Conversion into the oxide is unattractive because of sublimation losses, slowness of conversion and the unfavourable factor.[2c] The sulphide or oxide is often converted into molybdate and determined by the lead molybdate method, which is accurate only under rigorous conditions, is tedious and suffers interference from sulphate[5a] and many elements, especially iron, chromium, tungsten and vanadium. The oxine method is more suitable for semimicro amounts but titanium, vanadium, tungsten and uranium interfere even when complexed with EDTA.[5a]

Obviously, precipitation of molybdenum sulphide would be much more useful if the precipitate had constant composition and were suitable for direct determination. We have found that Mo(V) sulphide can be precipitated quantitatively from dilute acid solutions and not at all on complexation with EDTA,[2d] with possible uses for separation and determination of molybdenum, as described below.

EXPERIMENTAL

Reagents

Molybdenum solution. Sodium molybdate dihydrate was dissolved in water to give a stock solution containing 10 mg of Mo/ml. This was standardized by the cerimetric[6a] or the oxine method,[5a] and diluted to give concentrations of 500, 100 and 10 μg/ml.

Solutions of other elements. Prepared by dissolving suitable salts in water or dilute hydrochloric acid to give concentrations of 10 or 20 mg/ml.

Procedures

Precipitation of molybdenum(V) sulphide. A solution containing 5–100 mg of molybdenum was made $2M$ in hydrochloric acid and 10–15 ml in volume, boiled with 200 mg of hydrazine sulphate for 3–4 min in a covered beaker with frequent stirring, and diluted to $0.1N$ acidity. The solution was heated to about 90° and a rapid stream of hydrogen sulphide passed from a Kipp's apparatus for 15 min. The solution was reheated to about 90° and the precipitate immediately filtered off on a porosity-4 sintered-glass crucible and washed with four 5-ml portions of hot $0.1M$ hydrochloric acid saturated with hydrogen sulphide.

The filtrate was boiled free from hydrogen sulphide, then made just alkaline with sodium hydroxide and boiled with 5 ml of 6% hydrogen peroxide, then evaporated to 10–15 ml and subjected to the procedure above to recover the residual molybdenum ($< 0.3\%$). The precipitate was dried at $100 \pm 2°$ *in vacuo* for 1 hr, then cooled in a dry oxygen-free carbon dioxide atmosphere for 15 min (the vacuum being released slowly to avoid "blowing off" of the precipitate) and weighed quickly.

Separation from other elements by precipitation of molybdenum(V) sulphide. Solutions of molybdenum(VI) and either tungsten(VI), uranium(VI), vanadium(V), iron(III), nickel(II) or cobalt(II) were treated by the procedure above. Tartaric acid (3–4 g) was added to mask tungsten. Studies were made on co-precipitation of these elements, present in various ratios to molybdenum (Table 1). Each precipitate was washed 8 times with a total of 25 ml of hot $0.1M$ hydrochloric acid saturated with hydrogen sulphide.

Separation of other elements, by their precipitation as sulphides, from molybdenum(V) masked with EDTA. Solutions containing 20 mg of molybdenum and 10 mg of copper(II), bismuth(III), arsenic(III), antimony(III), tin(II), platinum(IV) or palladium(II), were adjusted to be $2M$ in hydrochloric acid and 10 ml in volume, boiled with 15 mg of hydrazine sulphate for 3–4 min in a covered beaker with frequent stirring, diluted 20-fold and heated to boiling again after addition of 150 mg of EDTA. The precipitation was then done as before. The amounts of hydrazine sulphate and EDTA were proportionately adjusted for other quantities of molybdenum.

Traces of bismuth, tin and arsenic were separated by adding 10 mg of a collector [copper(II) for bismuth; antimony(III) for tin or arsenic] and precipitating as just described.

Ferromolybdenum analysis. Finely powdered sample (0.1 g) was dissolved by gentle warming with 3 ml of concentrated hydrochloric acid and 1 ml of concentrated nitric acid. Nitrate was destroyed by careful addition of solid hydrazine. Any molybdenum blue was oxidized by bromine, the excess of which was boiled off. The solution was neutralized with sodium hydroxide and adjusted to be 2*M* in hydrochloric acid in 10–15 ml volume. The molybdenum was then precipitated.

Determination of elements. Milligram amounts of molybdenum were determined by the oxinate method[5a] or, in presence of EDTA, by cerimetric titration;[6a] microgram quantities were determined by the thiocyanate method.[7]

For determination of elements adsorbed on molybdenum(V) sulphide, the precipitate was dissolved in some water plus 8 ml of concentrated nitric acid, the solution was heated almost to dryness, and nitrate was destroyed by repeated heating to dryness with concentrated hydrochloric acid (3 ml each time). Any molybdenum blue formed was oxidized with bromine. The solution was neutralized with sodium hydroxide. Molybdenum was quantitatively extracted as molybdenum(V) xanthate[8] when tungsten was present, and as the molybdenum thiosulphato-complex[9] when vanadium, uranium, nickel, cobalt or iron was present. After oxidation of the xanthate or thiosulphate in the aqueous phase, the elements were determined by sensitive standard methods.

The molybdenum adsorbed on antimony, copper, bismuth and tin sulphide was determined by the thiocyanate method,[10] after dissolution of the precipitates as above.

RESULTS AND DISCUSSION

Molybdenum(VI) sulphide is precipitated more completely ($\sim 98.5\%$)[4a] from sulphuric acid than from other media. Molybdenum(V) also forms an insoluble sulphide[11] but this has not been investigated for analytical use. Molybdenum(V) obtained by reduction with hydrazine sulphate[6b] in 2*M* hydrochloric acid is quantitatively precipitated by passage of a rapid stream of hydrogen sulphide for 15 min into the solution (acidity 0.1*N*) at 90°. Less complete precipitation is obtained at lower temperature and with a shorter time of passage of the gas. Sulphuric acid medium is equally suitable. The precipitation decreases slightly as the acidity is increased (Fig. 1, curve A). More than 99.7% of the molybdenum is precipitated from 0.05–0.1*M* hydrochloric acid. The precipitate formed in $>0.05M$ hydrochloric acid is easily collected on a G-4 sintered-glass crucible, without need for aging. The precipitation is quantitative for molybdenum concentrations of 0.005–0.5 mg/ml under optimum conditions, though slightly lower at <0.01 mg/ml (Fig. 1, curve B). The formation of molybdenum blue is completely avoided as all the molybdenum is already in the quinquevalent state.

The traces of molybdenum in the filtrate can be recovered completely, if desired, by reprecipitation under the same conditions after expelling the hydrogen sulphide, oxidizing with peroxide, evaporating to about 20 ml and reducing with hydrazine to molybdenum(V). Without the reoxidation and reduction, no recovery is possible. Therefore, it seems that the molybdenum is present in the filtrate in the form of thiomolybdates. A collector is not necessary, unlike the case with molybdenum(VI).[12]

The precipitation of molybdenum(VI) sulphide is little affected by the presence of simple or complexing anions.[2a,b,e,4b] With 20 mg of molybdenum in 200 ml of solution, the precipitation of molybdenum(V) sulphide is not affected by 3–4 g of tartaric acid, 2 g of sodium or ammonium chloride and 1 g of sodium acetate or sulphate, but 1 g of sodium fluoride makes the precipitate slimy and the filtration very slow. Sodium citrate or oxalic acid (0.5 g) suppresses the precipitation almost completely and EDTA (0.15 g) does so completely. Oxidants interfere.

Separation from other elements by precipitating molybdenum(V) sulphide

Although quantitative information is not available, molybdenum(VI) sulphide is very much contaminated by iron,[2b] tungsten, vanadium,[1a] tin,[2b] copper,[4a] and perhaps cobalt, nickel, chromium, uranium. Therefore, reprecipitation is the rule. Precipitation from ammoniacal tartrate solution is preferred, but does not avoid contamination from vanadium and tungsten,[1a] without reprecipitation.

Molybdenum(V) belongs to the same qualitative analytical group as molybdenum(VI),[3b] so the same separations from other elements are possible with both. The adsorption of other elements on molybdenum(V) sulphide is shown in Table 1. It varies somewhat with the ratio of molybdenum to the element. Adsorption of tungsten, vanadium, iron and possibly other elements is much less than on molybdenum(VI) sulphide. Hence molybdenum can be separated from vanadium and tungsten even in acidic media, tungsten being kept in solution with tartaric acid. Acceptable accuracy for molybdenum can generally be obtained without reprecipitation (see Table 4).

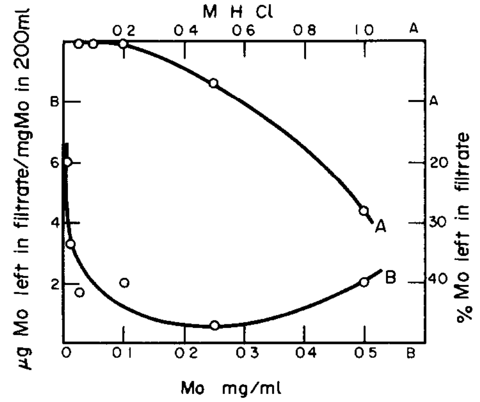

Fig. 1. Dependence of Mo(V) sulphide precipitation on HCl and Mo concentrations. A—Mo 0.1 mg/ml; B—0.1*M* HCl.

Table 1. Adsorption of elements on molybdenum(V) sulphide

Mo taken, *mg*	Element taken, *mg*	Weight adsorbed, *μg* W	V	Fe	Co	Ni	U
10	70	8	2	4	21	20	13
10	10	76	9	25	88	63	88
20	10	24	12	0*	—	—	28
70	10	126	141	77	294	301	441

* Significant for analysis of ferromolybdenum.
— Not determined.

Table 3. Adsorption of molybdenum(V) on sulphides of different elements in presence of EDTA

Mo taken, *mg*	Element taken, *mg*	Weight adsorbed, *μg* Cu	Bi	Sb	Sn
10	70	868	53	—*	—
10	40	—	—	—	216
20	10	38	13	8	0
40	10	—	—	—	21
70	10	5	3	3	—

* Hydrolysis takes place.

Separation from elements of the acid sulphide group by precipitation of the sulphides, masking molybdenum(V) with EDTA

Molybdenum(VI) cannot be separated from copper, bismuth, antimony, arsenic and tin by sulphide precipitation, as they are all precipitated, even in presence of the usual complexing anions.[1b] For separation other methods must be used,[1c,2b,5b] after precipitation of the sulphides, but these methods are tedious and give unsatisfactory results.

If complexed with EDTA, however, molybdenum(V) is not precipitated as sulphide from 0.2*M* hydrochloric acid or at pH 9, whereas antimony, bismuth, copper and tin, in their usual oxidation states after the hydrazine reduction, are precipitated quantitatively or nearly so (Table 2). However, at least 10 mg of these elements should be present in 200 ml, if necessary by addition; otherwise, precipitation is less quantitative. Traces of bismuth and tin in the filtrate can be collected by using 10 mg of copper(II) and antimony(III) respectively. Excess of hydrazine has little effect except on tin. More than 150 mg of EDTA in excess leads to incomplete precipitation of these elements. Arsenic is > 95% precipitated, but about 2% still remains unrecovered even after use of Sb(III) as collector for the traces left in the filtrate. Cadmium and lead are precipitated only in traces. When molybdenum is present with these elements, the sulphide precipitates adsorb traces of molybdenum (Table 3), but a single reprecipitation, if thought necessary, gives acceptable separation of molybdenum from these elements, though in the case of copper a reprecipitation is not so useful. When the ratio of molybdenum to tin is 4:1, the tin precipitate should be allowed to stand for 1 hr at 90° before filtration. At higher ratios, quantitative precipitation of tin is not possible.

Gravimetric determination of molybdenum(V) as sulphide

Molybdenum(VI) sulphide tends to be heavily contaminated by sulphur and other elements such as iron, tungsten and vanadium, which are usually present in molybdenum materials. Ignition to the oxide deals only with the sulphur problem, but is still not attractive because of the long time needed,[1a] losses due to volatilization and the poorer conversion factor. These drawbacks do not apply to molybdenum sulphide, which can be weighed as such. Further, the precipitation is 99.7–99.8% complete. The conversion factor is 0.475, corresponding to $Mo_2S_5 \cdot 3H_2O$. Alcohol, acetone, and ether cannot be used for washing the precipitate, because of its slight solubility in these solvents. For drying, the temperature should not be more than 120°, and the time less than 1 hr. Several samples, including ferromolybdenum, were analysed for molybdenum by this method, with satisfactory results (Tables 4 and 5). As the adsorption of iron, vanadium and tungsten is only about 0.2% even at high concentrations of molybdenum, the method can be used with acceptable error for samples containing

Table 2. Precipitation of some elements as sulphides after hydrazine reduction and EDTA complexation (element = 0.05 mg/ml; acidity = 0.1*M* HCl)

Element	Precipitation, % *A*	*B*	*C*
Sb(III)	100.0	100.0	100.0
Cu(II)	100.0	100.0	99.8
Bi(III)	99.8	99.6	99.4
Sn(II)	99.4	—	nil
As(III)	95.8	—	95.0
Pt(IV)	99.6	—	94.3
Pd(II)	97.0	91.0	50.0

Hydrazine sulphate, *A*—10 mg, *B*—50 mg, *C*—500 mg. EDTA, *A*—150 mg; *B*, *C*—500 mg.

Table 4. Analysis of samples by molybdenum(V) sulphide gravimetry

Sample composition Matrix*	Mo added, *mg*	Mo found, *mg*	Error, %
V(10)Co(5)Ni(5)Fe(5)	39.64	39.6	−0.1
Ni(5)Co(5)V(10)	39.99	40.1	+0.5
V(10)Ni(10)	49.55	49.5	−0.1
W(10)Mn(5)U(5)	54.50	54.6	+0.1
U(5)Mn(10)	59.46	59.4	−0.1
Fe(10)Co(10)	69.31	69.3	−0.1
Ferromolybdenum (SL-225) Mo = 58.9%† Cu = 0.25%		59.1‡	+0.4

* Number in brackets gives the amount in mg.
† By oxine method.
‡ Without separation of copper or correction for it.

Table 5. Analysis of molybdenum samples after the sulphide separation in presence of EDTA

Sample composition Matrix*	 Mo added, *mg*	Mo found,† *mg*	Error, %
Cu(10)	70.00	69.7	−0.4
Sb(10)	42.40	42.3	−0.2
Sb(10)	80.00	79.9	−0.1
Bi(10)	74.55	74.4	−0.1
Sn(10)	21.30	21.3	±0.0

* Number in brackets gives the amount in mg.

† After a single precipitation of the element as sulphide and cerimetric titration of Mo(V).

them. When cobalt, nickel and uranium are present, one reprecipitation would be necessary, but the loss of molybdenum must be taken into account.

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SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM IN CONCENTRATES AND BRASSES BY CHLOROFORM EXTRACTION OF THE TELLURIUM (IV) HEXABROMIDE–DIANTIPYRYLMETHANE COMPLEX AFTER SEPARATIONS BY IRON COLLECTION AND XANTHATE EXTRACTION

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Summary—A method for determining 0.0001–0.10% of tellurium in copper, nickel, molybdenum, lead and zinc concentrates is described. After sample decomposition, tellurium is separated from most of the matrix elements by co-precipitation with hydrous ferric oxide from an ammoniacal medium. After reprecipitation of tellurium and iron, the precipitate is dissolved in 12*M* hydrochloric acid, tellurium(VI) is reduced to the quadrivalent state by heating, and separated from iron, lead and other co-precipitated elements by chloroform extraction of its xanthate. The yellow ion-association complex formed between tellurium(IV) hexabromide and diantipyrylmethane is extracted into chloroform from a 2*M* sulphuric acid–0.6*M* potassium bromide medium. The molar absorptivity of the complex is 1.82×10^3 $1.\text{mole}^{-1}.\text{mm}^{-1}$ at 336 nm, the wavelength of maximum absorption. Small amounts of iron, copper and molybdenum are co-extracted as xanthates under the proposed conditions but do not cause error in the result. Interference from antimony, which is co-extracted as the chloro-complex, is eliminated by washing the extract with water. The proposed method is also applicable to brasses.

A current facet of the Canadian Certified Reference Materials Project sponsored by the Canada Centre for Mineral and Energy Technology involves the certification of various sulphide concentrates for both major and trace elements. As part of this project, the author is concerned with the development of methods for determining trace elements in concentrations as low as 1 ppm (10^{-4}%). Information obtained in previous work[1] involving the chloroform extraction of metal ethyl xanthates from hydrochloric acid media suggested the possibility that a single method for determining tellurium, selenium and arsenic might be developed, based on their co-precipitation with hydrous ferric oxide from an ammoniacal medium,[2] followed by their separation from iron by simultaneous extraction as the xanthates into chloroform and subsequent determination by flameless (carbon rod) atomic-absorption spectroscopy. However, this combined approach was ultimately abandoned because of the extremely poor reproducibility obtained for all three of the elements by the flameless technique. Consequently, an investigation was undertaken to develop a suitable spectrophotometric procedure for determining moderate and trace amounts of tellurium alone, based on the separations above, that would be applicable to diverse concentrates.

The most widely used methods for determining tellurium spectrophotometrically are based on the extraction of the diethyldithiocarbamate complex,[3] measurement of the absorbance of the hydrosol formed by reduction of tellurium with stannous chloride,[4] and formation of the thiourea complex.[5,6] The first two of these methods were not considered in the present work because of their low sensitivity and the instability of the complex and the colloidal sol. Tests with thiourea, which was used previously[1] and found to form a stable sensitive complex, showed that this method is subject to interference from selenium(IV) and from small amounts of iron(III) that are co-extracted with tellurium as the xanthate complex. Recently, methods based on the extraction of the ion-association complexes formed between tellurium(IV) hexahalides and pyrazolone or antipyrene derivatives have been reviewed,[7] and a method has been reported in which the tellurium(IV) hexabromide–diantipyrylmethane complex is extracted into dichloroethane.[8] In this method, the absorbance of the extract is measured at 450 nm (molar absorptivity = 4.2×10^2 $1.\text{mole}^{-1}.\text{mm}^{-1}$) although the absorption spectrum of the complex indicates that the molar absorptivity is at least 3–4 times greater at the wavelength of maximum absorption in the near ultraviolet. Preliminary tests using this method, in which absorbance measurements were made at the wavelength of maximum absorption, 336 nm, showed that moderate amounts of iron(III) and selenium(IV) do not interfere in the complex formation. Consequently, diantipyrylmethane was utilized in the present work, which de-

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scribes the successful determination of tellurium in copper, nickel, molybdenum, lead and zinc concentrates and brasses. Interference from copper during the separation of tellurium from iron by chloroform extraction of its xanthate is avoided by prior separation of the tellurium from copper by a double coprecipitation of tellurium with hydrous ferric oxide.

EXPERIMENTAL

Reagents

Standard tellurium solution, 10 *μg/ml.* Dissolve 0.1251 g of tellurium dioxide by heating gently with 25 ml of concentrated nitric acid, cool, and dilute to 500 ml with water. Dilute 10 ml of this stock solution to 200 ml with water. Prepare fresh as needed. (The tellurium dioxide used was found to be pure, by titration with potassium permanganate.)

Diantipyrylmethane, 4*% w/v solution in ethyl alcohol.* Prepare a fresh solution every 7 days (Note 1).

Iron(III) sulphate solution (1 *ml* ≅ 20 *mg of iron*). Dissolve 25 g of ferric sulphate monohydrate in hot water, add 10 ml of 50% v/v sulphuric acid, cool and dilute to 250 ml with water.

Potassium ethyl xanthate, 20*% w/v solution.* Prepare fresh as required.

Potassium bromide, 3*M solution.*

Potassium sulphate, 2.5*% w/v solution.*

Sulphuric acid, 10*M and* 50*% v/v.*

Nitric acid, 50*% v/v.*

Hydrochloric acid, 20*% v/v.*

Ammonia, 5*% v/v.*

Chloroform. Analytical-reagent grade and high-purity (alcohol- and peroxide-free).

Procedures

Calibration curve. Add 2 ml of 2.5% potassium sulphate solution and 2 or 3 drops of 50% sulphuric acid to each of eight 50-ml beakers; then, by burette, add to the last seven beakers 0.5, 1, 2, 3, 4, 5 and 6 ml, respectively, of standard 10 μg/ml tellurium solution. The first beaker contains the blank. Evaporate each solution to dryness or near dryness, cool, wash down the sides of the beaker with a small amount of water and evaporate to dryness again to ensure the removal of nitric acid. Add 5 ml of 10*M* sulphuric acid and 2 or 3 ml of water, heat gently for 2 or 3 min and cool to room temperature in a water-bath.

Transfer each solution to a 60-ml separatory funnel, marked at approximately 25 ml and containing 5 ml of 3*M* potassium bromide. Add 2 ml of 4% diantipyrylmethane solution, dilute the resulting solution to the mark with water, stopper, mix thoroughly and allow the solution to stand for 15 min to complete the complex formation. By pipette, add 10 ml of high-purity chloroform to each funnel, stopper and shake for 2 min. Allow several min for the layers to separate, then drain the chloroform layers into dry 15-ml centrifuge tubes and centrifuge for 1 min (Note 2). Determine the absorbance of the blank and each extract, at 336 nm, against chloroform as the reference solution, using 10-mm cells. Correct the absorbance value obtained for each tellurium bromide–diantipyrylmethane extract by subtracting that obtained for the blank. Plot μg of tellurium *vs.* absorbance.

Concentrates and brasses. Depending on the expected tellurium content and/or the iron content (Note 3), transfer 0.2–1 g of powdered sample, containing not more than ~150 mg of iron, to a 250-ml beaker. Add ~1.5 g of potassium chlorate (Note 4), moisten with a few ml of water, cover and carefully add 15 ml of concentrated nitric acid in small portions. Heat gently until the sample is decomposed, then remove the cover, add 25 ml of 50% sulphuric acid, wash down the sides of the beaker with a small amount of water, and carefully evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool, add ~100 ml of water, 5 ml of concentrated hydrochloric acid, and sufficient iron(III) sulphate solution, if necessary, for at least 80 mg of iron to be present. Cover and heat to dissolve the soluble salts.

Add sufficient concentrated ammonia solution to the resulting solution to precipitate iron as the hydrous oxide, then add 5 ml in excess and boil the solution to coagulate the precipitate. Allow it to settle, then filter the hot solution (Whatman No. 40 paper) and transfer the bulk of any insoluble material and any remaining globules of sulphur to the filter paper with a jet of 5% ammonia solution. Wash the paper and precipitate twice with 5% ammonia solution and discard the filtrate. Place the original beaker under the funnel and dissolve the precipitate with hot 20% hydrochloric acid contained in a wash-bottle. Wash the paper three times with the acid solution and discard the paper. Wash down the sides of the beaker with the hot acid solution, then reprecipitate the iron and filter as described above. Wash the beaker twice and the paper and precipitate three times with 5% ammonia solution. Place a 125-ml Erlenmeyer flask under the funnel, wash the precipitation beaker three times with concentrated hydrochloric acid from a plastic "squeeze" wash-bottle, and add the washings to the paper containing the precipitate. When the precipitate has dissolved, wash the paper three times with concentrated hydrochloric acid (Note 5), and discard it. Run a blank, with ~80 mg of iron(III) added, through the whole procedure.

Heat the blank and sample solutions in a hot water-bath at 90–95° for 30 min to ensure the complete reduction of tellurium(VI) to the quadrivalent state, then cool the solution to room temperature in a water- or ice-bath. Transfer each solution to a 125-ml separatory funnel, using concentrated hydrochloric acid to wash the flask, and dilute, if necessary, to ~50 ml with the concentrated acid. Add 10 ml of analytical-reagent grade chloroform, followed by 1 ml of freshly prepared 20% potassium ethyl xanthate solution, stopper and extract immediately (Note 6) by shaking for 1 min. Allow several min for the layers to separate, then drain the chloroform phase into a 125-ml separatory funnel. Extract the aqueous phase twice more, in a similar manner, with 10- and 5-ml portions of chloroform and 1 and 0.5 ml of xanthate solution, respectively, then wash the aqueous phase by shaking it for ~30 sec with 5 ml of chloroform. Add 15 ml water and 0.2 ml xanthate solution to the combined extracts, stopper, and shake for 1 min. Allow several min for the layers to separate, then drain the chloroform phase into a 150-ml beaker. Wash the aqueous phase three times, by shaking for ~30 sec each time, with 3 ml chloroform, and add the washings to the beaker containing the initial extract. Add 10 ml of 50% nitric acid to the combined extracts and heat in a hot water-bath to remove the chloroform. Add 0.5 ml of 50% sulphuric acid and 2 ml of 2.5% potassium sulphate solution, cover and heat until the volume of the solution has been reduced to ~3 ml. Remove the cover, wash down the sides of the beaker with water, and evaporate the solution to dryness or near dryness.

If the sample contains 60 μg or less of tellurium, evaporate both the sample and blank solutions to dryness or near dryness, after washing down the sides of the beakers with a small amount of water, to ensure the complete removal of nitric acid. Cool, add 5 ml of 10*M* sulphuric acid and 2 or 3 ml of water, heat gently for 2 or 3 min, cool to room temperature, and proceed with the determination of tellurium as described above (Note 7).

If the sample contains more than 60 μg of tellurium, add 10 ml of 50% nitric acid to both the sample and blank solutions and heat gently to dissolve the salts. Cool, transfer the solutions to volumetric flasks of appropriate size (50–200 ml) and dilute to volume with water. Transfer suitable aliquots (10–50 ml) of both solutions to 150-ml beakers, add 2 or 3 drops of 50% sulphuric acid and 2 ml of 2.5% potassium sulphate solution and proceed with the removal of nitric acid by evaporation and the subsequent determination of tellurium as described above.

Notes

1. Pure white diantipyrylmethane is recommended. The yellow compound sold by some manufacturers yields a high blank.
2. Filtration of the extracts through cotton-wool or filter paper to remove water droplets is not recommended, because of possible contamination from residual organic and other materials that absorb in the near ultraviolet.
3. Samples containing more than ~150 mg of iron should not be taken, because of the resultant slowness of the subsequent hydrous oxide filtration procedure, and particularly if a large amount of copper is present. In the presence of larger amounts of iron, sufficient copper is retained in the hydrous oxide precipitate, after a double precipitation, to cause low or negative results for tellurium.
4. The addition of potassium chlorate can be omitted for brass samples.
5. It is not necessary to remove all of the yellow iron colour from the filter paper. The total volume of the sample solution should be 40–50 ml at this stage.
6. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.
7. The presence of a small amount of co-extracted copper is indicated by the reddish colour obtained on addition of the sample solution to the potassium bromide solution in the separatory funnel. This colour disappears on dilution of the solution with water.

RESULTS

Extraction of the tellurium(IV) hexabromide–diantipyrylmethane complex

Busev and Babenko[8] found that the yellow 1:6:2 tellurium(IV) hexabromide–diantipyrylmethane ion-association complex can be extracted into chloroform and benzene but that it is most efficiently extracted with dichloroethane. Tests carried out with benzene, because dichloroethane was not immediately available, yielded extremely erratic results which were found to be caused by the presence of organic peroxides in the solvent. Subsequent tests with high-purity, peroxide-free (chromatographic quality) chloroform showed that up to at least 60 μg of tellurium contained in ~25 ml of solution can be extracted quantitatively in a single stage with 10 ml of chloroform. The extraction of larger amounts was not attempted because of the high absorbance of the resulting extract.

Busev and Babenko recommend measurement of the absorbance of the complex at 450 nm, but 336 nm, the wavelength of maximum absorption, was used in the present work because of the ~4-fold increase in sensitivity. The molar absorptivity at 336 nm is 1.82×10^3 $l.mole^{-1}.mm^{-1}$. Beer's law is obeyed over the range investigated, and the absorbance of the complex remains constant for at least 2 hr.

Factors influencing the formation and extraction of the tellurium complex

Effects of sulphuric acid and potassium bromide concentrations. Busev and Babenko[8] recommend the extraction of tellurium from a 1.8*M* hydrobromic acid–1*M* potassium bromide medium. However, initial tests in which the complex was extracted from hydrobromic acid media alone yielded high blank values, presumably caused by the co-extraction of residual bromine from the acid. Although this blank can be reduced by employing redistilled hydrobromic acid, subsequent tests showed that extraction from a sulphuric acid–potassium bromide medium is more satisfactory. The extraction of the complex is complete from solutions 1.5–3*M* in sulphuric acid and at least 0.5*M* in potassium bromide. Larger concentrations of potassium bromide do not affect the extraction. Extraction from 2*M* sulphuric acid–0.6*M* potassium bromide media was chosen for subsequent work.

Effects of diantipyrylmethane concentration and time. Tests performed with varying volumes of diantipyrylmethane solution showed that 1.5–2 ml of a 4% solution and approximately 15 min are required for complete complex formation under the conditions of the present investigation.

Separation of tellurium by extraction of its ethyl xanthate complex

Information obtained by the author in previous work[1] involving a study of the chloroform extraction of numerous metal ethyl xanthates from hydrochloric acid media showed that tellurium(IV) [or probably tellurium(II) after reduction by xanthate] can be quantitatively, or almost quantitatively extracted over a wide range of acidity. Consequently, it was considered that extraction from 12*M* hydrochloric acid, to minimize co-extraction of iron, copper, molybdenum and other elements, might be an effective means of separating small amounts of tellurium from large amounts of iron and from other co-precipitated elements after collection of tellurium by co-precipitation with hydrous ferric oxide from an ammoniacal medium; therefore the xanthate extraction procedure was investigated in the present work.

Preliminary experiments carried out with 12*M* hydrochloric acid containing up to 1 g of iron(III) showed that up to at least 1 mg of tellurium(IV) can be quantitatively extracted into chloroform as the xanthate in three successive extractions. Subsequent tests showed that if tellurium is present in the sexivalent state, prior reduction in a 12*M* hydrochloric acid medium, by heating at 90–95° for ~30 min,[9] is required in the presence of moderate amounts of iron(III). However, low or completely negative results were obtained for tellurium when the xanthate extraction procedure, after reduction of tellurium(VI) as described above, was applied to synthetic copper concentrate samples following a single separation of tellurium by co-precipitation with hydrous ferric oxides. Further work showed that the copper retained in the hydrous oxide precipitate, after a single precipitation, inhibits or completely prevents the extraction of tellurium as the xanthate. It is not known how the copper interferes, but tests showed that the inhibiting effect is much more pronounced in the presence of iron. Up to 50 mg of copper(II) alone will not interfere with the extraction of 50 μg of tellurium, but the same amount in the presence of 100 mg of iron(III) almost completely prevents extraction. Subsequent work showed that this interference effect can be avoided by removing the bulk of the copper retained in the initial hydrous ferric oxide precipitate, by performing a second precipitation.

Effect of diverse ions

It was found previously[1] that platinum(IV), palladium(II), gold(III), rhenium(VII) and selenium(IV) are partially or completely extracted into chloroform as xanthate complexes from 10M hydrochloric acid media, that germanium is extracted as the chloro-complex, and that arsenic(III) and arsenic(V) (after reduction by chloride[10]) are extracted as either xanthate- or chloro-complexes. In addition, it was found in the present work that small amounts of iron(III) are co-extracted from 12M hydrochloric acid media. Consequently, an investigation was made of the effects of moderate amounts of these ions on the determination of small amounts (50 μg) of tellurium. The results of these tests showed that up to at least 500 μg each of rhenium(VII), selenium(IV) and germanium, and up to at least 5 mg of iron(III), arsenic (III) and arsenic(V) do not interfere in the determination of tellurium by the proposed method. Although Busev and Babenko[8, 11] found that gold(III) interferes in their method because of its co-extraction into dichloroethane as the bromoaurate–diantipyrylmethane complex, up to at least 500 μg of gold(III) will not interfere in the present method. Small amounts of platinum(IV) (>50 μg) and palladium(II) (>25 μg) interfere during complex formation, but these elements are almost completely separated from tellurium during its co-precipitation from an ammoniacal medium with hydrous ferric oxide. Up to at least 200 μg of each will not interfere after a single ammonia separation of iron and tellurium. Residual copper and molybdenum, which are retained in the precipitate even after a double separation of iron and tellurium, are co-extracted to a slight extent from 12M hydrochloric acid media, but do not cause error in the tellurium result. Antimony(V), tin(IV) and bismuth are completely copreciptitated with tellurium and iron from ammoniacal media. Tin and bismuth do not interfere in the proposed method, but antimony(V) (more than approximately 1 mg) causes high results for tellurium because it is co-extracted, to a slight extent, as the chloro-complex, during the extraction of tellurium as the xanthate, and forms a similar extractable bromide-diantipyrylmethane complex. Interference from antimony (up to at least 50 mg) is eliminated in the present work by washing the tellurium xanthate extract with water. Large amounts of sulphate salts that are retained in the precipitate after a single precipitation and separation of tellurium may interfere in the subsequent reduction of tellurium(VI) in 12M hydrochloric acid medium. Consequently, a double precipitation is recommended. Nitrate salts interfere in a similar manner.

Applications

The proposed method was applied to the analysis of a series of five synthetic concentrates (*i.e.*, commercial mineralogical sulphide concentrates ground to finer than 200 mesh) in which the added tellurium was varied from 0.0005 to 0.10%. The standard tellurium solution was added directly to the powdered samples. Because of its high iron content, 0.5-g samples were taken of the copper concentrate; 1-g samples were taken of the remaining concentrates. The method was also applied to three standard reference cartridge-brass samples. The results of these analyses are given in Tables 1 and 2.

Table 1. Recovery of tellurium from synthetic concentrate samples

Matrix	Total Te present, %	Te found, %
Cu concentrate	0.0024_7	0.0026_0
	0.0029_7	0.0028_0
	0.0069_7	0.0072_5
	0.0120	0.012_0
	0 0520	0.051_1
	0.1020	0.100_7
Ni concentrate	0.0021_6	0.0022_1
	0.0026_6	0.0026_6
	0.0066_6	0.0067_4
	0.0117	0.011_4
	0.0517	0.051_1
	0.1017	0.099_8
Mo concentrate, NBS 333	0.0008_5	0.0008_8
	0.0013_5	0.0013_5
	0.0053_5	0.0052_0
	0.0103	0.010_0
	0.0503	0.049_2
	0.1003	0.100_2
Pb concentrate	0.0008_4	0.0008_0
	0.0013_4	0.0012_5
	0.0053_4	0.0049_5
	0.0103	0.010_2
	0.0503	0.049_6
	0.1003	0.098_4
Zn concentrate	0.0005_8	0.0005_5
	0.0010_8	0.0010_3
	0.0050_8	0.0048_0
	0.0101	0.010_1
	0.0501	0.050_0
	0.1001	0.100_2

Duplicate determinations of tellurium in the Cu, Ni, Mo, Pb and Zn concentrates by the proposed method gave 0.0020_5 and 0.0019_0, 0.0017_1 and 0.0016_0, 0.0004_4 and 0.0002_5, 0.0003_5 and 0.0003_3, 0.0000_6 and 0.0001_0%, respectively. The iron contents of the respective concentrates were 31.94, 1.58, 1.15, 8.40 and 11.10%.

Table 2. Determination of tellurium in N.B.S. cartridge brasses

Sample	Certified value, % Te	Te found, %
NBS-1100	0.0035	0.0034_8, 0.0034_3
NBS-1101	0.0015	0.0013_5, 0.0013_4
NBS-1102	0.0003	0.0000_8, 0.0000_8

DISCUSSION

Table 1 shows that the results obtained for the synthetic concentrate samples agree favourably with the total calculated amount of tellurium present. The results obtained (Table 2) for the first two of the National Bureau of Standards brass samples are in good agreement with the certified values, but that obtained for the third suggests that the certified value may be too high.

The proposed method is suitable for samples containing 0.0001% or more of tellurium. Probably samples containing approximately 0.01% or more can be analysed by flame atomic-absorption spectroscopy after removal of the chloroform from the tellurium xanthate extract by evaporation as described, followed by evaporation of the solution to dryness, dissolution of the residue in dilute nitric or hydrochloric acid, and dilution of the resulting solution to an appropriate volume (25 ml) with water.

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BEHAVIOUR OF TRACE IMPURITIES DURING CHEMICAL DISSOLUTION OF A METAL: PLATINUM ELEMENTS IN ALUMINIUM AND NICKEL

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Summary—In order to study the behaviour of trace impurities during aqueous dissolution of a sample, aluminium and nickel-based alloys containing 10^{-4}–1% Ir, Os or Ru were used. Yields of chemical separations such as distillation and ion-exchange were chosen as dissolution criteria. Dissolution of aluminium samples leads to precipitation of the three impurities. The Os and Ru precipitates can afterwards be dissolved by an oxidation procedure, in contrast to commercial powders of these elements. This behaviour may be explained in terms of the small grain-size of the precipitates. The iridium precipitates cannot be dissolved, which prevents quantitative separation of this element from an aluminium matrix. In the case of nickel alloys, these three impurities are dissolved and can be quantitatively separated.

In many analytical methods samples must be dissolved in aqueous media. In activation analysis, use of solutions of samples and standards is actually the easiest way to achieve identical and reproducible counting geometry. Dissolution is also needed when a chemical separation is included in the analytical procedure.

A proper dissolution method should result in a particular component being dissolved either completely (in which case it should also be brought to a definite oxidation state), or not at all. Depending on the chemical properties of the elements, this is not always easy to achieve. It may be a difficulty in the determination of Ru, Os and Ir when present as the metals in more electropositive matrices such as aluminium and nickel. These impurities should be deposited in the metallic state during the dissolution of the sample in either acidic or basic medium, and because of the difficulty of dissolving them it is not easy to see how to bring them to the oxidation state necessary for determination.

We wanted to study this problem with experimental conditions as close as possible to those encountered with an actual sample. For the purpose, we made alloys containing a very small but known quantity of each of these elements in aluminium or nickel[1] and irradiated them in a thermal neutron flux. Thus, we had aluminium or nickel samples doped with radioactive tracer of Ru, Os or Ir. In order to state whether the tracer dissolves or not, we thought that the best way was to submit the dissolved sample to a chemical separation. We assumed that the extent of dissolution of the tracer would be defined by the yield of the chemical separation, calculated from radioactivity measurements.

From the possible chemical separations we chose distillation for Ru and Os, which have volatile oxides, and ion-exchange for all three elements. Anion-exchange was performed in hydrochloric,[2,3] hydrobromic[4] or nitrite media,[5] and cation-exchange in hydrochloric acid–ethanol medium.[6]

EXPERIMENTAL

Experiments were performed on Al or Ni containing from 0.5 to 20,000 μg of Os, Ru or Ir per g of matrix and on commercial Os and Ru powders. Samples (2–100 mg) were irradiated for periods ranging from 30 min to 2 days, according to the concentrations, in a thermal-neutron flux of $3 \times 10^{12}\,n \cdot cm^{-2} \cdot sec^{-1}$ in the EL_3 reactor at Saclay. After application of the experimental procedures, the yield of the chemical separation was calculated from radioactivity measurements of the various chemical fractions, on a Ge(Li) detector coupled to a pulse-height analyser.

Distillation procedures

These were studied only with aluminium samples. We used a distillation apparatus consisting of a 250-ml flask wherein the samples were dissolved, a 10-cm distillation column, a condenser, and two receivers containing 20 ml of 9*M* sodium hydroxide.[7] The apparatus was flushed with air at a flow-rate of 200 ml/min. Various techniques were tried, as follows. The samples were dissolved in 10–15 ml of the acids and bases mentioned.

Procedure D_1 (*Os, Ru*). The sample was dissolved in 10 ml of sodium hydroxide 6*M*. The solution was then adjusted to be 6–8*M* in hydrochloric acid and the distillation performed according to Payne.[8] After addition of 10 ml of 20% perchloric acid, and then 15 ml of 20% sodium bromate solution, the distillation was continued for 30 min longer, and then for a further 40 min after dropwise addition of 15 ml of 20% sodium bromate solution. The radioactivities of the receiver solutions and of the residue were compared.

Procedure D_2 (*Os, Ru*). The sample was dissolved in 6*M* hydrochloric acid. The acidity was adjusted to be 8*M* and the solution treated as in procedure D_1.

Procedure D_3 (*Os*). The sample was dissolved in 6*M* sodium hydroxide. The solution was adjusted to be 12*M* in sulphuric acid and the distillation performed according to Chung and Beamish[9] after addition of 30 ml of 30% hydrogen peroxide.

Procedure D_4 (Os). The sample was dissolved in 6*M* hydrochloric acid and the distillation performed as in procedure D_3.

Procedure D_5 (Os). The sample was dissolved in 6*M* hydrochloric acid and the distillation performed from *aqua regia.*

Procedure D_6 (Os, Ru). The sample was dissolved in 6*M* hydrobromic acid. After evaporation the residue was treated with a solution of 6*M* hydrobromic acid containing 2% of bromine. The solution was evaporated (during the evaporations only 0.01% Ru and 0.67% Os were lost) and submitted to distillation procedure D_3 for Os and D_1 for Ru.

Procedure D_7 (Os). The sample was dissolved in 8*M* sulphuric acid and then treated as in procedure D_3.

Procedures using ion-exchange for aluminium samples

Procedure E_1 (Os, Ru). The sample was dissolved in a 6*M* hydrobromic acid–2% bromine solution. The resulting solution was adjusted to be 0.5*M* in hydrobromic acid and 0.0035*M* in bromine and passed through a column (height 12 cm, diameter 1 cm) of Dowex 1 × 4 resin, Br^- form, at a flow-rate of 1.5 ml/min. The column was washed with 20 ml of a solution having the same concentrations of the acid and bromine as the test solution. The radioactivities of the primary solution, of the resin and of the eluate were measured.

Procedure E_2 (Os, Ru). The sample was dissolved as in procedure E_2 and the solution was evaporated almost to dryness. The residue was dissolved in 1*M* sodium nitrite and adjusted to be 0.1*M* in nitrite at pH 6 in a volume of 30 ml. This solution was passed through a column (height 10 cm, diameter 1 cm) of Dowex 1 × 8 resin, NO_2^- form, at a flow-rate of 1 ml/min. The column was washed with 30 ml of 0.1*M* sodium nitrite at pH 6. The radioactivities were measured as in procedure E_1.

Procedure E_3 (Ir). The sample was dissolved in 6*M* hydrochloric acid. The solution was evaporated almost to dryness, treated with 0.5 ml of 0.5% ceric sulphate solution in 4*M* sulphuric acid and adjusted to be 1*M* in hydrochloric acid in a volume of 30 ml. The solution was passed through a column (height 15 cm, diameter 1 cm) of Dowex 1 × 8 resin, Cl^- form, at a flow-rate of 2 ml/min. The column was washed with 30 ml of 1*M* hydrochloric acid containing 0.05% ceric sulphate. The radioactivity measurements were performed as in procedure E_1.

Procedure E_4 (Ir). The sample was dissolved in 6*M* hydrochloric acid. Concentrated nitric acid was added in order to produce *aqua regia*, which was then evaporated almost to dryness. The residue was dissolved in 2*M* hydrochloric acid and oxidized with a cerium (IV) solution. The solution obtained (20 ml) was passed through a column (height 10 cm, diameter 0.6 cm) of Dowex 1 × 8 resin, Cl^- form, at a flow-rate of 2 ml/min. The column was washed with 20 ml of 2*M* hydrochloric acid containing 0.05% ceric sulphate. The measurements were performed as in procedure E_1.

Procedure E_5 (Ir). The sample (5-μg/g alloy only), and 30 mg of non-irradiated 0.4% alloy used as carrier, were dissolved in 5*M* sodium hydroxide. The solution was then treated with sulphuric acid and cerium (IV) and boiled for 30 min. This solution (20 ml), 1*M* in sulphuric acid, was passed through a column (height 10 cm, diameter 6 cm) of Dowex 1 × 8 resin, initially in the Cl^- form and previously treated with 0.05% ceric sulphate solution. The column was washed with 20 ml of 1*M* sulphuric acid containing 0.05% ceric sulphate. The radioactivity measurements were performed as in procedure E_1.

Procedure E_6 (Ir). The sample was dissolved in 6*M* hydrobromic acid–2% bromine solution. After evaporation almost to dryness, the residue was dissolved in more of the solvent mixture, again evaporated almost to dryness, and redissolved in 20 ml of 0.5*M* hydrobromic acid. This solution was filtered through a porosity 4 sintered-glass filter covered with an Ederol No. 4/M filter paper. The filtrate was adjusted to be 0.05*M* in hydrobromic acid–0.0035*M* bromine in 20 ml. The radioactivities of the filtrate and of the filter were measured. The filtrate was passed through a column (height 15 cm, diameter 1.2 cm) of Dowex 1 × 4 resin, Br^- form, at a flow-rate of 1 ml/min. The column was washed with 20 ml of 0.05*M* hydrobromic acid–0.0035*M* bromine. The radioactivities of the resin and of the eluate were measured.

Procedure E_7 (Ir). The sample was dissolved in 6*M* hydrochloric acid. Concentrated nitric acid was added in order to produce *aqua regia*, which was then evaporated almost to dryness. The residue was dissolved in 4*M* hydrochloric acid and oxidized with hydrogen peroxide. The solution was evaporated and adjusted to be 0.1*M* in hydrochloric acid and to contain 90% ethanol. This solution (40 ml) was passed through a column (height 10 cm, diameter 1 cm) of Dowex 50 × 8 resin, H^+ form, at a flow-rate of 2 ml/min. The column was washed with 40 ml of 0.1*M* hydrochloric acid–90% ethanol.

The eluate was adjusted to be 0.2*M* in sodium nitrite and passed through a Dowex 1 × 8 column as in procedure E_2. The yields of sorption on both columns were determined by radioactivity measurements.

Procedure E_8 (Ir). The sample was dissolved in 5 ml of the bath used for chemical polishing of aluminium[11] (70% phosphoric acid, 25% sulphuric acid, 5% nitric acid) at 90°. The solution was diluted to 60 ml and passed through Dowex 50 × 8 resin as in procedure E_7.

Procedure E_9 (Ir). The sample was dissolved in a 1:1 v/v nitric acid–hydrofluoric acid mixture.[12] The solution was evaporated in order to eliminate the acids and then made 0.1*M* in hydrochloric acid and to contain 90% ethanol. It was then treated as in procedure E_7.

Procedure using ion-exchange for nickel samples

Procedure E_{10} (Ir). The nickel sample was dissolved in 6*M* nitric acid. The solution was evaporated twice in presence of concentrated hydrochloric acid, in order to eliminate the nitric acid. The solution was then adjusted to be 0.1*M* in hydrochloric acid and to contain 90% ethanol, and passed through Dowex 50 × 8 and Dowex 1 × 8 resins as in procedure E_7.

RESULTS AND DISCUSSION

Separation yield with a nickel matrix

We did not observe a precipitate during the dissolution of a nickel sample. The separation yields of platinum elements were always very good. It seems that the electropositivity of the matrix has no effect

Table 1. Chemical separation yield of Ru in Al by various procedures (%)

Sample	Procedure				
	D_1	D_2	D_6	E_1	E_2
Al–Ru 0.34%	96.2	—	—	—	—
Al–Ru 0.30%	—	95.1	98.2	84.5	99.8
Al–Ru 50 μg/g	95.3	97.1	97.8	—	—
Ru commercial powder	≤0.5	≤0.7	≤0.7	—	—

Table 2. Chemical separation yield of Os in Al by various procedures (%)

Sample	Procedure D_1	D_2	D_3	D_4	D_5	D_6	D_7	E_1	E_2
Al–Os 2%	70	—	99.8	99.2	—	—	99.2	68.3	—
Al–Os 0.68%	—	79	99.7	—	99.9	99.9	—	—	98.6
Al–Os 50 μg/g	—	—	99.8	—	—	—	99.1	—	—
Al–Os 5 μg/g	—	—	99.5	—	—	⩾99.9	—	—	—
Os commercial powder	⩽0.2	—	⩽0.8	⩽0.7	1	⩽0.5	⩽0.1	—	—

when nitric acid is used for the dissolution. Platinum elements are probably dissolved as soon as they appear at the sample surface.

Separation yield with an aluminium matrix

In the case of aluminium we observed black precipitates during the dissolution of the less dilute alloys. The behaviour of these precipitates depends on the element concerned and on the further treatment.

In Tables 1 and 2 are presented the separation yields for Ru and Os. We did not apply procedures D_3, D_4, D_5 and D_7 to Ru, as these methods do not give quantitative distillation of this element, even if a soluble salt is used.[9] Such methods could not be used to test the dissolution of ruthenium.

Tables 1 and 2 show that the alloys and commercial powders exhibit completely opposite behaviour. The commercial powders could never be dissolved, whereas Os and Ru resulting from alloy dissolution were separated in 95–100% yield by methods D_3, D_4, D_5, D_6, D_7, E_2 and D_1, D_2, D_6, E_2 respectively.

Distillation of osmium after oxidation by bromate (methods D_1 and D_2) and sorption of Os and Ru on an anion-exchange resin in hydrobromic acid medium did not give quantitative separations. Low yields were obtained even when soluble salts (ammonium hexachloro-osmate and hexachlororuthenate) were used. The results showed that methods D_1, D_2 and E_1 could not be used to test the dissolution.

Table 3. Fixation of Ir from Al samples, on anion-exchange resin by various procedures (%)

Ir in alloy, w/w	Procedure E_3	E_4	E_5
10^{-2}	—	92.6	—
4×10^{-3}	—	97.1	—
2.9×10^{-3}	—	87.8	—
5×10^{-5}	86.7	95	—
3.2×10^{-5}	—	90.5	—
5×10^{-5}	—	88.7	88.5
5×10^{-6}	—	93.6	—

In the case of iridium neither of the ion-exchange methods leads generally to a quantitative separation (Table 3). The separation yield could not be correlated to the alloy concentration. Experiments performed with a soluble salt of iridium (tetrachloride obtained by electrolytic dissolution of Ir[10]) showed the same result, which could mean that the precipitate is dissolved during the oxidation process. However the presence of a black precipitate even after oxidation in the case of the 1% alloy, suggested that the ion-exchange resin might act as a filter. In order to check this hypothesis, we applied procedure E_6 in which the solution was filtered before passage through the resin. The results presented in Table 4 show that an appreciable fraction of the iridium was retained on the filter. This fraction was not very

Table 4. Separation of Ir from Al samples by procedure E_6. Ratio of fixation on filter to total quantity (F/T) and of fixation on resin to quantity introduced onto the resin after filtration [$R/(R + E)$]

Ir in alloy, w/w	Experiment 1 F/T, %	$R/(R + E)$, %	Experiment 2 F/T, %	$R/(R + E)$, %
10^{-2}	33.6	94.9	26.2	97.6
2.9×10^{-3}	40.6	93.9	38.3	95.7
5×10^{-5}	6.4	97.5	32.5	91.7
5×10^{-6}	28.6	85.4	38.9	88.5
5×10^{-7}	9.6	88.4	3.8	88.2

Table 5. Fixation of iridium on Dowex 50 X8 and Dowex 1 X8 resins from Al and Ni samples after various dissolution procedures

Alloy Matrix	Ir μg/g	Procedure	Retained on Dowex 50, %	Retained on Dowex 1, %
Al	5	E_7	94.1	100
Al	50	E_7	96.6	100
Al	2900	E_7	97.8	100
Al	2900	E_8	84.1	100
Al	2900	E_9	94.4	100
Ni	744	E_{10}	4.8 3.0 2.2	100

reproducible, however, and could not be correlated to the alloy concentration. When the filtrate was passed through the ion-exchange column, the sorption yield was more reproducible and varied as the alloy concentration.

In order to check the possibility of fixing iridium on a resin by a filtration mechanism we applied procedure E_7, which is analogous to procedure E_{10} applied to nickel (Table 5). In the case of the aluminium alloys, iridium is fixed on the cation-exchange resin, even at very low concentration, but this is not the case with the nickel matrix nor, more generally, with soluble iridium salts. It can be explained by the filtration effect, which probably occurs for all fixations of iridium on Dowex 1 resin without previous passage through a Dowex 50 column.

The direct dissolution of iridium from a nickel sample can be attributed to the oxidizing character of the nitric acid used for dissolution. We tried to use oxidizing dissolution baths with aluminium also (procedures E_8 and E_9), but they did not lead to a better dissolution of iridium.

Structure of the precipitates

The oxidation treatments did not lead to complete and reproducible dissolution of iridium precipitates resulting from aluminium alloys. These results are more in agreement with those expected from the metallic properties of Ir, than those for Os and Ru.

The difference between the behaviour of Os and Ru precipitates from the aluminium alloy and that of the commercial powders may be explained either by a difference in chemical composition, for instance the presence of oxides, or by a difference in the crystallite sizes. In order to choose between these postulates we took X-ray diffraction patterns of the available commercial powders (Os and Ru) and of the precipitates. In all cases we observed the characteristic peaks of metallic Ru, Os and Ir; we did not detect any other peak. We concluded that the precipitates were mainly composed of pure metal crystallites. A more detailed analysis allowed an estimate of the crystallite size from the formula[13,14]

$$D = \frac{0.9\,\lambda}{2\cos\theta\sqrt{\Delta^2 - \Delta_0^2}}$$

where D is the particle diameter, λ the wavelength of the incident X-ray (the K_α X-ray of cobalt in our case, $\lambda = 1.78$ Å), θ the Bragg angle, Δ the half-height width of the observed peak and Δ_0 the half-height width of a standard peak close to the one observed and given by a product with large well-crystallized grains (sodium chloride in this case).

The grain size of the precipitates was within the range 35–100 Å. For the commercial powders of Ru and Os the peak widths were close to those which result from the spectral width of the incident X-rays. We could only calculate a lower limit of 1000 Å for the grain size of the commercial powders.[15]

In order to confirm these results we made light- and electron-microscopy observations. The light-microscopy measurements gave a mean size of 0.01 mm for the commercial powders.

The precipitates obtained during alloy dissolution were deposited, after washing and centrifuging, on collodion-covered grids and observed with a Philips EM 300 electron microscope. At high magnification (about 200,000 ×) we saw individual grains and formations which seemed to be grain clusters. We could not establish a correlation between the grain or cluster size and the nature or concentration of the alloys. The diameter of individual grains varied from 20 to 50 Å, that of the clusters from 150 to 400 Å.

All these results seem to show that the precipitates are in the metallic state. Both methods lead to the same range of grain size for the precipitates: 20–100 Å. The grain size of the commercial powders was found to be at least 1000 times larger. This value could explain the difference in the dissolution behaviour of the powders and precipitates.

CONCLUSION

Using dilute alloys of Os, Ru and Ir we have shown the decisive influence of the method of sample dissolution on the chemical separations and consequently on the analytical results. As might be foreseen from the chemical properties, Os, Ru and Ir are not dissolved during the dissolution of the aluminium-based alloy either in acid or in basic aqueous solutions. Further treatment could not completely dissolve iridium and allow a quantitative separation of this element.

The Os and Ru precipitates obtained can be dissolved by using a suitable oxidation treatment and quantitatively separated for instance by distillation. On the contrary, commercial powders of the same two elements cannot be dissolved. This difference of behaviour seems to arise from grain size differences, and probably explains why alloying platinum elements with an acid-soluble metal facilitates their dissolution.[16] When the alloy is attacked with acids, the platinum elements form finely divided precipitates which are more easily dissolved than the initial samples. Osmium and ruthenium impurities can thus be brought into aqueous solution. Although iridium as impurity gives precipitates of the same grain size as Os and Ru, it cannot be directly brought into aqueous solution and other means of dissolution have to be used, for instance alkaline fusion. Sodium peroxide attack was successfully used by some authors for the determination of iridium in rocks and meteorites.[3,17,18] Unfortunately this procedure is not suitable for aluminium. For the determination of iridium in this metal we recommend dissolving the sample in hydrochloric acid, evaporating to dryness and attacking the residue with sodium peroxide.

We observed that Os, Ru and Ir are dissolved from a nickel-based alloy during the dissolution of the sample in nitric acid. The difference in behaviour of aluminium and nickel alloys may be explained by a difference either in the alloy structure or in the dissolution mechanism. It is difficult to discuss the influence of alloy structure as the phase diagrams and solubilities of platinum elements in aluminium and nickel are not well known. For the dissolution mechanisms there is a real difference: nickel is dissolved by oxidation with nitric acid, whereas aluminium is dissolved by oxidation with protons, yielding hydrogen.

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SELECTIVE DETERMINATION OF ARSENIC(III) AND ARSENIC(V) WITH AMMONIUM PYRROLIDINEDITHIOCARBAMATE, SODIUM DIETHYLDITHIOCARBAMATE AND DITHIZONE BY MEANS OF FLAMELESS ATOMIC-ABSORPTION SPECTROPHOTOMETRY WITH A CARBON-TUBE ATOMIZER

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Summary—The extraction behaviour of arsenic(III) and arsenic(V) with ammonium pyrrolidinedithiocarbamate, sodium diethyldithiocarbamate and dithizone in organic solvents has been investigated by means of flameless atomic-absorption spectrophotometry with a carbon-tube atomizer. The selective extraction of arsenic(III) and differential determination of arsenic(III) and arsenic(V) have been developed. With ammonium pyrrolidinedithiocarbamate and methyl isobutyl ketone or nitrobenzene, when the aqueous phase/solvent volume ratio is 5 and the injection volume in the carbon tube is 20 μl, the sensitivities for 1% absorption are 0.4 and 0.5 part per milliard of arsenic, respectively. The relative standard deviations are *ca.* 3%. Interference by many metal ions can be prevented by masking with EDTA. The proposed methods are applied satisfactorily for determination of As(III) and As(V) in various types of water.

Determination of arsenic in trace amounts has received increasing attention in connection with environmental pollution. Recently, a method involving the conversion of arsenic into arsine, and its subsequent introduction into the argon–hydrogen flame has been developed,[1–5] enhancing the sensitivity to the parts per milliard (ppM) level. Moreover, during the last few years there has been an increased interest in flameless methods for atomic-absorption analysis because of the increased sensitivity. In a previous paper[6] we reported an atomic-absorption spectrometric method with a carbon-tube atomizer for determinations of arsenic, antimony and selenium in aqueous solution. Neither the arsine method nor the carbon tube method will differentiate between arsenic(III) and arsenic(V), however.

The potential toxicity of arsenic is considered to depend on its oxidation state, but there are few techniques for determining the oxidation state of a trace amount of arsenic, though being able to do so would be extremely useful for understanding the biological function and availability of arsenic. From these aspects it appears very important to determine selectively arsenic(III) and arsenic(V). Solvent extraction followed by flameless atomic-absorption spectrophotometry seems profitable for this purpose. Extraction with ammonium pyrrolidinedithiocarbamate (APDC), sodium diethyldithiocarbamate (DDTC) and diphenylthiocarbazone (dithizone) has been widely used in atomic-absorption determination of various elements. Though these reagents, especially DDTC,[7–13] have been used for the extraction of arsenic, their combination with atomic absorption has scarcely been used for determination of the element, on account of the low sensitivity, only one report having been found by us in the literature.[14]

In this paper, we have studied the extraction behaviour of arsenic(III) and arsenic(V) with APDC, DDTC and dithizone in various organic solvents [carbon tetrachloride, methyl isobutyl ketone (MIBK) and nitrobenzene (NB)]. The paper further describes the selective extraction of arsenic(III) with these systems and the differential determination of arsenic(III) and arsenic(V) by the atomic-absorption method with a carbon-tube atomizer.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in polyethylene bottles.

Standard arsenic(III) solution, 1000 *ppm.* Prepared by dissolving 1.320 g of diarsenic trioxide in 10 ml of 10*M* sodium hydroxide, and diluting to 1000 ml with water. An aliquot of this solution was diluted with water to give a concentration of 0.4 ppm before use.

Standard arsenic(V), 1000 *ppm.* Prepared by dissolving 2.403 g of potassium dihydrogen arsenate in water and diluting to 1000 ml with water. An aliquot of this solution was diluted with water to give a concentration of 0.4 ppm before use.

Arsenic-76m solution. Prepared by diluting 1 mCi of the radioisotope arsenic-76m (arsenious acid in 1*M* hydrochloric acid) to a suitable concentration.

APDC solution, 1% *w/v aqueous.*

DDTC solution, 1% *w/v aqueous.*

Dithizone solution, 0.03% *w/v.* Prepared by dissolving 75 mg of refined dithizone in 250 ml of organic solvent.

Potassium iodide solution, 20% *w/v.*

Sodium thiosulphate solution, 1% *w/v.*

EDTA (disodium salt) solution, 5% *w/v.*

Buffer solution, *pH* 5.2. Prepared by mixing 1*M* acetic acid and 1*M* sodium acetate in suitable ratio.

Apparatus

Atomic-absorption measurements were made with a Nippon Jarrell-Ash Model AA-1 EW atomic-absorption spectrophotometer equipped with a Model FLA-10 flameless atomizer and a Model HU-10 furnace. Peak heights were recorded with a Yanaco Model YR-110 chart recorder. A Westinghouse arsenic hollow-cathode lamp was used as a light-source. Samples were placed in the carbon-tube with a Gilson Model P-20 digital micropipette. An Iwaki Model KM shaking apparatus was used for solvent extraction. Radioactivity measurements were made with an Aloka Model PSM-801 γ-ray spectrometer equipped with a 1.5 × 1 in. NaI(Tl) crystal.

Recommended general procedure

Arsenic(III) determination. Take an aliquot of a sample solution containing not more than 2 μg of arsenic(III), in a separatory funnel. Add 5 ml of the EDTA solution, 2 ml of the APDC solution and 5 ml of the acetate buffer solution. Dilute the mixture to 25 ml with water, the pH of the resulting solution being 5–5.6. Shake the funnel for 2–5 min with 10 ml of an organic solvent (MIBK or NB). Stand the funnel for 20–30 min and separate the organic phase.

Transfer 20 μl of the organic phase with the micropipette to the carbon-tube. Pass argon gas through the furnace at a flow-rate of 3 l./min, and then atomize the sample by the following heating sequence: drying for 30 sec at 30 A (*ca.* 350°), ashing for 120 sec at 70 A (*ca.* 1050°), atomization for 7 sec at 230 A (*ca.* 2400°). Record the absorption signal at 1937 Å. Run a reagent blank at the same instrumental settings and subtract it from the analytical value.

Total arsenic determination. Two methods are available as follows.

(*a*) *Extraction at* 1*N acidity.* Take an aliquot of a sample solution containing not more than 2 μg of arsenic, in a separatory funnel. Add 2 ml of 12*N* hydrochloric acid or sulphuric acid. Then add 5 ml of the EDTA solution and 2 ml of the APDC solution. Dilute the mixture to 25 ml with water, the acidity of the resulting solution being *ca.* 1*N*. Do the extraction and measure the atomic absorption as for arsenic(III).

(*b*) *Reduction of arsenic(V) to arsenic(III) and extraction at pH* 5.0–5.6. Take an aliquot of a sample solution containing not more than 2 μg of arsenic, in a separatory funnel. Add hydrochloric acid to adjust the acidity of the solution to *ca.* 0.5*N*. Then add 2 ml of the potassium iodide solution to reduce arsenic(V) to arsenic(III). After 5 min or more add 1 ml of the sodium thiosulphate solution. Add 5 ml of the EDTA solution and neutralize the solution with ammonia. Add 2 ml of the APDC solution, and adjust the pH to 5–5.6 with the buffer. Extract and measure as before.

The amount of arsenic(V) is estimated from the difference between total arsenic and arsenic(III).

Water analysis. Apply the general procedure to a 50-ml sample.

RESULTS AND DISCUSSION

Optimization of the atomization system

Heating conditions. The heating current and length of time for the dry, ash, and atomize steps of the atomization cycle were optimized as follows. At the drying stage, application of 30–40 A for 30 sec (*ca.* 350–500°) is suitable for removing the solvent. The temperature for the ashing stage considerably affects the arsenic atomization. Use of a current of less than 65 A for 120 sec (*ca.* 950°) gives a lower arsenic signal. This may be ascribed to insufficient decomposition of the organic extract. When the current is above 80 A (*ca.* 1200°), the signal is again lowered. This means that a considerable amount of arsenic is volatilized before the atomization stage. Accordingly the ashing current should be kept in the range 65–80 A for 120-sec heating. At the atomization stage, the arsenic peak height is maximal and constant over the tested current range of 220–260 A (*ca.* 2300–2700°) for 7-sec heating. From these results, a heating programme for the atomization of arsenic was chosen, as described in the general procedure.

Shielding-gas flow-rates. The peak signal of arsenic tends to decrease with increasing shielding-gas flow-rate in the tested range 0.5–5 l./min. This may be caused by the fact that the rate of diffusion of arsenic atoms in the carbon-tube is increased by increasing the flow-rate. On the other hand, the reagent blank signal increases considerably with a decrease in the flow-rate, which is possibly due to the molecular absorption of the products from atmospheric oxidation of the carbon tube. Accordingly, the flow-rate of argon gas was kept at 3 l./min.

Extraction

Extraction behaviour of As(III) and As(V). The extraction behaviour of arsenic(III) and arsenic(V) with ADPC, DDTC and dithizone in MIBK, nitrobenzene and carbon tetrachloride was investigated. The rather complicated effect of acidity on the extraction is shown in Figs. 1–3.

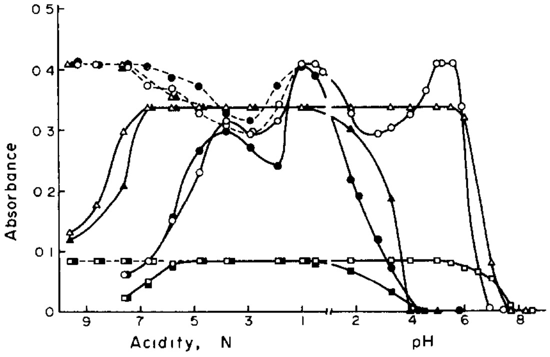

Fig. 1. Effect of pH and acidity on the extraction of As(III) and As(V) with APDC. ○, As(III)—MIBK; ●, As(V)—MIBK; △, As(III)—NB; ▲, As(V)—NB; □, As(III)—CCl$_4$; ■, As(V)—CCl$_4$; (——), hydrochloric acid medium; (- - -), sulphuric acid medium; aqueous phase, 25 ml; organic phase, 10 ml; As(III) or As(V), 2 μg.

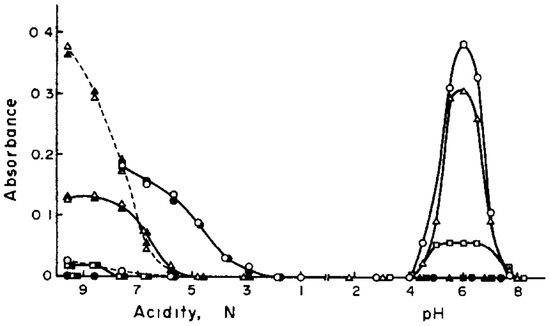

Fig. 2. Effect of pH and acidity on the extraction of As(III) and As(V) with DDTC. Symbols and conditions as for Fig. 1.

In the APDC system, in the pH ranges 4.0–5.6 (MIBK), 4.0–6.0 (NB), 4.0–6.0 (CCl_4), arsenic(III) is extracted whereas arsenic(V) is not. The extraction efficiency of the solvents increases in the order $CCl_4 < NB < MIBK$. On the other hand, in strongly acidic medium both arsenic(III) and arsenic(V) are well extracted from sulphuric acid into all three solvents (distribution ratio: MIBK 19, NB 19, CCl_4 0.25), but from hydrochloric acid medium the extraction is much decreased as the acidity increases. The extracted species in neutral medium should be $As(APDC)_3$, which is confirmed by continuous variation plots as described later, and the structure is assumed to be analogous to that[15] determined by X-ray analysis for $As(DDTC)_3$. The reason for the complicated behaviour of the APDC–MIBK system which shows three maxima on the absorbance–pH curve is not at present clear.

In the DDTC system, there is a very narrow pH range (at *ca.* pH 6.0) for selective extraction of arsenic(III) and the order of extraction efficiency of the solvents is similar to that for APDC.

Dithizone does not extract either arsenic(III) or arsenic(V) in the pH range 1–10. At high acidity only arsenic(III) is extracted, and even then but poorly.

Selective determination of As(III) and As(V). From these results it may be concluded that with APDC extraction into MIBK or NB from neutral medium is best for the selective separation of arsenic(III) and arsenic(V). Total arsenic is separately determined either by extraction from 1*N* acid medium or from neutral medium after reduction of arsenic(V) to arsenic(III).

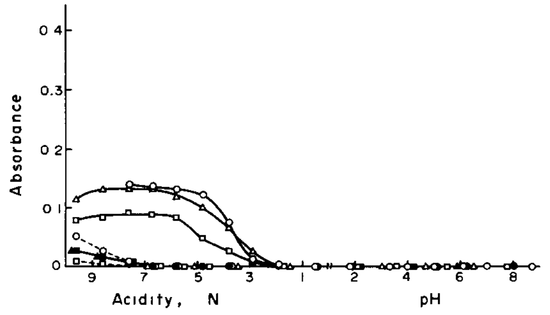

Fig. 3. Effect of pH and acidity on the extraction of As(III) and As(V) with dithizone. Symbols and conditions as for Fig. 1.

Table 1. Recovery tests

Extraction system	Arsenic added, *ng/ml* As(III)	As(V)	Arsenic found, *ng/ml* As(III)	As(total) *a**	*b**
APDC–MIBK	20	60	21	78	81
	40	40	41	77	80
	60	20	60	78	80
APDC–NB	20	60	20	80	81
	40	40	38	79	81
	60	20	59	80	82

* Procedure.

Recovery tests with known amounts of standard arsenic(III) and arsenic(V) showed (Table 1) that total arsenic can be determined with good recovery by both methods.

In the 1*N* acid method, the sensitivity is slightly higher with the APDC–MIBK system than with the APDC–NB system, but acidity has to be more carefully controlled.

In the reduction method, potassium iodide in 2–6*N* hydrochloric acid medium has been recommended for the reduction.[16] After completion of the reduction (half an hour in a heating bath), a reducing agent such as sodium thiosulphate or potassium metabisulphite is added to remove the iodine liberated. The tolerance ranges for these reagents were therefore determined, by tests with 2 μg of arsenic(V) and a final acidity of 0.6*N*. Thiosulphate will reduce arsenic(V) as well as remove iodine, but not completely, and Fig. 4 shows that the treatment with potassium iodide is essential, a concentration of at least 0.3% being necessary for complete reduction. The sodium thiosulphate concentration needed is 0.02–0.3%, and a large excess decreases the extraction of arsenic(III) by APDC. The optimum acidity is 0.3 *M* hydrochloric acid or above. It was also confirmed that the quantitative reduction to arsenic(III) requires not less than 5 min at room temperature.

Results of recovery tests for total arsenic are shown in Table 1.

Stability of the extracts. Extraction is quantitative in 15 sec shaking and continued shaking up to 20 min

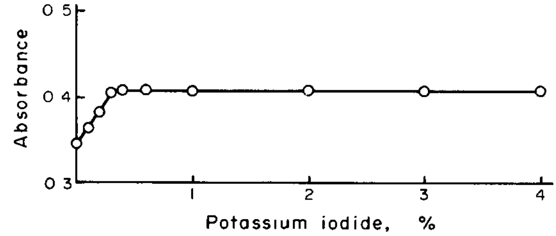

Fig. 4. Effect of potassium iodide concentration on reduction of As(V). As(V), 2 μg; sodium thiosulphate, 0.1%; aqueous phase 25 ml, organic phase 10 ml.

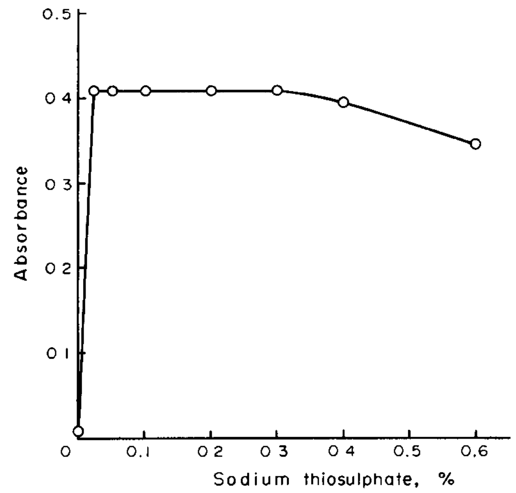

Fig. 5. Effect of sodium thiosulphate concentration on reduction of As(V) and removal of iodine. As(V), 2 μg; potassium iodide, 2%; aqueous phase 25 ml, organic phase 10 ml.

produces no further change in absorption. The absorption signal of the extract remains almost constant for at least 6 hr after the extraction.

Degree of extraction. This was investigated by the radio-tracer technique with ^{76m}As and a 1:1 volume-ratio of aqueous to organic phase. The results show that arsenic(III) is 95% extracted under these conditions (distribution ratio 19), while arsenic(V) is not appreciably extracted over the pH range used.

Composition of the extracted species. Continuous variation plots for the extraction process were made. The maximum absorption occurs at a mole-fraction of *ca.* 0.25 which suggests that the extracted species should have a composition of 1:3 (As:APDC).

Effect of phase-volume ratio on sensitivity. Although the degree of extraction appreciably decreases as the aqueous–organic phase-volume ratio (V_w/V_0) increases, arsenic(III) is extracted nearly quantitatively into the organic phase in a single extraction. To examine the effect of the volume ratio on the sensitivity of atomic absorption, 10 ml of MIBK or NB were used for the extraction from various volumes of aqueous phase, each containing 2 μg of arsenic(III). The result is shown in Fig. 6. With increasing V_w/V_0, the relative sensitivity in the case of NB appreciably decreases, while in the case of MIBK it remains almost unchanged owing to the solubility of MIBK in water (*ca.* 2%). If an appropriate V_w/V_0 ratio is chosen according to the arsenic content in sample, arsenic may be determined over a wide concentration range from ng/ml to μg/ml levels.

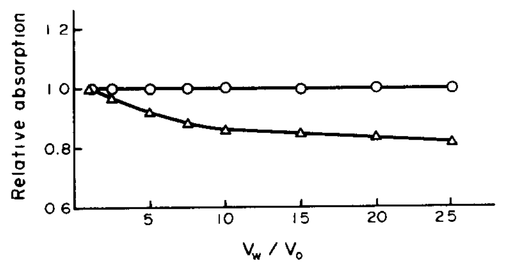

Fig. 6. Effect of initial volume ratio on atomic absorption of As. ○, MIBK; △, NB; As(III), 2 μg; initial volume of organic phase, 10 ml.

Calibration curve and precision

Under the established optimum conditions, the calibration curve was made, with the arsenic(III) solution as standard. Similar results are obtained with the arsenic(V) solution if the reduction procedure is used. The linearity is good over the range 2–40 ng/ml with an aqueous/organic solvent ratio of 5. The sensitivity for 1% absorption was found to be 0.4 ng/ml. The relative standard deviation was *ca.* 3% for 80 ng/ml of arsenic(III) (ten determinations, three injections of each).

Interference study

In the previous paper on arsenic determination by direct injection of aqueous samples,[6] large amounts of alkali and alkaline earth metals were found to interfere considerably with the determination. In the present investigation it was confirmed that these interferences could be avoided by the solvent extraction of arsenic before the atomic absorption analysis. However, large amounts of metal ions which react with APDC appreciably lower the degree of extraction of arsenic(III). In many cases, such interferences can be reduced by the use of EDTA as masking agent. Table 2 shows the effects of various ions; the data in parentheses were obtained with 1% of EDTA in the aqueous phase.

Table 2. Permissible amount of foreign ions in determination of 2 μg of As/25 ml (to give <10% error)

Ion	Added as	Limit [Ion]/[As]
Fe^{3+}	Chloride	2 (1000)
Co^{2+}	Chloride	110 (1000)
Ni^{2+}	Chloride	620 (1000)
Mn^{2+}	Chloride	19 (1000)
Cu^{2+}	Sulphate	25 (25)
Zn^{2+}	Chloride	55 (1000)
Al^{3+}	Potassium alum	900 (1000)
Cr^{3+}	Nitrate	280 (1000)
Pb^{2+}	Nitrate	80 (450)
Ag^{+}	Sulphate	140 (200)
Hg^{2+}	Chloride	130 (200)
Sn^{2+}	Sulphate	400 (1000)
Cd^{2+}	Sulphate	7 (7)
Bi^{3+}	Chloride	8 (8)
Se^{4+}	Selenious acid	75 (75)
Te^{4+}	Tellurous acid	25 (25)
Sb^{3+}	Chloride	1 (1)
S^{2-}	Sodium salt	150 (150)

The following are tolerable in 1000-fold ratio to As: Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, . Br^-, I^-, NO_3^-, CN^-, CH_3COO^-. Values in parentheses apply when 1% EDTA is present.

Table 3. Analytical results on various samples

Sample	As (total), *ng/ml* added	found	As(III), *ng/ml* added	found	As(V), *ng/ml* added	found
River water A	—	17	—	3	—	14
River water A	8	25	8	11	—	14
River water A	16	32	16	19	—	13
River water B	—	19	—	5	—	14
River water B	8	26	8	14	—	12
River water B	16	35	16	21	—	14
River water B	16	34	—	5	16	29
Waste water	—	11	—	4	—	7
Waste water	8	19	8	13	—	6
Waste water	16	27	16	20	—	7
Sea-water A	—	ND	—	ND	—	ND
Sea-water A	8	8	8	8	—	ND
Sea-water A	24	24	24	24	—	ND
Sea-water B	—	3	—	ND	—	3
Sea-water B	16	19	16	16	—	3
Sea-water B	16	18	—	ND	16	18

ND: not detected.

Application to water analysis

The results of the selective determination of arsenic(III) and arsenic(V) in various types of water are presented in Table 3 together with those of the recovery test run on the samples. All the samples used were acidified with hydrochloric acid to *ca.* pH 1 immediately after sampling. According to the method proposed here, ng/ml levels of arsenic(III) and arsenic(V) in waste water or sea-water can be selectively determined.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF PYRROLE DERIVATIVES

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Omosi[1] determined carbazole by a method based on nitrosation. Matraka and Navratil[2] determined carbazole polarographically. Furusawa *et al.*[3] determined carbazole with xanthydrol in glacial acetic acid. Byrom and Turnbull[4] used *p*-dimethylaminobenzaldehyde in aqueous trifluoroacetic acid for determination of indole and its derivatives. Furusawa *et al.*[5] determined carbazole with maleic anhydride in anthracene. Sawicki *et al.*[6] used *p*-nitrosophenol in benzene for the spectrophotometric determination of carbazole. In the present work a simple rapid ultraviolet procedure is described for the microgram determination of indole, carbazole, indole-3-propionic acid and indole-3-butyric acid. It was observed that reaction of a few drops of concentrated sulphuric acid in presence of acetic anhydride with these pyrrole derivatives leads to the rapid formation of products ranging from yellow to violet in colour.

EXPERIMENTAL

Reagents

Stock solutions of the pyrrole derivatives were prepared by dissolving 10–15 mg of the compound (analytical grade) in acetic anhydride and making up to the mark in 50-ml standard flasks.

Procedure

A 2-ml aliquot of stock solution was transferred to a 25-ml standard flask, 1 or 2 drops of concentrated sulphuric acid were added and the mixture was allowed to stand for about 5 min, then gently shaken and made up to the mark with chloroform for indole or carbon tetrachloride (except for indole). The absorbance was measured against a reagent blank at the appropriate wavelength.

Calibration curves were prepared by treating various aliquots of standard solutions as described.

Table 1. Absorption maxima of the reaction products

Compound	Colour	λ_{max}, *nm*
Indole	Violet	350
Carbazole	Blue	315
Indole-3-propionic acid	Violet	290
Indole-3-butyric acid	Light yellow	308

RESULTS AND DISCUSSION

Between 5 and 35 mg of indole, indole-3-propionic acid, indole-3-butyric acid and carbazole were determined with a general maximum deviation of 0.2 μg. Beer's law is obeyed up to 40 μg of each compound (in 25 ml of solution). If acetic acid is used in place of acetic anhydride or water instead of chloroform or carbon tetrachloride for dilution the colours formed are less intense. Ethanol cannot be used as solvent because the sulphuric acid reacts with it.

The absorbance of the blank is almost zero and the absorbance of the products is constant for at least 48 hr. The amount of sulphuric acid is not critical, but if dilute sulphuric acid is used, the colours obtained are less intense. The amount of acetic anhydride is also not critical.

The principal virtues of this method are its reproducibility, simplicity and speed.

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Summary—A simple, reliable and rapid method for the spectrophotometric determination of some pyrrole derivatives with concentrated sulphuric acid has been developed. The results show a maximum deviation of about 0.2 μg.

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DETERMINATION OF AMINOCRESOL ISOMERS BY HIGH-SPEED LIQUID CHROMATOGRAPHY

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The intramolecular migration of aromatic ring substituents (NIH shift), which occurs during hydroxylation by cytochrome P-450 mono-oxygenases had been observed usually from the NIH shift of deuterium, tritium or chloride.[1] The NIH shift of an alkyl group has also been found to occur in liver microsomes.[2] It may be considered that *p*-toluidine is a simple compound for a model substrate to observe the occurrence of methyl migration during hydroxylation.

It is well known that aminophenols can be determined by colorimetric, spectrometric, isotopic or liquid-chromatography methods.[3–7]

The present paper describes simultaneous determination of aminocresol isomers by use of a commercially available high-speed liquid chromatograph. This method was applied to the aminocresols and *p*-aminophenol formed by the model system of cytochrome P-450, for evaluating the capability of the chemical model system to detect the NIH shift occurring during hydroxylation.[8]

EXPERIMENTAL

High-speed liquid chromatography

A Du Pont Model 840 liquid chromatograph equipped with an ultraviolet detector (254 nm) was employed. The column was a Du Pont analytical column packed with Zipax SCX (1 m × 2.1 mm i.d.). The separation of aminocresol isomers was achieved with H_3PO_4–KH_2PO_4 buffer solution of various pH values as mobile phase, at 25° and a flow-rate of 0.64 ml/min. Samples of 10 μl were injected directly into the column through the septum.

Chemicals

4-Hydroxy-*m*-toluidine [I], 3-hydroxy-*p*-toluidine [II], 2-hydroxy-*p*-toluidine [III] and *p*-aminophenol, used as standards, were purified by sublimation before use. Haemin chloride and all other reagents were of analytical-reagent grade. The acetone used for reaction and the ether and chloroform for extraction were redistilled.

Reaction mixture

The reaction mixture used as a model system contained the following reagents; cysteine $10^{-1}M$, haemin chloride $10^{-3}M$, *p*-toluidine $10^{-1}M$, and sodium hydroxide. The reaction mixture was adjusted to 10 ml with acetone (80%), and the pH to 4. The mixture was vigorously shaken in an air atmosphere, at 40°, and stopped after 2 hr by addition of 0.5 ml of $2M$ hydrochloric acid.

Separation of aminocresols from reaction mixture

Aminocresols formed by the model system were extracted from the reaction mixture according to the separation method developed by Brodie.[9]

After evaporation of the acetone in the reaction mixture, at reduced pressure and a temperature below 40°, the remaining aqueous solution was saturated with sodium chloride, the pH adjusted to 7.5 and the solution shaken with 25 ml of ether. The ether layer (20 ml) was shaken with 3 ml of $0.1M$ hydrochloric acid, and the acid phase (2 ml), after separation, was extracted with an equal volume of chloroform to remove the excess of *p*-toluidine and the remaining ether, and then analysed.

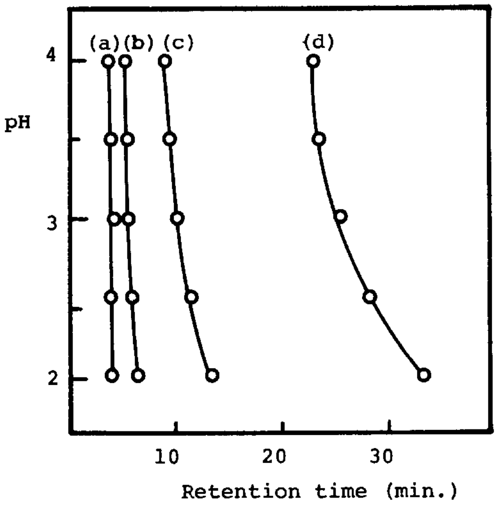

Fig. 1. Effect of pH of mobile phase on retention time of aminocresol isomers and *p*-aminophenol. Eluent $0.1M$ H_3PO_4–$0.1M$ KH_2PO_4; flow-rate 0.64 ml/min; column temperature 25° (a) *p*-Aminophenol, (b) 4-hydroxy-*m*-toluidine [I], (c) 3-hydroxy-*p*-toluidine [II], (d) 2-hydroxy-*p*-toluidine [III].

RESULTS AND DISCUSSION

Selection of mobile phase

Aminocresol isomers and *p*-aminophenol were separated with mobile phases consisting of $0.1M$ H_3PO_4–$0.1M$ KH_2PO_4 buffer solutions at pH 2.0, 2.5, 3.0, 3.5 and 4.0. In Fig. 1, it is seen that with a mobile phase of high pH, the time needed for separation of the four compounds was reduced but the resolution was inadequate, whereas, with a low-pH buffer solution the resolution was satisfactory but the time for separation longer. Hence pH 3 was chosen as a suitable compromise. With various concentrations of phosphate buffer (0.02, 0.05, 0.1, 0.3 and $0.5M$) as mobile phase, the four compounds were separated at pH 3. Figure 2 shows that high concentrations give fast but poor separation whereas low concentrations give good but slow separation. Hence a $0.1M$ buffer was chosen as eluent.

In Fig. 3, a chromatographic separation of three aminocresols and *p*-aminophenol is shown. The resolution values (R_s) of the adjacent peaks, *i.e.*, between the *p*-aminophenol peak and [I], between [I] and [II], and between [II] and [III], were 1.5, 4, and 5.4, respectively. As resolution in

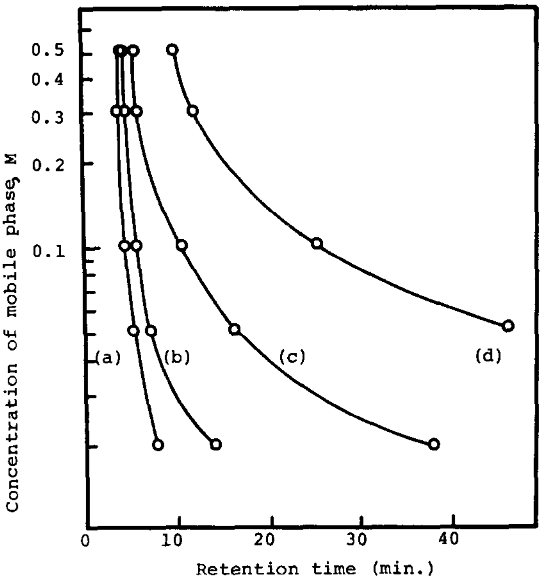

Fig. 2. Retention time of aminocresol isomers and *p*-aminophenol at various concentrations of mobile phase. Conditions are the same as those given for Fig. 1. (a) *p*-Aminophenol, (b) [I], (c) [II], (d) [III].

high-speed separation is adequate when R_s is greater than unity,[10] the separation conditions for Fig. 3 were used for the determination of the four compounds.

Determination of reaction products

Figure 4 shows a typical chromatogram obtained from the reaction mixture. It was confirmed that *p*-toluidine was hydroxylated by the model system, the products being mainly [I], [II] and [III]; only a trace amount of *p*-aminophenol was detected. The result agreed with that obtained by thin-layer chromatography (cellulose:silica gel G = 5:2; eluent butyl ether–ethyl acetate–acetic acid 50:50:5; detection by iodine vapour; R_f values [I] 0.11, [II] 0.33, [III] 0.41, *p*-toluidine 0.61).

For determination of [I], [II] and [III], a known amount of standard sample dissolved in 0.1*M* phosphate buffer (pH 7.5) was subjected to the procedure. In this case a known amount of cysteine (65 mg) was added to the buffer solution in order to give the same conditions as for the reaction mixture. The amounts and peak-heights of [I], [II], [III] and *p*-aminophenol gave a straight line relationship over the range studied (0–600 μg). The recovery was >95%. The method gave accurate and reproducible results.

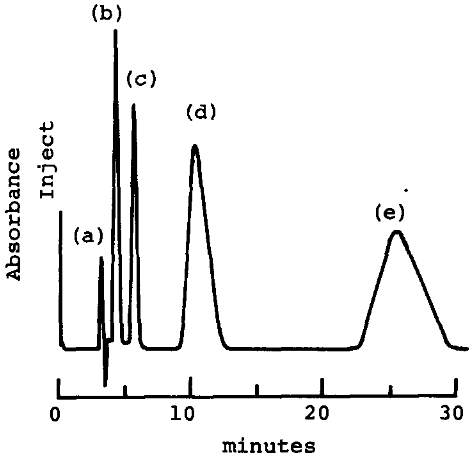

Fig. 3. Chromatogram for the separation of aminocresol isomers and *p*-aminophenol. Eluent 0.1*M* H_3PO_4–KH_2PO_4 (pH 3); flow-rate 0.64 ml/min; column temperature 25°. (a) Solvent front, (b) *p*-aminophenol, (c) [I], (d) [II], (e) [III]

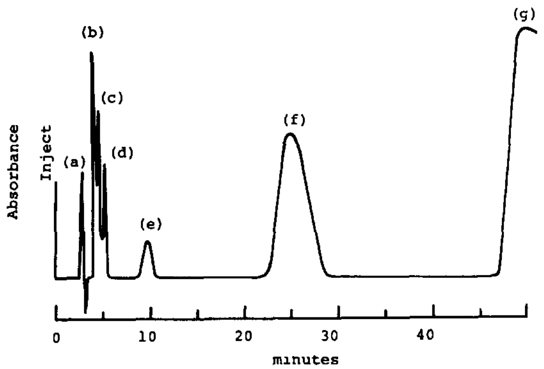

Fig. 4. Typical chromatogram of extracted reaction mixture. The reaction vessel contained, in a total volume of 10 ml (80% acetone), *p*-toluidine $10^{-1}M$, haemin chloride $10^{-3}M$ and cysteine $10^{-1}M$, and was incubated for 2 hr at pH 4 and 40° in air. Conditions are the same as those given for Fig. 3. (a) Solvent front, (b) *p*-aminophenol, (c) unknown peak, (d) [I], (e) [II], (f) [III], (g) *p*-toluidine.

Table 1 shows typical results of the hydroxylation of *p*-toluidine by the haemin–cysteine model system, providing positive evidence of methyl migration during hydroxylation of *p*-toluidine.

The method described is suitable for the simultaneous determination of aminocresol isomers in a sample. Further, it may be applied for the detection of aminocresols in biological materials such as liver microsomal fractions, since aqueous samples can be analysed.

Table 1. Methyl migration and hydroxylation of *p*-toluidine by haemin–cysteine model system

pH	[I], μg	[II], μg	[III], μg	*p*-Aminophenol, μg
4	51 ± 4	26	280 ± 31	trace
6	48 ± 7	trace	127 ± 4	trace
7	61 ± 4	trace	120 ± 8	trace

Conditions are the same as those given for Fig. 4. Values are mean ± standard deviation of four experiments.

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Summary—Aminocresol isomers (4-hydroxy-*m*-toluidine [I], 3-hydroxy-*p*-toluidine [II], 2-hydroxy-*p*-toluidine [III]) and *p*-aminophenol have been separated and determined by a high-speed liquid chromatographic method. Since this method is applicable in aqueous media, it was used to investigate the suitability of a haemin–cysteine system as a model for the cytochrome P-450 mono-oxygenase system, by determination of the [I], [II], [III] and *p*-aminophenol formed.

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EXTRACTION CHROMATOGRAPHY OF CHLORIDE COMPLEXES OF OSMIUM (III, IV AND VI) ON PAPER TREATED WITH TRIBUTYL PHOSPHATE AND AMBERLITE LA-1 HYDROCHLORIDE

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Osmium and ruthenium are usually separated from other platinum metals by oxidation to the volatile oxides OsO_4 and RuO_4 and distillation. The absorption of osmium tetroxide in hydrochloric acid leads to the formation of various chloride complexes of osmium, depending on the concentration of the acid and on the temperature.[1,2] The literature on the chromatographic separation of osmium complexes is somewhat scanty. Apart from the papers describing the separation of platinum metals, including osmium(IV)[3–5] or osmium(VIII),[6] there are only a few works concerned with the separation of some osmium(IV) or osmium(VI) halide complexes. Using paper chromatography, Rallo[7] separated the complex anion OsI_6^{2-} from mixed chloride–iodide complexes of osmium(IV) formed during reduction of OsO_4 by alkali metal iodides in hydrochloric acid media. Meier *et al.* investigated the chromatographic behaviour of the complex anions $OsCl_6^{2-}$, $OsBr_6^{2-}$ and $OsO_2Cl_4^{2-}$, developing the chromatograms with mixtures of oxo-solvents with hydrochloric or hydrobromic acid[8] or with aqueous solutions of hydrochloric acid and ammonium or alkali metal chloride.[9]

Extraction chromatography on paper treated with Amberlite LA-1 hydrochloride has been found to be useful in the separation of some platinum metals;[10] therefore the possibility of use of this chromatographic technique in separation of the chloride complexes of osmium(III, IV and VI) and in separation of osmium from ruthenium was investigated in the present work.

EXPERIMENTAL

Materials

Amberlite LA-1 and tributyl phosphate (TBP) were used as the extractants without further purification. The samples were spotted as 1% solutions of $(NH_4)_2OsCl_6$ in 6*M* hydrochloric acid and aqueous solutions of OsO_4. Solutions of the chloride complexes of osmium(VI) and osmium(III) were prepared by methods described in the literature.[1,2,11] The remaining reagents were of analytical grade.

Procedure

Benzene solutions (0.2*M*) of TBP or Amberlite LA-1 hydrochloride were used as impregnating solutions. Amberlite LA-1 was converted into the hydrochloride by shaking a 0.2*M* solution of it in benzene with an equal volume of 1*M* hydrochloric acid, separating the phases and filtering the organic phase through cellulose. The paper chromatography was performed in the manner described previously.[10] Descending development over a distance of 16 cm required from 2 hr 10 min to 3 hr, depending on the hydrochloric acid concentrations in the mobile phase. The complex anion $OsCl_6^{2-}$ forms a well-defined yellow spot on the chromatograms, which reacts very slowly with thiourea, changing to rose. The spots of other chloride complexes of osmium and also those of ruthenium were identified by spraying the chromatograms with a saturated solution of thiourea in 1*M* hydrochloric acid.

RESULTS AND DISCUSSION

The most promising extractants for the platinum metals appeared to be high molecular-weight amines or quaternary ammonium compounds and neutral organophosphorus compounds; some of them have been used in extraction of the chloride complexes of osmium. The complex anion $OsCl_6^{2-}$ is strongly extracted by tertiary and secondary amines from hydrochloric acid[12,13] as well as in a lesser degree by solutions of TBP in organic solvents.[14] The extraction of the complex anion $OsO_2Cl_4^{2-}$ from hydrochloric acid by primary, secondary and tertiary amines was investigated by Bolshakov *et al.*[15]

Liquid–liquid extraction and extraction chromatography are closely correlated practically as well as theoretically.[16] The R_F *vs.* eluent hydrochloric acid concentration relationships for extraction chromatography are available only for the anion $OsCl_6^{2-}$ on paper treated with tri-n-octylamine and Amberlite LA-2[17] and for the oxy-anion OsO_5^{2-} on thin layers of cellulose treated with TBP.[6] In view of the very high affinity of $OsCl_6^{2-}$ for tri-n-octylamine hydrochloride ($R_F = 0$ even at high concentrations of hydrochloric acid in the mobile phase), the chromatographic systems Amberlite LA-1–HCl and TBP–HCl were chosen in our investigations. The results obtained for chloride complexes of osmium are summarized in Table 1 (and presented graphically in the form of R_F *vs.* [HCl] relationships in Fig. 1). Table 1 also gives the chromatographic data

Summary—Aminocresol isomers (4-hydroxy-*m*-toluidine [I], 3-hydroxy-*p*-toluidine [II], 2-hydroxy-*p*-toluidine [III]) and *p*-aminophenol have been separated and determined by a high-speed liquid chromatographic method. Since this method is applicable in aqueous media, it was used to investigate the suitability of a haemin–cysteine system as a model for the cytochrome P-450 mono-oxygenase system, by determination of the [I], [II], [III] and *p*-aminophenol formed.

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EXPERIMENTAL

Materials

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Table 1. $R_F \times 100$ for chloride complexes of osmium and ruthenium as a function of the molarity of HCl in the eluent (paper impregnated with 0.2*M* solutions of Amberlite LA-1 hydrochloride or tributyl phosphate in benzene)

Complex anion	Amberlite LA-1 [HCl], *M*						TBP [HCl], *M*					
	1	2	4	6	8	10	1	2	4	6	8	10
$OsCl_6^{2-}$	0	0	0	2	8	10	58	34	24	26	30	36
$OsCl_6^{3-}$	3	4	6	11	17	21	24	16	12	8	14	20
$OsO_2Cl_4^{2-}$	0	0	2	4	8	—	40	40	30	34	42	52
OsO_4^*	I 0 II 3	I 0 II 4	I 2 II 6	I 4 II 12	I 8 II 17	I 10 II 20	—	—	—	30	44	54
$RuCl_6^{3-}$	—	30–70 ↔	70↑	76	88	86	88	90	88	88	90	86
$RuCl_6^{2-}$	82↑	80↑	80↑	74	86	86	88	88	90	86	90	80

* Double spots in the Amberlite LA-1 system.

for the chloride complexes of ruthenium(III and IV) which are formed during absorption of RuO_4 by hydrochloric acid.

All chloride complexes of osmium are strongly retained on paper treated with Amberlite LA-1 hydrochloride; nevertheless, $OsCl_6^{2-}$ was found to have a higher affinity than $OsCl_6^{3-}$ for the amine salt. The R_F values of all the complexes of osmium investigated increase (decreasing extraction) with increasing concentration of hydrochloric acid in the eluent, in agreement with liquid–liquid extraction data.[11,12,14] The differences between the R_F values of the complex anions $OsCl_6^{2-}$ and $OsO_2Cl_4^{2-}$ are too low to permit their separation; nevertheless it is possible to separate osmium(III) from osmium(IV) or osmium(VI) complexes by development of the chromatograms with 8 or 10*M* hydrochloric acid. Chloride complexes of ruthenium(III) and in a lesser degree those of ruthenium(IV) form elongated spots in this chromatographic system at [HCl] < 6*M*. It is possible to achieve a good separation of osmium from ruthenium by development of the chromatograms with more concentrated hydrochloric acid. It is worthwhile mentioning the chromatographic behaviour of osmium tetroxide on paper treated with Amberlite LA-1 hydrochloride—two rose spots were visible after development with 6—10*M* hydrochloric acid and spraying with thiourea in hydrochloric acid, their R_F values corresponding to $OsCl_6^{3-}$ and $OsO_2Cl_4^{2-}$. It seems that OsO_4 is strongly bound by the amine salt and reduced during elution with hydrochloric acid, in contrast to the TBP–HCl chromatographic system where osmium could not be identified after development with dilute hydrochloric acid (< 6*M*) owing to the high volatility of OsO_4.

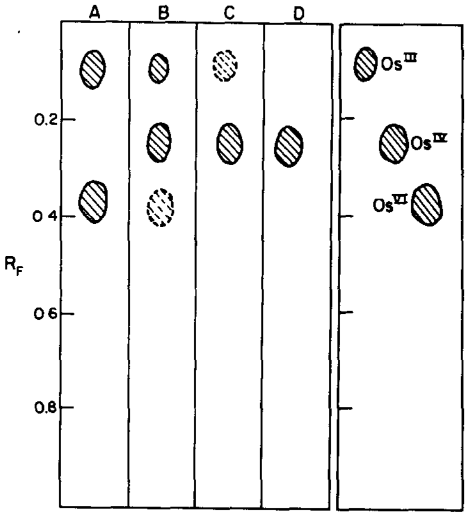

Fig. 1. Chromatographic separations of products of reduction of OsO_4 in concentrated HCl, obtained on paper impregnated with 0.2*M* TBP in benzene and eluted with 6*M* HCl: A—solution spotted immediately after dissolution of OsO_4 in cold concentrated HCl; B—the same, after 5 min heating on the water-bath; C—the same, after 30 min heating; D—solution obtained after evaporation of the solution of OsO_4 in concentrated HCl almost to dryness on the water-bath and dissolution of the residue in 6*M* HCl.

The chloride complexes of osmium(III, IV and VI) have distinctly different R_F values in extraction chromatography on paper treated with TBP, increasing in the order $OsCl_6^{3-} < OsCl_6^{2-} < OsO_2Cl_4^{2-}$. The curves of R_F *vs.* [HCl] show minima (maximal extraction) at 4*M* hydrochloric acid for $OsCl_6^{2-}$ and $OsO_2Cl_4^{2-}$ and at 6*M* hydrochloric acid for $OsCl_6^{3-}$. The maximal extraction of osmium(IV) in the system TBP–HCl was also reported by Meier *et al.*,[14] so our experiments confirm the analogies between extraction chromatography and liquid–liquid extraction. The chloride complexes of neither ruthenium(III) nor ruthenium(IV) are retained on paper treated with TBP and they can be easily separated from the chloride complexes of osmium.

The different R_F values of the various chloride complexes of osmium obtainable in the TBP–HCl system, combined with the colours of the zones (only $OsCl_6^{2-}$ forms a yellow zone, the others are colourless) and the rapidity of the reaction with thiorea, can be useful in identification of the oxidation states of osmium and in investigations of the reduction mechanism of osmium tetroxide in solution. The behaviour on evaporation of osmium tetroxide dissolved in concentrated hydrochloric acid is also interesting from the viewpoint of the conditions of preparation of platinum metal samples for chromatographic analysis; therefore some chromatographic experiments were carried out on solutions of OsO_4 in concentrated hydrochloric acid, heated for various periods of time on the water-bath (Fig. 1).

The results obtained indicate that OsO_4 absorbed by the cold concentrated acid is reduced to $OsO_2Cl_4^{2-}$ and $OsCl_6^{3-}$. After heating of the solution a yellow spot of $OsCl_6^{2-}$ appears, the colour intensity of which increases with time of heating, whereas the intensities of colour of the spots corresponding to $OsCl_6^{3-}$ and $OsO_2Cl_4^{2-}$ (visible after spraying with thiourea in hydrochloric acid) decrease. After evaporation of the acidic solution to dryness and dissolution of the residue in 6*M* hydrochloric acid, only the yellow spot of $OsCl_6^{2-}$ is visible. It seems that $OsO_2Cl_4^{2-}$, one of the products of reduction of OsO_4 by hydrochloric acid, oxidized the complex anion $OsCl_6^{3-}$, forming the most stable inert complex anion $OsCl_6^{2-}$.

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Summary—The complex anions $OsCl_6^{2-}$, $OsO_2Cl_4^{2-}$ and $OsCl_6^{3-}$ were separated by extraction chromatography on paper treated with tributyl phosphate and developed with hydrochloric acid. The chloride complexes of osmium and ruthenium can also be separated in the system TBP–HCl or Amberlite LA-1 hydrochloride–HCl.

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THE DETERMINATION OF SELENIUM AND OTHER IMPURITIES IN HIGH-PURITY COPPER BY FLAMELESS ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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The determination of traces of selenium in high-purity copper is of importance because of the effect of this element on the annealing properties. The methods of analysis in common use in the copper industry involve separation of the selenium from the dissolved copper by ion-exchange,[1] co-precipitation with ferric hydroxide[2] or lanthanum hydroxide,[3] or reduction by hypophosphorous acid and co-precipitation with arsenic.[4] The separated selenium is determined either colorimetrically using 3,3′-diaminobenzidine[5] or by atomic absorption. These procedures are slow and require skill and practice. Other techniques, such as gas chromatography[6] or hydride generation[7] appear impracticable with copper as the parent material.

A method has been devised involving co-precipitation of selenium, together with bismuth, antimony and tellurium, with ferric hydroxide and collection of the precipitate on a filter paper disc. Punched out portions of the dried disc are analysed by flameless atomic-absorption spectrophotometry (F.A.A.S.) Proficiency in the technique is soon acquired and results can be obtained within little more than an hour of sample receipt.

EXPERIMENTAL

Apparatus

A Varian Model AA-4 spectrophotometer with Model 63 carbon rod atomizer and an Oxford Instruments 3000-series chart-recorder were used.

Reagents

Ferric nitrate solution, 2%.

Standard Bi, Sb and Te solutions for atomic absorption. B.D.H. solutions were used.

Stock solution of selenium, 1000 *ppm*. Made by dissolving 1 g of pure Se in 10 ml of nitric acid and diluting to 1000 ml with distilled water.

*Whatman CF*11 *cellulose powder.*

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Purified copper solution. Five 20-g samples of cathode copper drillings are each dissolved in 80 ml of nitric acid in 600-ml beakers, 20 ml of ferric nitrate solution are added to each, the solutions are diluted with water to *ca.* 300 ml and the temperature is raised to 75–85°. Concentrated ammonia is added, with stirring, until the solutions become dark green, a level spatula-spoonful of Whatman's CF11 is added as filter aid and the solutions are brought to the boil. After half a minute of boiling the covered beakers are set aside overnight to allow the coagulated ferric hydroxide and occluded impurities to settle, after which the blue supernatant liquor is decanted through a 541 filter paper. The precipitation and filtration procedure are repeated twice with further additions of ferric nitrate, the five liquors combined, acidified with 10 ml of concentrated nitric acid and made up to 2 litres with distilled water.

Analytical-grade reagents were used whenever possible.

Acknowledgement—Thanks are due to Prof. Dr. E. Soczewiński for helpful discussions and for his interest in this work.

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Summary—The complex anions $OsCl_6^{2-}$, $OsO_2Cl_4^{2-}$ and $OsCl_6^{3-}$ were separated by extraction chromatography on paper treated with tributyl phosphate and developed with hydrochloric acid. The chloride complexes of osmium and ruthenium can also be separated in the system TBP–HCl or Amberlite LA-1 hydrochloride–HCl.

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THE DETERMINATION OF SELENIUM AND OTHER IMPURITIES IN HIGH-PURITY COPPER BY FLAMELESS ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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(*Received* 5 *April* 1976. *Accepted* 1 *May* 1976)

The determination of traces of selenium in high-purity copper is of importance because of the effect of this element on the annealing properties. The methods of analysis in common use in the copper industry involve separation of the selenium from the dissolved copper by ion-exchange,[1] co-precipitation with ferric hydroxide[2] or lanthanum hydroxide,[3] or reduction by hypophosphorous acid and co-precipitation with arsenic.[4] The separated selenium is determined either colorimetrically using 3,3′-diaminobenzidine[5] or by atomic absorption. These procedures are slow and require skill and practice. Other techniques, such as gas chromatography[6] or hydride generation[7] appear impracticable with copper as the parent material.

A method has been devised involving co-precipitation of selenium, together with bismuth, antimony and tellurium, with ferric hydroxide and collection of the precipitate on a filter paper disc. Punched out portions of the dried disc are analysed by flameless atomic-absorption spectrophotometry (F.A.A.S.) Proficiency in the technique is soon acquired and results can be obtained within little more than an hour of sample receipt.

EXPERIMENTAL

Apparatus

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Reagents

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Purified copper solution. Five 20-g samples of cathode copper drillings are each dissolved in 80 ml of nitric acid in 600-ml beakers, 20 ml of ferric nitrate solution are added to each, the solutions are diluted with water to *ca.* 300 ml and the temperature is raised to 75–85°. Concentrated ammonia is added, with stirring, until the solutions become dark green, a level spatula-spoonful of Whatman's CF11 is added as filter aid and the solutions are brought to the boil. After half a minute of boiling the covered beakers are set aside overnight to allow the coagulated ferric hydroxide and occluded impurities to settle, after which the blue supernatant liquor is decanted through a 541 filter paper. The precipitation and filtration procedure are repeated twice with further additions of ferric nitrate, the five liquors combined, acidified with 10 ml of concentrated nitric acid and made up to 2 litres with distilled water.

Analytical-grade reagents were used whenever possible.

Table 1. Operating conditions for spectrophotometer

Element	Wavelength, *nm*	Spectral band width, *Å*	Ashing		Atomization	
			Voltage setting	*sec*	Voltage setting	*sec*
Se	196.1	9.9	7	12	7	3
Te	214.3	3.3	7	12	7	3
Bi	223.1	1.7	7	12	5.5	3
Sb	217.6	3.3	7	12	8	3

Procedures

Standards. To 20-ml portions of the purified copper solution in 150-ml beakers are added 0, 1, 2, 4 or 6 ml of a freshly prepared solution containing 0.5 ppm Se and Sb and 0.25 ppm, Bi and Te, followed by 1 ml of ferric nitrate solution and water to make up to 80 ml. The solutions are brought almost to boiling point, concentrated ammonia solution is added carefully until they turn green, 0.01 g of Whatman CF11 is added and the ferric hydroxide is coagulated by boiling for half a minute. After settling for 15 min the sediments are collected on 542 discs in Gooch crucibles by filtration under suction. To ensure an even deposit on the disc most of the supernatant liquor is decanted through the filter, the suction is removed, and the residue is swirled and poured quickly into the crucible. Gentle vibration is applied throughout, by such means as holding the rotating shaft of a stirrer motor against the crucible. After the precipitate has settled in the crucible the suction is re-applied and the disc finally washed carefully with 1 ml of water from a pipette. The discs are dried at 100° before their analysis.

Samples. One-gram samples are dissolved in 5 ml of concentrated nitric acid, 1 ml of ferric nitrate solution is added to each and the same procedure followed as for the standards.

Instrument operation. The appropriate monochromator wavelengths, spectral band-widths and instrument settings are shown in Table 1.

A graphite cup is used as furnace in the atomizer work head and oxygen-free nitrogen as the inert gas. After decontamination of the cup by preliminary atomization cycles 5/64-in. (2-mm) samples punched from the filter disc are dropped into it and subjected to the appropriate ashing and atomization cycles. The absorbances are recorded at a chart-speed of 2 cm/min and recorder sensitivity of 2 mV full-scale deflection. For highest accuracy, duplicate precipitate discs should be prepared and a number of replicate samples atomized, interspersed among standards.

RESULTS AND DISCUSSION

Results

Past experience had shown that although ferric hydroxide reproducibly collected selenium and many other impurities from copper solutions at a pH of 2.5–3.0, only about 90% was collected in one precipitation. The treatment of the standards in the same way as the samples obviated the need for more than one precipitation. For example, when three 0.5-μg amounts of selenium were precipitated and six samples from across the diameter of each disc were analysed, the relative standard deviations ranged from about 7 to 10%.

Figure 1 represents a typical series of recorder traces for 0, 0.25, 0.5 1.0 and 1.5 μg selenium standards. A large smoke signal occurs during ashing as the cellulose pyrolyses. A dull red heat (ashing voltage setting 7) is required for complete ashing but no loss of any of the four elements occurs. The blank atomization peak is higher for selenium than for the other elements. Use of the hydrogen continuum lamp showed that this was caused by background absorption.

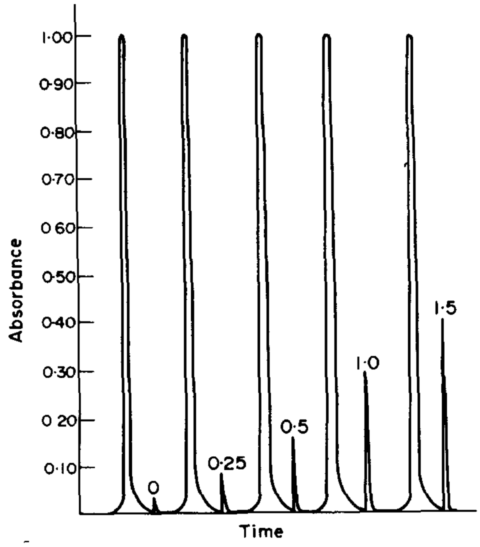

Fig. 1. Recorder traces for selenium (number of μg is shown above each peak).

Comparison of results obtained for selenium in high-purity copper by this method, by the conventional colorimetric method and by mass spectrometry show good agreement (Table 2).

A sample of electrolytic copper from the European Bureau of Standards was also analysed, and gave a mean of 0.12 ppm Se, standard deviation 0.04 ppm (duplicate precipitations, 4 analyses on each), compared with a range of quoted figures of 0.14–0.46 ppm Se, mean 0.22 ppm (9 laboratories, 4 techniques).

Typical absorbance curves for the Bi, Sb and Te standards are shown in Fig. 2.

No samples with well-established tellurium content were available and there was only one, namely the European

Table 2. Comparison of Se results (ppm) obtained by proposed method with those obtained by colorimetry and mass spectrometry

Sample	Proposed method	Colorimetry	Mass spectrometry
Rod 1	0.40	0.35	
Rod 2	0.95	0.8	
Rod 3	0.75	0.8	
Rod 4	2.2	2.0	
Cathode 1	0.50		0.6
Cathode 2	0.40		0.3

Table 3. Comparison of Bi results (ppm) obtained by proposed method by other methods

Sample	Proposed method	Other methods
BICC standard 1	0.45	0.42 (powder arc spectrography)
BICC standard 2	0.90	0.8 (powder arc spectrography)
European bureau of standards copper	0.12	Mean 0.2 ppm (range 0.046–0.53 ppm, 9 laboratories, 4 techniques)

Bureau of Standards sample, with quoted antimony figures [mean content 0.6 ppm with a range of 0.2–1.42 ppm (11) laboratories, 6 techniques)]. The result obtained by the proposed procedure was 0.56 ppm (s.d. 0.04 ppm, 2 precipitations, 4 atomizations on each). Three samples were available for comparison of bismuth content and the results are given in Table 3.

The sensitivity of the method and non-linearity of the curves (illustrated by Fig. 2) show the method to be most suitable for impurity levels below about 1 ppm. The upper limit can be extended by using a 0.5-g sample, no significant difference having been observed in the results obtained for impurities precipitated from 1-g and 0.5-g copper samples. With less than 0.5 g of copper in solution the ferric hydroxide precipitate tends to be too flocculent to spread evenly over the filter disc. A method of extending the upper limit which is often preferable is to use a less sensitive spectral line such as the 203.9 nm line for selenium.

The satisfactory agreement with the colorimetric method for selenium when the 203.9-nm line is used is exemplified by the results for two samples, 4.6 and 12 ppm by the present method, 4.8 and 12.2 ppm by colorimetry.

Interferences

The most likely impurities to interfere with any of the four elements are those co-precipitated with ferric hydroxide, namely, the other three elements and As, Sn, Pb. These are unlikely to be present at a level of more than 20 ppm in high-purity copper and no interference was observed at this level. During the precipitation stage small amounts of copper hydroxide may also precipitate, indicated by a cloudiness of the supernatant liquor. The presence of this amount of copper on the filter disc does not interfere with the determination.

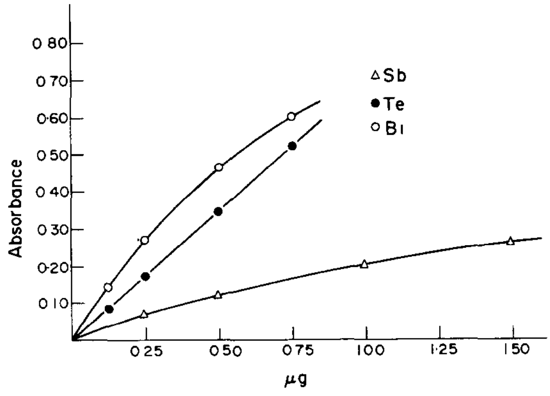

Fig. 2. Calibration curves for Sb, Te and Bi at 217.6, 214.3 and 223.1 nm respectively.

Discussion

The use of F.A.A.S. for direct determination of selenium in solutions of high-purity copper is impracticable because of both the high detection limits and the masking of the selenium absorption peak by large non-atomic absorption peaks. The same problem occurs to a lesser extent with the other three elements. Reduction of the selenium in solution to the metal and co-precipitation with arsenic is slow and the F.A.A.S. part of the procedure erratic. Although concentration by co-precipitation with lanthanum hydroxide has been used successfully for the determination of larger amounts of impurities the technique was found to be unsuccessful with F.A.A.S. owing to the occurrence of a large lanthanum peak during atomization.

Co-precipitation with ferric hydroxide is difficult on the large scale but quite simple from solutions of 1 g of copper. Precipitation at a pH of approx. 3 rather than from ammoniacal solution gives a residue which spreads more uniformly over the filter disc. The amounts of ferric nitrate solution and Whatman CF11 specified are the optimum for the production of a readily filterable solution and an even, coherent deposit on the filter.

The method has been in routine use for a year and has resulted in considerable savings of time and effort. Attempts to determine arsenic by this procedure have proved unsuccessful owing to high extraneous peaks during atomization and erratic response for the arsenic. A modified technique is being developed, with promising results.

Acknowledgements—The author wishes to express his thanks to Messrs. R. Evans, W. Price and D. Reeves for assistance with the experimental work and to the Directors of BICC Metals Ltd. for permission to publish this paper.

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Summary—Se, Te, Bi and Sb are co-precipitated with ferric hydroxide from a solution of 1 g of the copper. The precipitate is collected on a filter disc and punched samples are taken for flameless atomic-absorption analysis. Less than 0.5 ppm of the four elements can be rapidly determined.

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APPLICATION OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—III

EXTENSION OF CALIBRATION CURVES

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The useful range of analytical calibration curves in flame atomic-absorption spectroscopy (AAS), assuming normal instrumental alignment, is limited to an upper analyte solution concentration of 10–100 ppm. Some extension may be obtained by use of less strongly absorbing atomic lines, such as the 2614 Å line for lead. In some instances, useful extensions may be achieved by use of non-resonance lines. Thus Thompson[1] has described the determination of calcium at concentrations up to 1500 ppm by use of the germanium 4226.57 Å line. Similarly Dagnall *et al.*[2] have examined the fluorescence of bismuth at 2061.2 Å excited by the 2061.63 Å line from an iodine electrodeless discharge lamp. Norris and West[3] have tabulated a number of potential spectral interferences in AAS which in principle could be used in an analogous manner.

In these techniques, the spectrometer requires some adjustment specific to the individual element considered, before the high concentration section of the calibration curve can be obtained. In addition, suitable low-sensitivity lines are available for only a limited number of elements, and even in these cases the range extension available is governed by the spectroscopic parameters of the system, rather than being subject to operator control.

The present work describes a generally applicable technique by which an extended range calibration curve may be obtained by using the Zeeman affect. Single beam AAS measurements are made on the σ-components of the Zeeman multiplet. The σ-components are displaced into the wings of an analyte absorption profile to an extent governed by the magnitude of the applied magnetic field, as in the measurement of line profiles by Zeeman scanning.[4–6] Thus the upper limit of the calibration curve may be extended simply by increasing the magnetic field strength, without moving the spectrometer off the optimum resonance line for the particular element considered. Since the σ-components may be selected electronically, the extension of range thus obtained may be controlled readily with either manual or automated instrumentation.

EXPERIMENTAL

The elements chosen for examination were Ca, Cd and Cu, the 4227, 2288 and 3248 Å lines being used. At the magnetic field strengths available, these lines show respectively a normal Zeeman triplet, a normal triplet with hyperfine structure, and an anomalous multiplet. The spectrometer used was that described in a previous communication.[7] The instrument was set up and operated as previously described, except that the amplifier was balanced to pass only signals generated by the σ optical channel. All instrumental parameters (lamp-current, monochromator slit-width, photomultiplier voltage, *etc.*) were optimized for each element to give the best zero-field sensitivity, and were left unaltered as the field strength was increased. The spectral sources used were modifications of an earlier design.[8] All anode electrodes were cut from 0.01-in. zirconium sheet (Alpha Products); copper and cadmium electrodes were prepared from copper foil and cadmium-coated copper foil as described previously.[8] The calcium electrode was prepared by immersing 1-mm^2 mesh stainless-steel gauze in fused calcium chloride and filing the cooled salt coating flush with the original mesh surface. During operation, sufficient metal was thus exposed to permit formation of a stable plasma, while volatilization of the deposited calcium chloride provided the required source of calcium atoms in the vapour phase. This technique is convenient for preparing cathodes for chemically reactive elements, and gives an operational lifetime comparable to that of the metallic cathodes used previously (the calcium lamp used here is still operable after some 0.5 ampere-hours). However the intensity was found to be only about 1% of that of a commercial source for a given power dissipation.

To assemble each lamp, platinum wire was attached to the base of each electrode. Electrodes were separated by 1-mm thick horseshoe-shaped insulators (Fig. 1) which were cut from 1/2" diameter silica discs. The whole assembly was mounted in a preformed Pyrex glass case (Fig. 1), with copper shims inserted behind the anode to hold the assembly in place. Silica capillary insulators were pushed over the platinum wires and the wires sealed into the case. A silica window was attached to the front of the lamp with epoxy resin cement. The lamps were conditioned and sodium deposited as described previously.[8]

This procedure extends lamp shelf-life almost indefinitely. In addition it improves lamp intensity because of reduced quenching within the plasma through the use of silica insulators.

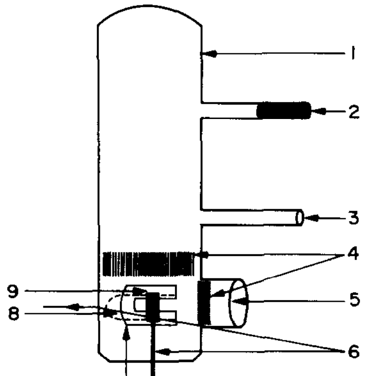

Fig. 1. Lamp assembly: 1—Pyrex lamp casing, 2—sodium, 3—side-arm for evacuation, 4—tapered regions, 5—quartz window, 6—platinum wire connectors, 7—quartz horseshoe insulator, 8—zirconium anode, 9—cathode.

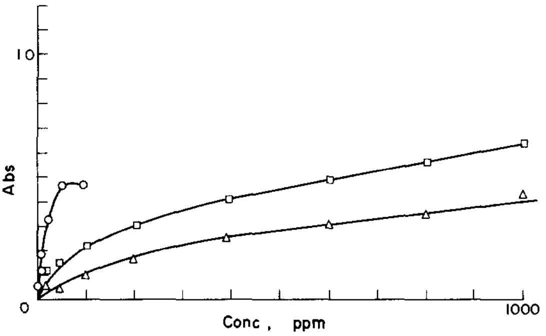

Fig 2. Calibration curves for calcium: ○ zero field, □ 6.6 kG, △ 15 kG.

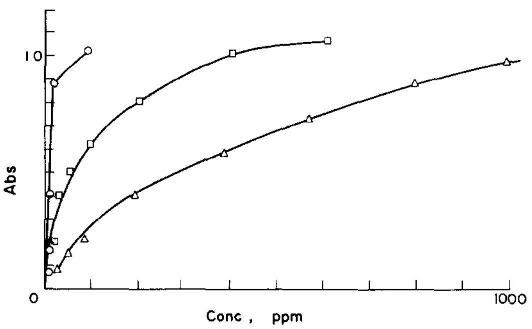

Fig. 4. Calibration curves for copper: ○ zero field, □ 6.6 kG, △ 16 kG.

RESULTS AND DISCUSSION

Figures 2–4 show the calibration curves obtained for calcium, cadmium and copper at field strengths from 0 to 16 kG. The extension obtained for cadmium is less than that for calcium or copper. This arises from the larger line-width observed for cadmium, this being due to isotopic hyperfine structure.[9] An analogous effect has been observed during Zeeman background-correction measurements on mercury.[10]

All the calibration curves obtained here show some departures from linearity and this arises from the following causes. De Galan and Samaey have shown that non-linear calibration curves are inherent whenever the monochromator bandpass covers more than one source-line.[11] This is true in the present case, since all the σ-components of the Zeeman multiplet, including hyperfine structure, are transmitted when the present techniques are used. It should, however, be pointed out that this defect is not inherent in the method, since σ_+ and σ_- components are separable, given parallel optical and magnetic axes[4] rather than the mutually perpendicular orientation used for the present study.

With the present orientation, minimum curvature can be expected for singlet transitions without hyperfine structure (*i.e.*, a single atomic line at ν_0 giving a normal Zeeman triplet with two σ-components spaced symmetrically about ν_0). Even in this situation, however, linear plots will not be attained with atmospheric absorption cells, because of the asymmetry in the analyte absorption profile, caused by pressure broadening.

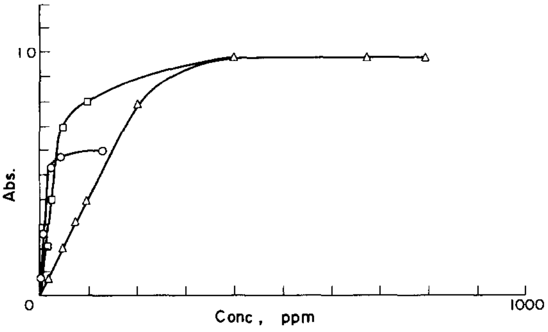

Fig. 3. Calibration curves for cadmium: ○ zero field, □ 6.6 kG, △ 16 kG.

CONCLUSIONS

The technique is of potential value in extending the working range of atomic-absorption spectroscopy. The method is of value for instruments employing the Zeeman effect for background correction, since such instruments can generate ambiguous data owing to the maxima observed in their calibration curves.[7] The present technique thus offers a means whereby such ambiguity may be removed by utilizing signals which are automatically available to any spectrometer of this type.

Acknowledgements—The authors are indebted to the National Research Council of Canada for financial support of this work.

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Summary—An application of the Zeeman effect is described by which calibration curves applicable to high analyte concentrations may be obtained. The procedure uses single-beam measurements on the displaced σ-components of the Zeeman multiplet, and thus permits controlled desensitization of an atomic-absorption signal to be obtained, simply by increasing the magnetic field strength, while leaving the monochromator permanently set on the optimum analytical line for the element considered Calibration curves for Ca, Cd and Cu are given for applied field strengths from 0 to 16 kG.

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SELECTIVE COMPLEXATION OF PALLADIUM AND OSMIUM WITH SUBSTITUTED PYRIMIDINETHIOLS

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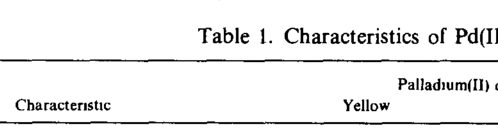
As a continuation of our studies on 1-substituted-4,4,6-trimethyl-1*H*,4*H*-2-pyrimidinethiols as analytical reagents,[1] the applications of the 1-amino- (**I**), 1-anilino- (**II**) and 1-(2′,4′-dinitroanilino)- (**III**) derivatives have been investigated. Of the metals belonging to the iron and platinum groups, only Pd(II) and Os(VIII) react instantly with the present compounds to form coloured complexes, at room temperature. The complexes are extractable into non-polar solvents and may be used for the spectrophotometric determination of the two metals.

EXPERIMENTAL

Reagents

Standard solutions of Pd(II) and Os(VIII) were prepared by dissolving appropriate amounts of anhydrous $PdCl_2$ in 1.0*M* hydrochloric acid and OsO_4 in 1.0*M* sodium hydroxide.

The thiols (**I**) and (**II**) were prepared by the method of Mathes[2] and melted at 209–210° and 170–171° respectively. To synthesize (**III**), 2,4-dinitrophenylhydrazine (3.96 g; 0.02 mole) and 2-methyl-2-isothiocyanato-4-pentanone (3.14 g; 0.02 mole) were taken in 50 ml of ethanol, 3 or 4 drops of conc. sulphuric acid were added and the mixture was refluxed for 5 hr on a steam-bath. The solvent was removed under reduced pressure and the residue washed with water. After 2 or 3 crystallizations from acetic acid, the m.p. was 223–224°. Calculated: C, 46.29%; H, 4.45%; N, 20.77%; found C, 45.9%; H, 5.0%; N, 20.5%.



Standard solutions (0.01*M*) of the ligands were prepared by dissolving appropriate amounts of (**I**) in dimethylsulphoxide (DMSO) and (**II**) and (**III**) in chloroform.

The pH of the solutions were adjusted with acetate buffers and dilute sodium hydroxide solution and hydrochloric acid. All other reagents used were of analytical grade. Demineralized water was used throughout.

RESULTS

The solutions of (**I**) and (**II**) are colourless and do not absorb significantly in the visible region. However, (**III**), being light yellow in colour, absorbs in this region and consequently a reagent blank was used in the complexation study. When a few drops of any of these reagents were added to either Pd(II) or Os(VIII) solution, two distinct coloured complexes appeared, depending upon the pH of the solution. It was established by the method of continuous variations that the metal to ligand ratio was 1:2. Except for the complexes of (**I**), the complexes were completely extractable into chloroform, carbon tetrachloride, benzene or n-butanol, and suitable for extractive determinations. Thiol (**I**) is insoluble in common organic solvents, so it was studied in 60% DMSO medium. The other complexes were investigated in chloroform in which their absorbance was maximum and constant. The characteristics of Pd and Os complexes of (**I**), Pd complexes of (**II**) and (**III**) and Os complexes of (**II**) and (**III**) are summarized in Tables 1, 2 and 3 respectively. The Os-complex, formed in acidic medium, showed a slight shift in λ_{max} towards shorter wavelength with time. The maximum shift was attained after 1 hr at room temperature or heating for 5 min on a steam-bath. Because of the poor solubility of (**I**) and its complexes in common organic solvents (except DMSO), comparative lack of selectivity and low sensitivity (*cf.* Tables 1–3), (**II**) and (**III**) are far better reagents for spectrophotometric determination of Pd(II) and Os(VIII).

Procedure

Adjust the acidity or pH of a Pd(II) or Os(VIII) solution (Table 2 or 3), add 10 ml of 0.02*M* (**II**) or (**III**) (in chloroform) and shake for 20 min. Allow to settle and remove the organic layer. For the determination of Os, keep the extract for 1 hr or heat it for 5 min on a steam-bath, if

Table 1. Characteristics of Pd(II) and Os complexes with thiol (**I**)

Characteristic	Palladium(II) complex Yellow	 Red	Osmium complex Red	 Green
λ_{max}, *nm*	365	480	520–530	675
ϵ_{max}, 10^3 *l mole*$^{-1}$.*cm*$^{-1}$	4.0	1.2	4.0	2.0
Reagent ratio for full colour development	25	10	20	35
Medium for maximum absorbance	0.01–0.75*M* HCl, $HClO_4$, HNO_3 or H_2SO_4	pH 4.5–6.5	0.5–1.5*M* HCl, $HClO_4$, HNO_3 or H_2SO_4	pH 8.0–9.0
Stability in the solvent, *hr*	12	12	24	12
Beer's law upper limit, *ppm*	24	86	40	76
Accurate range of determination, *ppm*	5–20	16–75	10–35	15–68
Sandell sensitivity, *μg/cm*^{2}	0.027	0.090	0.048	0.095
Standard deviation* (from 8 samples)	0.0065	0.0085	0.0089	0.0068

* Of the absorbance for 18.4 ppm of palladium and 19.0 ppm of osmium.

Table 2. Characteristics of Pd(II)-complexes with the thiols (II) and (III)

Characteristic	Palladium(II) complex with (II) Yellow	Red	Palladium(II) complex with (III) Yellow	Green
λ_{max}, *nm*	370	490	440–450	670
ϵ_{max}, 10^3 *l. mole^{-1} cm^{-1}*	7.2	2.0	9.0	2.6
Reagent ratio for full colour development	30	10	50	30
Medium for maximum absorbance	0.01–1.0*M* HCl, $HClO_4$, HNO_3 or H_2SO_4	pH 5.0–6.0	0.1–1.0*N* HCl, $HClO_4$, HNO_3 or H_2SO_4	pH 2.8–6.3
Stability in the solvent, *hr*	5–6	5–6	3–4	3–4
Beer's law upper limit, *ppm*	15	48	12	44
Accurate range of determination, *ppm*	4–14	10–40	3–11	10–39
Sandell sensitivity, *μg/cm^2*	0.015	0.054	0.012	0.041
Standard deviation* (from 8 samples)	0.0048	0.0067	0.0035	0.0052

* Of the absorbance for 10.7 ppm of palladium.

Table 3. Characteristics of Os-complexes with the thiols (II) and (III)

Characteristic	Osmium(VIII) complex with (II) Red	Green	Osmium complex with (III) Red	Blue
λ_{max}, *nm*	520–530	675	480–490	610
ϵ_{max}, 10^3 *l mole^{-1} cm^{-1}*	14.4	8.0	5.6	4.0
Reagent ratio for full colour development	15	25	60	80
Medium for maximum absorbance	0.8–1.8*M* HCl, $HClO_4$, HNO_3 or H_2SO_4	pH 8.0–9.5	0.5–1.5*M* HCl, $HClO_4$, HNO_3 or H_2SO_4	pH 8.5–9.5
Stability in the solvent, *hr*	24	12	12	5–6
Beer's law upper limit, *ppm*	14	23	38	42
Accurate range of determination, *ppm*	3–13	5–20	9–32	10–39
Sandell sensitivity, *μg/cm^2*	0.013	0.024	0.034	0.048
Standard deviation* (from 8 samples)	0.0069	0.0058	0.0076	0.0064

* Of the absorbance for 11.6 ppm of osmium.

Table 4. Tolerance limits (ppm)

	Thiol(II)				Thiol (III)			
	Pd		Os		Pd		Os	
Ion	yellow	red	red	green	yellow	green	red	blue
F^-	10^4	10^4	10^3	10^3	10^4	10^4	10^3	500
I^-	200	100	400	200	200	50	200	50
NO_2^-	500	500	50	50	400	400	50	20
SCN^-	2×10^3	100	100	100	10^3	150	Int	Int.
$S_2O_3^{2-}$	10	10	50	50	10	10	Int	Int
oxalate	5×10^3	5×10^3	2×10^3	2×10^3	2×10^3	2×10^3	2×10^3	10^3
tartrate	5×10^3	5×10^3	200	200	2×10^3	2×10^3	100	50
EDTA	3×10^3	3×10^3	10^3	10^3	2×10^3	2×10^3	10^3	200
PO_4^{3-}, BO_3^{3-}	5×10^3	5×10^3	2×10^3	2×10^3	2×10^3	2×10^3	2×10^3	10^3
citrate	5×10^3	2×10^3	10^3	10^3	1.5×10^3	1.5×10^3	10^3	10^3
Cu^{2+}	4×10^3	3×10^3	4×10^3	4×10^3	4×10^3	2×10^3	2×10^3	2×10^3
Hg^{2+}	3×10^3	800	3×10^3	800	2×10^3	200	10^3	500
Sn^{4+}	2×10^3	10^3	10^3	500	2×10^3	10^3	10^3	200
V^{4+}	3×10^3	2×10^3	2×10^3	2×10^3	2×10^3	2×10^3	10^3	500
Mn^{2+}	5×10^3	5×10^3	5×10^3	5×10^3	5×10^3	5×10^3	2×10^3	10^3
Fe^{3+}	5×10^3	3×10^3	5×10^3	2×10^3	2×10^3	10^3	2×10^3	10^3
Co^{2+}, Ni^{2+}	5×10^3	2×10^3	5×10^3	2×10^3	2×10^3	10^3	2×10^3	10^3
Ru^{3+}, Rh^{3+}	2×10^3	10^3	2×10^3	10^3	10^3	10^3	10^3	10^3
Pd^{2+}	—	—	Int	10	—	—	Int	10
Os^{8+}	Int.	Int	—	—	Int	Int.	—	—
Ir^{3+}	5×10^3	2×10^3	10^3	10^3	2×10^3	2×10^3	10^3	10^3
Pt^{4+}	5×10^3	2×10^3	2×10^3	2×10^3	2×10^3	2×10^3	2×10^3	2×10^3

Int. = interference.

extracted from acidic solution. Make up to volume, measure its absorbance at λ_{max} of the complex against a solvent blank [or reagent blank in case of the (III)] and calculate the amount of the metal from a calibration graph.

Diverse ions

The effect of a large number of diverse ions on the determination of 10.7 ppm of Pd and 11.6 ppm of Os with (II) and (III) was investigated. Up to 10^4 ppm of Cl^-, Br^-, NO_3^-, ClO_4^-, CH_3COO^-, SO_4^{2-}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+} gave no interference, nor did 5×10^3 ppm of Pb^{2+}, in any of the complexation reactions. Silver interfered when present at the 10 ppm level, and cyanide and thiourea must be absent. The other tolerance limits are incorporated in Table 4. It is evident that the determinations can be accomplished in the presence of large amounts of many species, including all the other metals of the iron and platinum groups.

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Summary—1-Amino-, 1-anilino- and 1-(2′,4′-dinitroanilino)- 4,4,6-trimethyl-1*H*,4*H*-2-pyrimidinethiols react with Pd(II) and Os(VIII), forming coloured complexes extractable into non-polar organic solvents. The optimum conditions for the complexation have been established. Beer's law is obeyed and by an extractive spectrophotometric procedure, microgram quantities of the two metals are determined in the presence of large amounts of diverse ions, including all the other metals of the iron and platinum groups.

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DETERMINATION OF AMERICIUM AND CURIUM BY USING ION-EXCHANGE IN NITRIC ACID–METHANOL MEDIUM FOR ENVIRONMENTAL ANALYSIS

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(*Received* 16 *March* 1976. *Accepted* 29 *April* 1976)

Transplutonic elements are only slightly sorbed on anion-exchangers from hydrochloric or nitric acid media, but the presence of alcohol in the media enhances the anion-exchange of these elements, especially in nitric and sulphuric acid media. Von Haidvogel *et al.*[1] showed this enhancement in thin-layer chromatography; the sorption of transplutonic elements increased with increasing alcohol content and the binding with the ion-exchanger was stronger in nitric acid medium than in sulphuric acid medium. Guseva *et al.*[2,3] separated americium from curium, both at relatively high level, in a nitric acid–methanol medium, observing that the greater the atomic number, the stronger the sorption.

In the present work a method has been developed for determining americium and curium in environmental samples, on the basis of the difference between the sorption characteristics of these elements on anion-exchangers in an acid–methanol system and those of plutonium, polonium, thorium, *etc.* The method also permits us to perform sequential determination of plutonium, when necessary. The radiochemical separation of americium from curium is not generally required, since modern α-spectrometry resolves the major α-peak of ^{241}Am (5.49 MeV) from those of ^{242}Cm (6.10 MeV) and ^{244}Cm (5.80 MeV), which possibly co-exist with ^{241}Am in environmental samples.

EXPERIMENTAL

Reagents

Nitric acid–methanol mixtures: 1*M* HNO_3–90% CH_3OH solution (10*M* nitric acid–methanol) (1:9 v/v) and 0.5*M* HNO_3–70% CH_3OH solution (5*M* nitric acid–water–methanol, 1:2:7 v/v).

First anion-exchange resin column: Dowex 1 (X8, 100–200 mesh), bore 1 cm, volume 10 ml.

Second anion-exchange resin column: Dowex 1 (X2, 50–100 mesh), bore 1 cm, volume 20 ml.

Cation-exchange resin column: Dowex 50 (X8, 200–400 mesh), bore 1 cm, volume 5 ml.

Americium-243 solution in 1*M* nitric acid (5 dpm/ml): chemical yield monitor for ^{241}Am.

Plutonium-236 or plutonium-242 solution in 1*M* nitric acid (5 dpm/ml): chemical yield monitor for ^{238}Pu and ^{239,240}Pu.

Sample pretreatment

Biological or sediment samples are dried at 105–110°, weighed and placed in a porcelain crucible to which the chemical yield monitors, a few dpm each of ^{243}Am and ^{236}Pu or ^{242}Pu, are normally added. After drying again, the samples are ashed at 500° overnight. The ash obtained is leached with a mixture of concentrated nitric and hydrochloric acids and a few ml of 30% hydrogen peroxide.

Water samples are acidified, and iron carrier (50 mg of Fe^{3+}) is added.

The actinides are co-precipitated with ferric hydroxide by adding ammonia. The precipitate is centrifuged and dissolved in 9–12*M* hydrochloric acid. After the addition of a few drops of 30% hydrogen peroxide, the solution is heated and kept at 80° for 20 min. The acidity of the solution is finally adjusted to 9*M* in hydrochloric acid.

Ion-exchange

After cooling, the solution is passed through the first column of Dowex 1 and then through the Dowex 50 column, which is directly connected to the first column, at a flow-rate of 2 ml/min. Iron(III) is sorbed on the Dowex 1 column with plutonium(IV) as well as any uranium and polonium. Thorium is sorbed on the Dowex 50 column. Tervalent actinides, americium and curium, on the other hand, pass through both columns. The columns are washed with 50 ml of 9*M* hydrochloric acid, then the effluent and washings are combined and evaporated to dryness. The residue is dissolved in 1*M* HNO_3–90% CH_3OH solution (50–100 ml).

In order to obtain further purification of americium and curium, the solution is passed through the second Dowex 1 column at a flow-rate of 2 ml/min. Americium and curium are sorbed on the column with other impurities, such as remaining plutonium, polonium, thorium *etc.* The column is washed with 60 ml of 1*M* HNO_3–90% CH_3OH mixture. The tervalent actinides are then eluted with 0.5*M* HNO_3–70% CH_3OH mixture (70 ml).

When the plutonium determination is required, plutonium can be eluted from the first Dowex 1 column with

Summary—1-Amino-, 1-anilino- and 1-(2′,4′-dinitroanilino)- 4,4,6-trimethyl-1*H*,4*H*-2-pyrimidinethiols react with Pd(II) and Os(VIII), forming coloured complexes extractable into non-polar organic solvents. The optimum conditions for the complexation have been established. Beer's law is obeyed and by an extractive spectrophotometric procedure, microgram quantities of the two metals are determined in the presence of large amounts of diverse ions, including all the other metals of the iron and platinum groups.

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When the plutonium determination is required, plutonium can be eluted from the first Dowex 1 column with

1.2M hydrochloric acid after washing with 7.2M nitric acid and determined by the procedure described by Talvitie.[4]

Electro-deposition

The eluate which contains americium and curium is evaporated to dryness and the residue is dissolved with 0.8 ml of conc. sulphuric acid. The solution is diluted with distilled water and adjusted to pH 2 with ammonia, the final volume being about 10 ml. The electro-deposition of americium and curium from this solution onto a stainless-steel disc is performed at a current of 1.2 A for 1 hr, with a disposable polyethylene vial as electrolysis cell. A similar procedure for the electrodeposition of plutonium has already been described.[5]

Alpha-spectrometry

In the present work, the α-spectrometry for americium and curium was carried out by using a silicon surface-barrier detector having a sensitive area of 300 mm^2. The resolution of α-spectra was 35–40 keV for the ^{241}Am peak (5.49 MeV) in terms of the full width at half maximum. The least detectable activity was 0.01 pCi for a 1000-min count under these conditions.

RESULTS AND DISCUSSION

The key to precise determinations of americium in environmental samples is to obtain good decontamination from naturally-occurring α-emitters, such as ^{210}Po (α-energy, 5.30 MeV) and ^{228}Th (5.42 MeV) as well as from the artificial fall-out radionuclides such as ^{238}Pu (5.49 MeV). Their α-energies would interfere with the α-spectrometry of ^{241}Am (5.49 MeV) or of the yield monitor ^{243}Am (5.28 MeV). For curium determinations separation from ^{236}Pu (5.76 MeV) is essential when ^{236}Pu has been used as the yield monitor for plutonium, as its α-peak overlaps that of ^{244}Cm (5.80 MeV).

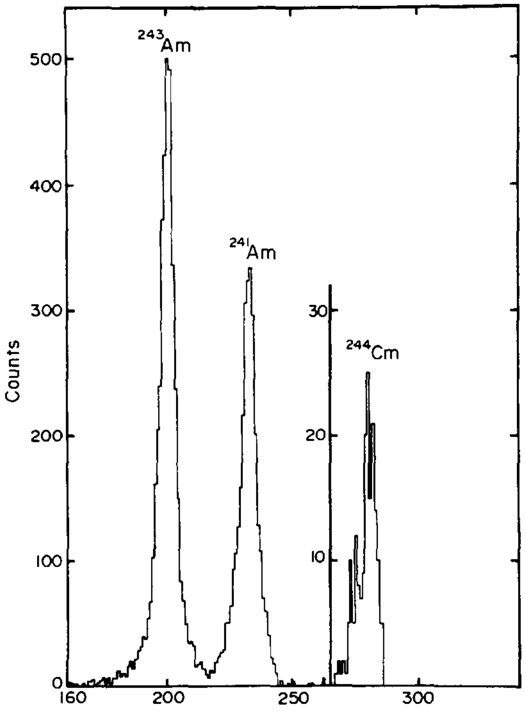

Fig. 1. Alpha-spectrum of IAEA intercalibration sample AG-I-1 (seaweed, 1 g dry, 18 dpm ^{243}Am added). Counting time: 3800 min.

Table 1. Comparisons between the probable concentrations of transuranic element in IAEA reference samples and the results obtained in the present work

Sample No.	Matrix	Probable concentration, *pCi/kg* ^{238}Pu	^{239,240}Pu	^{241}Am	^{244}Cm	Results of this work, *pCi/kg* ^{238}Pu	^{239,240}Pu	^{241}Am	^{244}Cm
AG-I-1	Seaweed	$(3.8 \pm 0.1) \times 10^3$	$(27.0 \pm 0.5) \times 10^3$	$(5.2 \pm 0.2) \times 10^3$	30	$(3.8 \pm 0.3) \times 10^3$	$(31 \pm 2) \times 10^3$	$(5.9 \pm 0.2) \times 10^3$	30 ± 5
SD-B-1	Sediment	$(0.43 \pm 0.03) \times 10^2$	$(9.6 \pm 0.3) \times 10^2$	—	—	$(0.56 \pm 0.10) \times 10^2$	$(9.7 \pm 0.9) \times 10^2$	$(0.23 \pm 0.05) \times 10^2$	N.D.*
SW-I-3	Seawater	0.018 ± 0.001	0.11 ± 0.01	0.028 ± 0.002†	<0.002	0.026 ± 0.008	0.11 ± 0.01	0.034 ± 0.006§	N.D.*

* Not detected.
† Activity in Dec. 1974.
§ Activity in Oct. 1975.

The decontamination of polonium by the present procedure was verified by analysing samples which were known to contain relatively high levels of ^{210}Po, without adding any yield monitor. The decontamination factor for ^{210}Po is estimated to be of the order of 10^5.

However, since it was also observed that ^{210}Pb is strongly sorbed on the anion-exchange resin from the nitric acid–methanol medium, it is possible that a small fraction of the ^{210}Pb may be carried over to the americium fraction and interfere with the α-spectrometry of ^{243}Am, when the content of ^{210}Pb in the samples is exceptionally high. The interference comes from the build-up of ^{210}Po through β-decay of ^{210}Pb (half-life: 19.4 y) with an equilibrium time of approximately 6 months. This difficulty can be overcome by using clean ^{242}Cm or ^{244}Cm as the yield monitor for americium measurements, since it has been experimentally proved that there is practically no difference between the chemical yields of americium and curium in the present procedure.

The decontamination of ^{228}Th was tested either by spiking known amounts of ^{230}Th (α-energy, 4.69 MeV) or by verifying absence of the ^{224}Ra-peak (5.68 MeV) which should be built up during two weeks from the separation if the thorium decontamination has been incomplete. These tests indicated that the procedures decontaminate ^{228}Th by a factor of at least 10^4.

The absence of the $^{239,240}Pu$-peak (5.16 MeV) in the α-spectra obtained through the present procedure confirmed sufficient decontamination of $^{239,240}Pu$ as well as of ^{238}Pu. The activity of $^{239,240}Pu$ is 10–20 times that of ^{238}Pu in normal environmental samples.

To illustrate the decontamination from the interfering radionuclides mentioned above, an α-spectrogram obtained for the IAEA intercalibration sample, AG-I-1 (seaweed) by the present procedure is given in Fig. 1. The α-peaks of ^{243}Am, ^{241}Am and ^{244}Cm are seen to be clean.

If the plutonium and thorium were not preseparated through the first anion-exchange, about 10% of the plutonium and thorium would follow americium in the $0.5M$ HNO_3–70% CH_3OH eluate. Plutonium and thorium are also strongly sorbed on Dowex 1 from $1M$ HNO_3–90% CH_3OH, but partially eluted with $0.5M$ HNO_3–70% CH_3OH. Polonium is also sorbed, but not eluted under these conditions.

Since ^{243}Am often contains some ^{244}Cm as an impurity, a serious error may be introduced into curium determination when the curium concentrations are low and ^{243}Am is used as the yield monitor for ^{241}Am. This difficulty can be avoided by repeating the procedure without adding any yield monitor. In this case, the previously determined ^{241}Am concentration of the sample is used to measure the yield since, as has been mentioned, the chemical yield of ^{241}Am is practically identical to that of ^{242}Cm or ^{244}Cm.

The method described above was applied to several IAEA reference samples, such as AG-I-1 (seaweed), SD-B-1 (marine sediment) and SW-I-3 (seawater), for which the probable concentrations are already known for ^{238}Pu and $^{239,240}Pu$ as well as ^{241}Am.[6] The results of these analyses are given in Table 1. The recovery of americium in these analyses varied between 30 and 95%. Nevertheless, the results presented in Table 1 are in good agreement with the given probable concentrations, showing the usefulness of the present method for the determination of americium and curium in environmental samples.

A major part of ^{241}Am in the environment today results from the decay of ^{241}Pu (half-life 13.6 y, β-emitter) deposited as radioactive fall-out or from nuclear installations.[7] The method presented here is being used for studying the environmental behaviour of americium and curium isotopes originating from various sources.

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Summary—A method is presented for the determination of americium and curium isotopes in environmental samples, an ion-exchange clean-up procedure being used.

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DETERMINATION OF TRACES OF INDIUM, MANGANESE, ARSENIC AND ANTIMONY IN ZINC BY NEUTRON-ACTIVATION ANALYSIS*

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Zinc metal is available in different degrees of purity, from the so-called "five nines zinc" (99.999 + % Zn) to the grade with more than 1.6% of impurities. Among the main impurities in commercial zinc are iron, copper and lead, but many others (arsenic, antimony, tin, cadmium, germanium, indium, thallium, manganese and gallium) influence the mechanical, electrical and anticorrosion properties of zinc metal.[1–4] Some trace elements (10^{-4}–10^{-6}% of iron, manganese, copper, nickel and cobalt) may also change the luminescence properties of zinc sulphide.[5–8] The trace element composition also indicates the origin of the zinc ore.

Destructive and non-destructive activation analysis are both suitable for the determination of trace elements in high-purity materials but because the activity of ^{69m}Zn and of ^{64}Cu interferes in the determination of short-lived isotopes and the activity of ^{65}Zn interferes in the determination of long-lived isotopes, non-destructive analysis using high-resolution spectrometry is impracticable. Thus destructive methods for Cu, Ni, Co, Fe, Mn,[6,7,9] for Hg, U, Yb,[10] for Mo, Re,[11] for Te, Se, As, Sb[12] and for Co, Cd, Fe, In[13] in electrolytic zinc sulphate solutions, and for Co, Ag,[14] for 13 trace elements,[15] for Ge,[16] for Cu, Fe, Co, Ni[9] and for 27 trace elements [17] in zinc metal, have been reported. Experience in analysis of standard reference materials shows that chemical separations are essential for the majority of elements in the very low concentration range. The aim of the present work was to extend the applicability of methods for pure chemical reagents,[18,19] biological materials,[20–22] glasses [21–24] and calcium carbonate[24] to materials requiring a separation of gram quantities of the active matrix before the determination of microgram and submicrogram quantities of trace elements. Separations with very high decontamination factors are essential.

The present paper gives an account of the destructive determination of the trace elements indium, manganese, arsenic and antimony in different samples of pure zinc metal, by solvent extraction techniques. The various samples analysed included the NBS standard Zn 683, for which results for these four elements have not previously been published.[25]

EXPERIMENTAL

Irradiation

For the determination of indium and manganese, the samples (0.2–1.0 g) and standards, sealed in plastic tubes, were irradiated for 30–40 min in the Institute's reactor TRIGA MK.II at a neutron-flux of 4×10^{12} n.cm^{-2}.sec^{-1}, the pneumatic transfer system being used.

In the determination of arsenic and antimony, the samples, sealed in plastic tubes, were irradiated together with the standard for 18–20 hr at a neutron-flux of approximately 2×10^{12} n.cm^{-2}.sec^{-1}.

Nuclear data

The most important nuclear data for the elements determined are given in Table 1.[26]

Apparatus

Quantitative determinations of individual elements were based on activity measurements of the separated radionuclides at the γ-ray energies indicated in italics in Table 1. They were counted in a 3 × 3 in. well-type (NaI(Tl) detector connected to a 250-channel analyser.

Reagents and solutions

Apart from mineral acids and hydrogen peroxide used in the dissolution of samples, the following reagents were

Table 1. Relevant nuclear characteristics of arsenic, indium, manganese, antimony and zinc[26]

Stable isotope	Abundance, %	Reaction	Cross section, *barn*	Half-life	γ-Ray energy, *MeV*
^{75}As	100	^{75}As(n,γ)^{76}As	4.3	26.4 hr	*0.56*, 0.66
^{115}In	95.7	^{115}In(n,γ)^{116m}In	65	54 min	0.42, 0.82, 1.10, *1.29*
^{55}Mn	100	^{55}Mn(n,γ)^{56}Mn	13.3	2.58 hr	*0.85*, 1.81, 2.11
^{121}Sb	57.3	^{121}Sb(n,γ)^{122}Sb	6.2	2.70 d	*0.56*, 0.69
^{123}Sb	42.7	^{123}Sb(n,γ)^{124}Sb	4.3	60.3 d	0.60, 0.65, 1.69
^{64}Zn	48.9	^{64}Zn(n,γ)^{65}Zn	0.78	244 d	1.12
		^{64}Zn(n,p)^{64}Cu		12.7 hr	0.51, 1.34
^{66}Zn	27.8	^{66}Zn(n,p)^{66}Cu		5.1 min	1.04
^{67}Zn	4.1	^{67}Zn(n,p)^{67}Cu		61.9 hr	0.09, 0.18
^{68}Zn	18.6	^{68}Zn(n,γ)^{69m}Zn	0.09	13.9 hr	0.44
		^{68}Zn(n,p)^{68}Cu		30 sec	1.08, 1.26

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required. For the determination of indium and manganese: solutions of ammonium citrate (40%), potassium cyanide (5%), sodium diethyldithiocarbamate (1%), Cresol Red (0.1%), lanthanum nitrate in 0.1*M* nitric acid (La = 10 mg/ml), and ammonia, concentrated hydrobromic acid, carbon tetrachloride and alcohol. For the determination of arsenic and antimony: 5*M* and 0.5*M* potassium iodide, toluene and alcohol.

Standards were prepared from spectroscopically pure reagents (metallic indium, potassium permanganate, arsenic trioxide and antimony trioxide) and contained 0.1% w/w of the elements determined. The solutions were 0.1*M* with respect to nitric acid (hydrochloric acid for antimony) and after appropriate dilution, were used as carriers or standards.

Dissolution of samples

After irradiation, but before their dissolution, the surface contamination of the samples (except in the case of zinc dust) was removed by etching them in nitric acid (1 + 1) followed by washing in doubly distilled water and then 96% alcohol. After washing, the samples were dried, weighed and dropped into a Kjeldahl flask together with carriers (50 μg of indium, 250 μg of manganese, 500 μg of arsenic, 1 mg of antimony, 1 mg of copper and 10 mg of lanthanum) and heated in a mixture of nitric and sulphuric acids until SO_3 fumes appeared.

Determination of indium and manganese

After dissolution of the samples, a few ml of concentrated hydrobromic acid were added to the Kjeldahl flask and heating continued (to remove volatile bromides) until SO_3 fumes appeared. The solution was cooled and quantitatively transferred to a centrifuge tube. An excess of ammonia was added until the precipitate of zinc hydroxide was completely dissolved. To the ammoniacal solution a few ml of 32% hydrogen peroxide were added to precipitate manganese together with lanthanum and indium hydroxides. After 10 min heating on a water-bath, the solution was discarded, the remaining precipitate washed with a mixture of 1*M* ammonia and a few drops of hydrogen peroxide and centrifuged again.

The hydroxides were dissolved in 6*M* hydrochloric acid (5 ml) and quantitatively transferred to a separatory funnel. After addition of 5 ml of sodium diethyldithiocarbamate solution, indium and manganese were extracted as the diethyldithiocarbamates at pH 8–9 (Cresol Red) into 10 ml of carbon tetrachloride in the presence of ammonium citrate (5 ml) and potassium cyanide solutions (5 ml). Manganese was isolated from indium by the selective stripping of the organic phase with a 1:1 mixture of 4*M* hydrochloric acid and sodium diethyldithiocarbamate solution, which holds back indium in the organic phase.

After separation of manganese, the organic phase was mineralized with a mixture of sulphuric and nitric acid, cooled and transferred to a 5-ml counting vial. The activity of the 1.29-MeV ^{116m}In peak was measured and compared with the activity of the standard. The chemical yields, which were better than 98%, were determined by re-irradiation. The aqueous phase containing manganese was mineralized in the same way and transferred to a counting vial. The activity of the 0.85-MeV ^{56}Mn peak was measured and compared with that of the standard. The chemical yield was determined spectrophotometrically by the periodate method and was about 90%.

Determination of arsenic and antimony

After dissolution of the samples, the solution was transferred to a separatory funnel and diluted to a volume of 18 ml in which 13.4 ml of free 9*M* sulphuric acid were present. Then 2 ml of 0.5*M* of potassium iodide and exactly 15 ml of toluene were added and the mixture was shaken for 3 min. The aqueous phase was discarded and the organic phase washed with 10 ml of 6*M* sulphuric acid/0.05*M* potassium iodide. Antimony was stripped from the organic phase with two 5-ml portions of 6*M* hydrochloric acid/0.5*M* potassium iodide, being shaken for 2 min each time. The stripping solutions were collected in a 10-ml counting vial and the activity of the 0.56-MeV ^{122}Sb peak was measured and compared with that of the standard.

The activity of arsenic was measured in two ways, depending on the quantity in the sample. At high levels of arsenic, an aliquot of the organic phase (after separation of antimony) was transferred directly to the counting vial; at low levels the arsenic from the whole of the organic phase was stripped into dilute mineral acid. In both cases the activity of the isolated ^{76}As was measured in a counting vial at 0.56 MeV and compared with that of the standard. The yields for arsenic and antimony were shown by tracer experiments to be quantitative.

RESULTS AND DISCUSSION

Owing to the high activity of the matrix and the presence of copper isotopes arising from (n,p) parasite reactions, non-destructive activation analysis for determination of trace elements in different samples of zinc metal and its compounds is usually impracticable. For separation of gram quantities of zinc matrix from microgram and sub-microgram quantities of short-lived or long-lived isotopes, one-step separation methods usually fail. With a combination of two or more separation procedures or by repeated application of a single but very selective separation procedure, the decontamination factors required for such a separation can be obtained.

Since the larger quantities of zinc interfere with the extraction and determination of indium and manganese, even in the presence of larger quantities of potassium cyanide, both elements were (before extraction with sodium diethyldithiocarbamate) quantitatively co-precipitated with lanthanum hydroxide in the presence of excess of ammonia. Tracer experiments with ^{56}Mn and ^{116m}In confirmed that co-precipitation was quantitative. The quantities of indium and manganese carriers suitable for diethyldithiocarbamate extraction and yield determination are small enough to make their co-precipitation on lanthanum hydroxide desirable. This isolation of indium and manganese is convenient, since most of the matrix and those elements soluble in excess of ammonia are removed, *e.g.*, copper, which arises from the reactions ^{64}Zn(n,p)^{64}Cu and ^{67}Zn(n,p)^{67}Cu. The γ-spectra obtained by this method are clean and identical with the γ-spectra of the standards, for both elements.

In samples which had more than 100 ppm of cadmium, in addition to the peaks of ^{116m}In there was a peak due to the 0.34-MeV ^{115m}In activity ($t_{1/2}$ = 4.5 hr). This arises as a daughter of ^{115}Cd after the ^{114}Vd(n,γ) reaction. Since the γ-energy of ^{115m}In is lower than the energies of the ^{116m}In isotopes, the presence of ^{115m}In does not interfere with the evaluation of indium in the samples.

Determination of arsenic and antimony in different samples of zinc metals is based upon the extraction of the tri-iodides of both elements into toluene. From the extraction curves[27] it can be seen that both elements are quantitatively extracted into the organic phase from 6*M* sulphuric acid/0.05*M* potassium iodide. The high degree of extraction permits washing of the organic phase without appreciable loss of arsenic and antimony and so increases the degree of decontamination. The basis for the separation of the elements from the organic phase is the difference in the extraction coefficients of their iodides (for arsenic ~600, for antimony ~0.05) from 6*M* hydrochloric acid/0.5*M* potassium iodide solution into toluene.[22]

For samples with a high concentration of antimony compared with arsenic, traces of antimony in the organic

Table 2. Results for indium, manganese, arsenic and antimony in different samples of zinc metal (*ng/g*)*

	In			Mn			As			Sb		
Sample	*n*	*A*	*σ*	*n*	*A*	*σ*	*n*	*A*	*σ*	*n*	*A*	*σ**
Zn Malinckrodt	3	0.68	—	3	370	—	6	5.5	0.7	4	154	14
Zn-SRM 683 NBS	7	0.93	0.09	7	56	4	7	2.5	0.3	6	506	17
Zn-pulvis Kemika	4	8310	315	5	4650	240	5	410	11	5	175	6
Zn-grobes Pulver Riedel de Haen	8	10	1	4	3790	440	3	26	—	5	48	5

* *n* is the number of determinations, *A* the average value and *σ* the standard deviation.

phase must be stripped a second time with 6*M* hydrochloric acid/0.5*M* potassium iodide. Similarly, for samples with a very high arsenic–antimony ratio, the antimony stripped from the organic phase should be washed with toluene to remove traces of arsenic.

The procedure is simple, fast and quantitative. The two elements are cleanly separated from zinc (the 0.44-MeV peak from ^{69m}Zn was not observed). In the analysis of zinc samples for arsenic and antimony it is essential to dissolve them in the presence of nitric acid, or low results may be obtained by the loss of the volatile hydrides.

The results for indium, manganese, arsenic and antimony are summarized in Table 2. We have been unable to check the accuracy of our results directly on zinc reference samples, since these are not available. From the high chemical yields, the clean γ-spectra and the good reproducibility of the results it is concluded that the values for indium, manganese, arsenic and antimony are close to the true values.

CONCLUSION

The solvent extraction method described is superior to earlier methods, involving precipitation, distillation or ion-exchange separations and has the advantages of simplicity and speed. The radiochemical purity of the separated fractions allows determinations to be made at the nanogram level.

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Summary—Destructive activation determination of the trace elements indium, manganese, arsenic and antimony in different samples of pure zinc metal by solvent extraction techniques is described. Determination of indium and manganese is based on the quantitative co-precipitation of both elements with lanthanum hydroxide, followed by their extraction with sodium diethyldithiocarbamate in the presence of potassium cyanide and their subsequent separation by selective stripping. The quantitative determination of arsenic and antimony is based on the extraction of their iodides from sulphuric acid solution with toluene.

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OPTIMIZATION OF SILICATE ROCK DECOMPOSITION FOR DETERMINATION OF MAJOR ELEMENTS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Some of the most useful methods employed in silicate analysis for major elements are flame photometry, colorimetry, and atomic-absorption spectrophotometry (AAS); all of them require prior dissolution of the sample. Much has been written about silicate rock decomposition, but in the authors' opinion most of the methods described present serious inconveniences for work in a routine laboratory where instrumental techniques are employed. The method applied has to fulfil certain requirements dictated by the nature of the work. Geochemistry laboratories are usually concerned with determination of SiO_2, TiO_2, Al_2O_3, total iron as Fe_2O_3, MgO, CaO, Na_2O, K_2O and P_2O_5. At present, all these except phosphorus and titanium oxides can be determined advantageously by AAS. Phosphorus cannot be determined directly by AAS, and the sensitivity for titanium is low. Colorimetric methods are preferred in both cases and so it is important not to introduce into the matrix components which interfere with the colorimetric and AAS determinations.

A very important aspect of AAS and the other techniques mentioned, and one that is directly connected with sample decomposition is the use of standards. For some elements many authors have successfully used standard solutions prepared from pure salts, but the results for elements such as silicon and aluminium are not very good. The use of artificial standards may produce poor results because of the differences in bulk composition and in physical properties between natural samples and artificial standard matrices. Thus it is highly desirable to use the various standard rocks with a well-established composition, but doing so demands that the solutions prepared from them have certain qualities, one being good stability so that they can be used for more than one set of samples, saving both time and material. Another requirement is that the level of dissolved solids in the matrix must be low in order to facilitate accurate determinations. It is also preferable to be able to use the same standard solution for all the determinations.

The present paper reports a rapid and versatile method for decomposition of silicate rocks, to give a solution which contains all the elements of the rock but only a low total amount of solids. The master solution can be treated in various ways to stabilize it with respect to various components and it is possible to determine all the major elements by atomic absorption and/or colorimetry. The most important methods described for silicate rock decomposition have been investigated and their useful aspects put together and in some cases improved to obtain the final procedure.

EXPERIMENTAL

Reagents

All chemicals used were analytical reagent grade.

Flux. A 1:1 mixture of boric acid and lithium carbonate.

EDTA solution. Prepared by dissolving 2 g of the acid in 250 ml of distilled water containing 10 ml of concentrated ammonia solution and diluting to 1 litre. Stored in a plastic bottle.

Fluoboric acid solution. This contains 30 g of boric acid and 30 ml of 45% hydrofluoric acid per litre.

Potassium and barium nitrate buffer solutions. These contain 10,000 ppm of potassium and barium respectively.

RESULTS AND DISCUSSION

Classical schemes

These usually involve separate attack on two samples, which we consider a serious inconvenience for economic and rapid work.

Methods designed for atomic-absorption analysis

There is a great variety of published methods but we will consider only those established on the basis of a single attack and further determination of all the major elements in the solution obtained. The methods are essentially variants of two themes.

Pressure vessel decomposition.[1–5] Hydrofluoric acid is used alone or together with other acids in a hermetically sealed bomb. The fluorides are then stabilized with alcohol, aluminium chloride, or more often boric acid. The last produces good results but has two main inconveniences: (*i*) some resistant minerals such as zircon, tourmaline, cassiterite, titanium oxides and in some cases polymorphous alumina are not completely decomposed; (*ii*) the fluoride anions produced cause the inconveniences discussed below.

Lithium metaborate fusion.[6–10] This flux has been shown to be one of the most effective in silicate rock decomposition, giving complete fusion of most silicate rock minerals. On the other hand we have found that a mixture of lithium carbonate and boric acid gives faster decomposition of minerals such as zircon concentrates. The product can be dissolved in hydrofluoric, nitric, hydrochloric acid and so on. The most important variants are the following.

(*a*) *Nitric acid.*[6–8] In this case the stability of silicon and aluminium species in the solution is somewhat questionable. We have found that polymerization begins after about 8 hr, as shown in Fig. 1, which refers to a solution prepared from a typical granodiorite. The apparent concentration of silicon in solution has been found to be the same after 20 hr, irrespective of the silica content of the original rock (from 50 to 96%). An equilibrium between the silica precipitated and the solution seems to be established after this time. In spite of these inconveniences the method has the advantages of simplicity and rapidity (it takes about 15 min to dissolve the fusion product), the matrix is very suitable for flame and colorimetric determinations because nitrate does not produce interferences, and the amount of solids in solution is low.

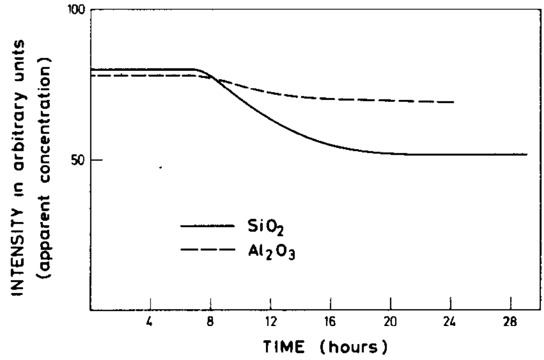

Fig. 1. Stability of signal for silicon and aluminium in a granodiorite rock. The same sample solution was measured at different times, and always compared with a fresh sample solution.

(*b*) *Hydrofluoric acid.* The fluorides can be stabilized with boric acid[9] or by direct dissolution with fluoboric acid.[10] The matrix is the same in both cases. The advantage of this method is that the solutions can be stored for a long time, but this is outweighed by several disadvantages. The high concentration of boron depresses the aluminium AAS signal by about 30% and increases the background by a factor of about ten, perhaps by formation of refractory compounds in the flame. The presence of fluoride interferes with the colorimetric determination of titanium, and in AAS if the amount of fluoride is high there is attack on any titanium parts of the instrument exposed to the sample. The amount of dissolved solids is also excessive, about 3.5% in Saavedra's method[10] and 2.2 or 1.3% respectively for the two solutions obtained by Abbey's method,[9] as we have found by evaporation of the solvent from different samples. In our experience, no atomizer can work satisfactory with solutions which contain more than 1% of solids. These problems also arise with the solution obtained by the pressure vessel method.

(*c*) *Complexing reagents.*[11] This method is very promising although it has not been employed to determine the total range of major elements. So far it has been mainly applied for determining alkali and alkaline earth metals. In our experience it is difficult to obtain clear solutions and the amount of solids in the matrix is also excessive.

Interferences

Some interference problems have been discussed above, and we will summarize some others here.

Chemical interferences. These can be classified into two groups.

(*a*) *Inter-element effects.* The most important are those produced by aluminium, silicate and sulphate in conjunction with calcium and magnesium. They can be overcome by using protecting agents, generally chelating agents such as EDTA[12] or releasing agents such as lanthanum, barium and strontium. In our experience barium is superior to strontium, Fig. 2, because of its lower ionization potential and its ability to form stronger Al-O-metal complexes.

(*b*) *Components introduced by chemical reagents.* The most important is that produced by fluoborate anions, described above.

Ionization interferences. These are important not only for alkali metals in an acetylene/air flame but also for alkaline earth metals, aluminium and silicon in an acetylene/nitrous oxide flame. The signals for aluminium and silicon decrease by about 20 and 5% respectively. We find potassium effective in suppressing these interferences.

The combined method

There is no doubt that the advantageous aspects of the different methods can be combined in a single procedure. We have taken Ingamell's method as a basis. In our opinion it is the most suitable, apart from the stability of the solutions.

We have found that if a small amount of EDTA is added before dilution to final volume, the apparent content of most ions except those derived from silica remains constant for several months. The apparent content of silica starts to change after 30 hr but less than in the absence of EDTA and the solution can be kept stable for months if some fluoborate is also added (Fig. 3), irrespective of the nature of the rock sample.

The nitrate–EDTA system produces no interelement interferences and the ionization interferences are suppressed by addition of barium for determination of alkali and alkaline earth metals, and of potassium for determination of silicon and aluminium.

Procedure

Weight 0.2000 g of the finely powdered sample into a gold or platinum crucible. Add 1.0 g of the 1:1 $LiCO_3$/H_3BO_3 mixture and heat in a furnace at 950° for 15 min. Remove the crucible from the furnace, rotate the melt over the wall in the usual way and return the crucible to the furnace for 5 min. Swirl the melt and cool the crucible quickly by putting it into a flat container with demineralized water in it, simultaneously adding a small amount of water to the crucible. Wash the outside of the crucible with demineralized water, place a small Teflon-covered magnetic bar in the crucible and put this into a 100-ml beaker. Add 5 ml of concentrated nitric acid to the crucible and set the beaker on a magnetic stirrer. Stir, with heating at 70–80°, until all the fusion cake has disintegrated. Transfer the solution to a 200-ml flask, add 20 ml of EDTA

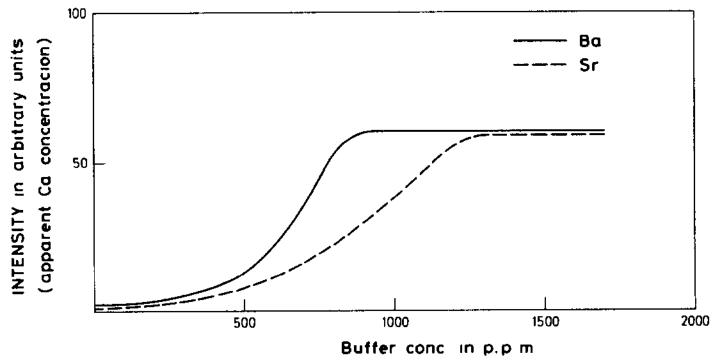

Fig. 2. Releasing effect of barium and strontium on the calcium signal. The effect on magnesium is similar.

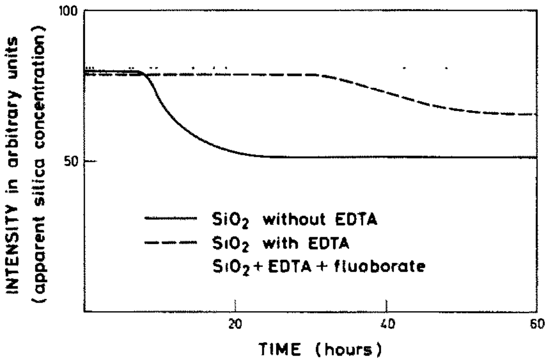

Fig. 3. Stability of signal for silicon in three different matrices, measured at different times and compared with that for a fresh solution.

solution and make up to volume with demineralized water. Prepare the solutions as follows.

Solution (*A*) *for Si and Mn.* Transfer a 25-ml aliquot immediately into a 50-ml flask, add 5 ml of fluoborate solution and 5 ml of the potassium buffer and dilute to volume with demineralized water.

Solution (*B*) *for Al and Mn.* To another 25-ml aliquot in a 50-ml flask add 5 ml of the potassium buffer and make up to volume with demineralized water. This solution is better than (A) for manganese determination.

Solution (*C*) *for Ca, Mg, Fe, Na, K, Ti,*[13] *P.*[14] Transfer a 5-ml aliquot to a 50-ml volumetric flask, add 5 ml of the barium buffer and make up to volume with demineralized water.

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Summary—A rapid method for sample decomposition of silicate rocks and further accurate determination of major elements by atomic-absorption spectrometry is described. The solutions obtained were stabilized so that the measurements were comparable with those made on standard rocks solutions. Interferences were avoided. The most important methods of silicate rock decomposition were applied, and the useful characteristics from each were combined, and in some cases improved, to obtain the final procedure.

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NON-DESTRUCTIVE RADIOCHEMICAL METHOD FOR DETERMINING CARBON CONCENTRATIONS IN THIN SHEET 3% Si–Fe ALLOY

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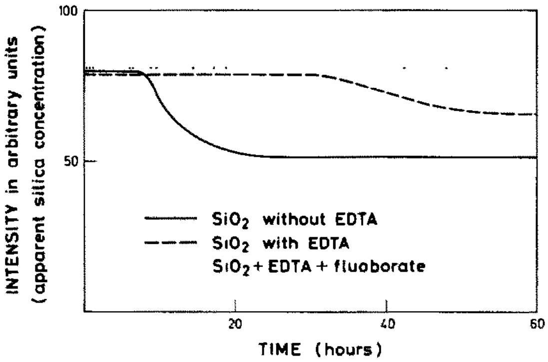

Fig. 3. Stability of signal for silicon in three different matrices, measured at different times and compared with that for a fresh solution.

solution and make up to volume with demineralized water. Prepare the solutions as follows.

Solution (A) for Si and Mn. Transfer a 25-ml aliquot immediately into a 50-ml flask, add 5 ml of fluoborate solution and 5 ml of the potassium buffer and dilute to volume with demineralized water.

Solution (B) for Al and Mn. To another 25-ml aliquot in a 50-ml flask add 5 ml of the potassium buffer and make up to volume with demineralized water. This solution is better than (A) for manganese determination.

Solution (C) for Ca, Mg, Fe, Na, K, Ti,[13] *P.*[14] Transfer a 5-ml aliquot to a 50-ml volumetric flask, add 5 ml of the barium buffer and make up to volume with demineralized water.

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Summary—A rapid method for sample decomposition of silicate rocks and further accurate determination of major elements by atomic-absorption spectrometry is described. The solutions obtained were stabilized so that the measurements were comparable with those made on standard rocks solutions. Interferences were avoided. The most important methods of silicate rock decomposition were applied, and the useful characteristics from each were combined, and in some cases improved, to obtain the final procedure.

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NON-DESTRUCTIVE RADIOCHEMICAL METHOD FOR DETERMINING CARBON CONCENTRATIONS IN THIN SHEET 3% Si–Fe ALLOY

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The carbon concentration in cold-rolled silicon–iron steel is typically above 200 ppm before decarburization. Carbon removal is necessary because of the undesirable magnetic losses imparted to fully processed (110)[001] 3% Si-Fe by impurities such as carbon. Hence accurate analytical methods are required to determine the effectiveness of decarburization annealing.

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Commercial carbon analysers are available which are designed to eliminate some of the sources of error inherent in classical procedures. In this laboratory, the Leco carbon analyser, which also uses a destructive method, is used for routine carbon determinations. The CO_2 generated from combustion of the sample in pure oxygen is measured by thermal conductivity after separation on a gas-solid chromatographic column. The method is more sensitive and faster than classical procedures, but is limited to carbon concentrations above the 60 ppm level.[1]

Radiochemical techniques are often applicable where conventional wet methods fail. In this laboratory, Goldman[2] developed a sensitive radiochemical procedure for measuring sulphur concentrations as low as 1 ppm by doping 3% silicon–iron with ^{35}S, a weak β-particle emitter. This material was used as a standard for measuring the accuracy of the Kriege–Wolfe method for accurate sulphur determination at the 1-ppm level.[3] Carbon-14 emits β-radiation comparable in energy to ^{35}S β-radiation,[4] but has a much longer half-life (5700 years for ^{14}C, 87 days for ^{35}S). Therefore, it seemed feasible to develop a radiochemical procedure for determining carbon in 3% silicon–iron by using ^{14}C as a tracer element. This paper describes a radiochemical procedure for measuring carbon concentrations by counting the β-radiation emanating from disks of ^{14}C-doped 3% silicon–iron. This technique is non-destructive and permits rapid analysis before and after annealing.

EXPERIMENTAL

Sample preparation

Ingots of 3% Si-Fe doped with ^{14}C were melted as follows. First, prepurified iron was vacuum-melted by induction heating. Second, additions of silicon, manganese and sulphur were made. The silicon reacts with oxygen, thus moderating any subsequent carbon–oxygen reactions which could produce a low recovery of ^{14}C. Third, helium was admitted to the vacuum system to a pressure of ~200 mmHg and the melt was cooled until a light crust appeared on its surface. The ^{14}C and the balance of the carbon (as Fe_3C) were added. To ensure that the ^{14}C dissolved after the Fe_3C, the ^{14}C powder (~6 mCi) was sealed in an iron capsule. Fourth, the melt temperature was increased to complete the mixing and dissolution of the carbon, and the melt was poured into a slab-like mould. The total mass of the alloy was about 2.5 kg. The composition was 3.20% Si, 0.08% Mn, 0.010% C, 0.025% S, <0.001% O, <0.001% N, balance Fe.

The ingot was processed to a final gauge of 0.30 mm in the following manner: (1) hot-rolled in argon at 1050° from an initial thickness of 25 mm to a thickness of 1.9 mm; (2) pickled to remove surface oxide; (3) cold-rolled to 0.63 mm; (4) annealed in helium at 800° for ~10 min; (5) cold-rolled to final gauge of 0.30 mm.

Carbon removal

Carbon was removed from samples of the 0.30-mm thick sheet by isothermal annealing in dry hydrogen (dew point −60°). Under these conditions carbon is removed as methane. Samples were in the form of circular disks 25.4 mm in diameter. Before annealing, samples were chemically polished with a 1:1 v/v mixture of phosphoric acid and 30% hydrogen peroxide solution. The polishing procedure removed a layer of material approximately 0.025 mm thick from each surface, and rendered these surfaces clean and free from surface oxides and imperfections. The isothermal annealing procedure involved the following steps: (1) the sample was mounted upright in a slot cut in a small stainless-steel annealing boat; (2) the boat was placed in the heating zone of an Inconel tube furnace and held at the required temperature for a predetermined time; (3) the boat was quickly withdrawn into a water-cooled chamber. Because of the small combined mass of the boat and sample (~10 g), rapid heating (at ~30°/sec) to isothermal soak temperatures between 800° and 1000° was achieved.

Radiochemical method

The radiochemical technique for carbon analysis is based on the supposition that the carbon is uniformly dispersed through the sheet thickness. Thus, low energy β-particles emitted from a thin surface layer can be correlated with the bulk carbon content. A 25.4-mm diameter disk of ^{14}C-doped 3% Si-Fe was placed in a circular groove in a brass block. The block was firmly seated in the sliding tray of the entrance port of a "castle" containing a Geiger-Müller (GM) end-window tube. Sliding the tray inward placed the sample in close proximity to the window of the GM tube. Thus, the counting geometry was constant. The GM tube was designed to operate at 1500 V and was equipped with a thin mica window 90% efficient in passing β-radiation. The dead-time was 200 μsec, and since the surface activity was always less than 20,000 cpm, no correction was necessary. The surface activity of the ^{14}C-doped disks was counted with a Tracer Lab Superscaler coupled to the output of the GM tube. The activity of both surfaces of a disk was measured, and the average value used to correlate ^{14}C activity with carbon concentration. Fixed-time counting was used. For samples with surface activities > 1000 cpm, a 3-min count was made for each surface of the disk. Longer counting times, *e.g.*, 10 min, were employed for surface activities < 1000 cpm. In all cases, the background activity (~20–30 cpm) was subtracted from the measured activity.

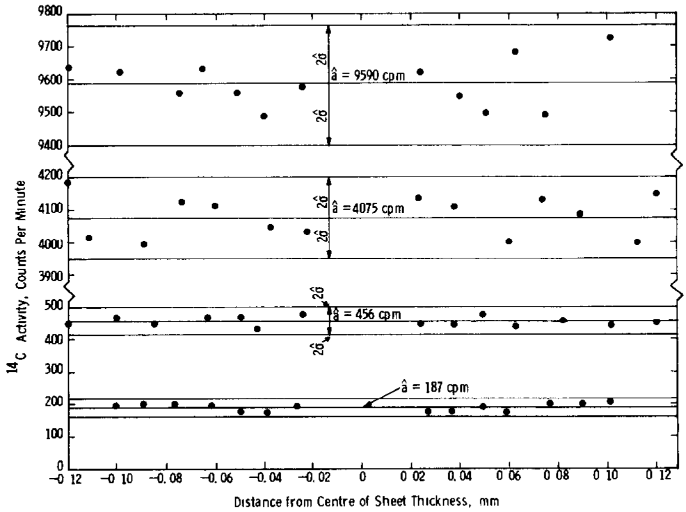

Fig. 1. Variation of ^{14}C activity as a function of sheet thickness.

RESULTS AND DISCUSSION

Disk samples of cold-rolled 0.30-mm thick sheet had ^{14}C surface activities of about 10,000 cpm which was equivalent to only about 1% of the total ^{14}C added during the melting operation. In other words, the measured radiation was associated with β-particles emanating from a surface layer only 1.5 μm thick. Consequently, it was necessary to establish that the ^{14}C surface activity was independent of sheet thickness and total carbon concentration, which is tantamount to testing for the existence of carbon gradients between the two surfaces. Testing for uniformity of ^{14}C concentration as a function of sheet thickness and total carbon concentration was done for four samples having ^{14}C surface activities ranging between ~ 180 (~ 1.5 ppm C) and 9600 cpm (~ 87 ppm C). How the carbon concentrations given in parentheses were obtained will become apparent shortly. The ^{14}C surface activity of each surface of these samples was measured at each thickness before thinning to the next thickness. The results are summarized in Fig. 1. These data show that the ^{14}C surface activity as a function of sheet thickness was within $\pm 2\hat{\sigma}$ of $\hat{a}$, where $\hat{a}$ is the estimate of the ^{14}C surface activity and $\hat{\sigma}$ is the estimate of the standard deviation from the mean. The value for $\hat{a}$ was obtained by averaging the ^{14}C surface activities based on measurements at various thicknesses, while $\hat{\sigma}$ was estimated to be $\sqrt{\hat{a}}$ which is a well-known relationship for radioactive decay processes.[4] The data in Fig. 1 are equivalent to accepting at a confidence level of 95% the hypothesis that ^{14}C is uniformly distributed through the sheet thickness.

Table 1 lists the carbon concentrations of twelve samples of ^{14}C-doped 3% Si-Fe having carbon concentrations > 60 ppm (according to the Leco method), and the corresponding ^{14}C surface activities. It was assumed that carbon measured by the Leco method was sufficiently precise for carbon concentrations > 60 ppm.[1] These data were used to calibrate the ^{14}C method. It is seen in Table 1 that 1 ppm of carbon corresponds to 110 cpm, compared to a background count of ~ 30 cpm. Thus, the limit of detection is about 1 ppm or slightly less, and in principle, could be lowered still further by using more ^{14}C in the melting procedure. Carbon concentrations determined by the Leco method and the ^{14}C method are shown in Fig. 2 for carbon concentrations ranging from 1.5 to 110 ppm. The agreement is excellent in the range 20–110 ppm. The linear correlation coefficient, ρ, in this range is $+0.96$ (23 variates). For carbon concentrations below 20 ppm (^{14}C method) the agreement is poorer, with a ρ of $+0.54$ (11 variates) in the range 1.5–20 ppm.

The ^{14}C radiochemical method described in this work was used to study carbon removal in 3% Si–Fe, as a function of annealing time, temperature and atmosphere.

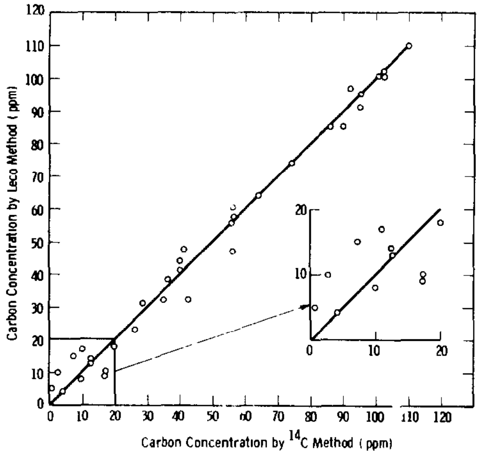

Fig. 2. Relationship between results of carbon measurement by the ^{14}C and Leco combustion methods.

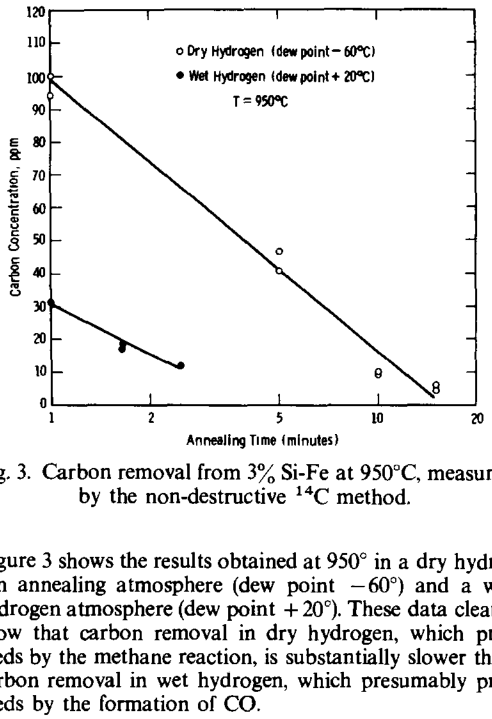

Fig. 3. Carbon removal from 3% Si-Fe at 950°C, measured by the non-destructive ^{14}C method.

Figure 3 shows the results obtained at 950° in a dry hydrogen annealing atmosphere (dew point −60°) and a wet hydrogen atmosphere (dew point +20°). These data clearly show that carbon removal in dry hydrogen, which proceeds by the methane reaction, is substantially slower than carbon removal in wet hydrogen, which presumably proceeds by the formation of CO.

Table 1. Calibration data for the ^{14}C carbon determination method

Carbon by Leco method, *ppm*	^{14}C surface radioactivity, *cpm*	Ratio $^{14}C/C^*$, *cpm/ppm*
60	6200	103
64	7000	109
74	8200	111
85	9500	112
85	9900	116
91	10500	115
95	10500	111
97	10200	105
101	11100	110
101	11300	112
102	11200	110
110	12100	110

*Mean = 110 cpm/ppm, 95% confidence interval: 110 ± 3.6

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4. C. Leymonie, *Radioactive Tracers In Physical Metallurgy*, Wiley, New York, 1963.

Summary—A non-destructive radiochemical method for determining carbon concentrations in thin sheet 3% Si-Fe has been developed. An ingot of 3% Si-Fe was doped with ^{14}C during the melting operation, and subsequently processed to give a 0.30-mm thick sheet. Decarburizing annealing conditions were controlled in order to obtain sheets having final carbon concentrations in the range 1.5–110 ppm. The β-radiation emanating from a thin surface layer of these sheets was found to be independent of sheet thickness, and linearly correlated to the bulk carbon content determined by the Leco carbon analyser, in the range 1.5–110 ppm. The radiochemical method is more sensitive for carbon concentrations below 20 ppm than techniques which rely on sample combustion.

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A STUDY ON THE THEORY OF ACTION OF REVERSIBLE REDOX INDICATORS

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In the traditional treatment for a two-colour indicator it was generally assumed that each of the two colours masks the other such that the first visible change in colour occurs only when 10% of the indicator has changed from one form to the other, and the last visible change occurs when 90% has changed. Thus, it could be said that 10% in one form is effectively invisible in the presence of 90% in the other form.

In more recent treatments such as Bishop's,[1] this idea has been amended to read instead "when colour 1 has ten times the intensity of colour 2 the indicator appears to be completely of colour 1. Thus, when $\epsilon_{ox}[\mathrm{Ind_{ox}}] = 10\epsilon_{red}[\mathrm{Ind_{red}}]$ the indicator appears to the eye to be completely oxidized, and when $10\epsilon_{ox}[\mathrm{Ind_{ox}}] = \epsilon_{red}[\mathrm{Ind_{red}}]$ the indicator appears to be completely reduced." Another recent treatment[2] questions the validity of this 10:1 ratio, and instead uses a variable ratio. These treatments, however, ignore the colour-sensitivity of the eye, and describe the situation in which the eye is replaced by a spectrophotometer. We shall use the term "theoretical" in connection with them, but will use the same approach.

Treatments of one-colour indicators have generally been quite different: the usual assumption is that the coloured form is not visible until a certain finite concentration is present, and that this critical concentration depends on the molar absorptivity of the species, on the depth of solution through which the colour is viewed, and on the minimum absorbance that the individual is able to detect at the particular wavelength. If this is true for the one colour of a one-colour indicator, then it must also hold for the two colours of a two-colour indicator, although if the colours are strong or if the concentration is high, it may not be observable. However, if the colours are weak or the concentration is low, it may be that one form is not observable in the presence of the other, irrespective of the fraction present, because the absorbance of that form is less than the minimum detectable. It may even happen that the colour of one form disappears before the colour of the other form becomes visible.

The present treatment develops this idea by postulating that a certain minimum concentration of an indicator species, in addition to the "theoretical" fraction in the "invisible" form, must be present before the species becomes discernible to the eye, and that this minimum concentration is the same as the minimum concentration which would be defined for a one-colour indicator.

Unsymmetrical stoichiometries occur only rarely, and their mathematical treatment is involved and time-consuming, so the treatment here has been confined to the symmetrical case with $n_{ind} = 1$. Also, the depth of the solution of which the colour is viewed has been assumed to be constant and equal to 1 cm. However, the theory is readily modified for higher values of n and for greater depth of solution.

SYMBOLS USED

E'_0	the conditional potential, or indicator constant, for the indicator.
E_{trans}	the transition potential—the potential at the point where the two colours have equal intensity.
E_{low}	the potential at the point where the second form of the indicator first becomes visible.
E_{high}	the potential at the point where the first form of the indicator finally becomes invisible.
A_c, A'_c	the critical absorbances—the minimum absorbances of the oxidized and reduced forms of the indicator that the individual is able to detect at the wavelength of maximum absorption.
m, m'	the concentrations of the oxidized and reduced forms of the indicator, in the absence of the other form, corresponding to the critical absorbance.
C_r	molar concentration of the indicator, added in reduced form.
x	fraction of indicator oxidized.
N	critical ratio of the absorbances of the two indicator forms (traditionally, $N = 10$).
ϵ_{ox}	molar absorptivity of the oxidized form of the indicator at its absorption maximum.
ϵ_{red}	molar absorptivity of the reduced form of the indicator at its absorption maximum.
k	$\epsilon_{red}/\epsilon_{ox}$.
k'	k/N.
k''	$1/Nk$.

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k'	k/N.
k''	$1/Nk$.

THEORY

At the point where the colour of the oxidized form just becomes visible (the point corresponding to E_{low}), we can regard the absorbance of the oxidized form as composed of two parts, one imperceptible to the eye against the background of the reduced form, and the other the critical absorbance. Setting the imperceptible part equal to the background gives:

$$\epsilon_{\text{ox}} C_r x = (1/N)[\epsilon_{\text{red}} C_r(1 - x)] + A_c \qquad (1)$$

$$= (1/N)[\epsilon_{\text{red}} C_r(1 - x)] + \epsilon_{\text{ox}} m \qquad (2)$$

Substituting $k = \epsilon_{\text{red}}/\epsilon_{\text{ox}}$ and transposing gives

$$m = C_r x - (1/N)[kC_r(1 - x)] \qquad (3)$$

and further substitution of $k' = k/N$ gives

$$m = C_r[x(1 + k') - k'] \qquad (4)$$

The potential at this point is given by:

$$E_{\text{low}} = E_0' + 0.059 \log\left(\frac{x}{1 - x}\right) \qquad (5)$$

Substitution in this expression for x from equation (4) gives, on simplification:

$$E_{\text{low}} = E_0' + 0.059 \log\left[\frac{(m + k'C_r)}{(C_r - m)}\right] \qquad (6)$$

At the point where the colour of the reduced form just disappears (the point corresponding to E_{high}), similar reasoning gives:

$$\epsilon_{\text{red}} C_r(1 - x) = (1/N)\epsilon_{\text{ox}} C_r x + A_c' \qquad (7)$$

$$= (1/N)\epsilon_{\text{ox}} C_r x + \epsilon_{\text{red}} m' \qquad (8)$$

and substituting $k'' = 1/(Nk) = \epsilon_{\text{ox}}/N\epsilon_{\text{red}}$ gives:

$$m' = C_r[1 - x(1 + k'')] \qquad (9)$$

The potential at this point is given by:

$$E_{\text{high}} = E_0' + 0.059 \log\left(\frac{x}{1 - x}\right) \qquad (10)$$

and substitution for x from equation (9) gives

$$E_{\text{high}} = E_0' + 0.059 \log\left[\frac{(C_r - m')}{(m' + k''C_r)}\right] \qquad (11)$$

The transition interval, ΔE, is given by

$$\Delta E = E_{\text{high}} - E_{\text{low}}$$

$$= 0.059 \log\left[\frac{(C_r - m')(C_r - m)}{(m' + k''C_r)(m + k'C_r)}\right] \qquad (12)$$

and the transition potential is given by

$$E_{\text{trans}} = \frac{E_{\text{low}} + E_{\text{high}}}{2}$$

$$= E_0' + \frac{0.059}{2} \log\left[\frac{(C_r - m')(m + k'C_r)}{(m' + k''C_r)(C_r - m)}\right] \qquad (13)$$

Let us now see how these equations can be simplified when applied to specific situations.

(*a*) A one-colour indicator with colourless reduced form:

$$\epsilon_{\text{red}} = 0, \quad \text{so} \quad k = 0 = k',$$

and equation (6) reduces to

$$E_{\text{low}} = E_0' + 0.059 \log\left[\frac{m}{C_r - m}\right] \qquad (14)$$

E_{high} and E_{trans} are irrelevant because the eye is incapable of judging when the corresponding colour intensities have been reached.

(*b*) A one-colour indicator with a colourless oxidized form:

$$\epsilon_{\text{ox}} = 0,\ k = \infty \text{ and } k'' = 0,$$

so equation (11) reduces to

$$E_{\text{high}} = E_0' + 0.059 \log\left[\frac{C_r - m'}{m'}\right] \qquad (15)$$

E_{low} and E_{trans} are irrelevant in this case.

(*c*) A "normal" two-colour indicator (with both colours reasonably intense) m and $m' \ll C_r$ and equation (6) reduces to

$$E_{\text{low}} = E_0' + 0.059 \log\left[\frac{k'C_r}{C_r}\right]$$

$$= E_0' + 0.059 \log k'$$

$$= E_0' + 0.059 \log(\epsilon_{\text{red}}/N\epsilon_{\text{ox}}) \qquad (16)$$

and equation (11) reduces to

$$E_{\text{high}} = E_0' + 0.059 \log\left[\frac{C_r}{k''C_r}\right]$$

$$= E_0' + 0.059 \log(N\epsilon_{\text{red}}/\epsilon_{\text{ox}}) \qquad (17)$$

Equation (12) reduces to

$$\Delta E = 0.059 \log\left[\frac{C_r^2}{k'k''C_r^2}\right]$$

$$= 0.059 \log\left[\frac{N}{k} \cdot \frac{Nk}{1}\right]$$

$$= 0.118 \log N \qquad (18)$$

For $N = 10$, this becomes $\Delta E = 118$ mV.

$$E_{\text{trans}} = E_0' + \frac{0.059}{2} \log k^2$$

$$= E_0' + 0.059 \log(\epsilon_{\text{red}}/\epsilon_{\text{ox}}). \qquad (19)$$

(*d*) For a two-colour indicator with coloured forms of equal absorptivity, $\epsilon_{\text{red}} = \epsilon_{\text{ox}}$, and $k = 1$. Hence equation (6) becomes

$$E_{\text{low}} = E_0' + 0.059 \log\left[\frac{m + C_r/N}{C_r - m}\right] \qquad (20)$$

and equation (11) becomes

$$E_{\text{high}} = E_0' + 0.059 \log\left[\frac{C_r - m'}{m' + C_r/N}\right] \qquad (21)$$

and if the colours are reasonably intense, m and $m' \ll C_r$, they become

$$E_{\text{low}} = E_0' + 0.059 \log(1/N) \qquad (22)$$

$$E_{\text{high}} = E_0' + 0.059 \log N \qquad (23)$$

and again $\Delta E = 0.118 \log N$.

These simplified forms of the equations are in agreement with the equations derived for the same situations by other authors. However, the real test of this new treatment is its ability to deal with a situation which cannot be adequately treated by other theories. A suitable case is the indicator ferroin, which is sometimes considered as a one-colour indicator[3] and sometimes as a two-colour indicator. This arises because the two forms have strikingly different absorptivities ($\epsilon_{\text{red}}:\epsilon_{\text{ox}} = 20:1$). Its conditional potential in 1*M* sulphuric acid is 1.06 V,[4,5] and the point normally taken as the end-point corresponds to a potential of 1.12–1.14 V.[4,5]

In practical titrations with ferroin, the point normally taken as the end-point is the point where the pink colour of the reduced form just disappears, and this corresponds to E_{high} as defined above, and NOT to E_{trans}.

When the equation derived for two-colour indicators by Bishop[1] is applied to ferroin, the value found for E_{high} is 1.20 V, which obviously disagrees with the experimental evidence.

Applying the present treatment, and taking $m = 4.5 \times 10^{-5}M$ and $m' = 2.0 \times 10^{-6}M$, the following results are obtained:

(1) with 2 ml of 0.025*M* indicator per 100 ml of titration solution (*i.e.*, $C_r = 5 \times 10^{-4}M$)

$E_{high} = 1.18$ V

$E_{low} = 1.08$ V

(2) with 0.2 ml of 0.025*M* indicator per 100 ml of titration solution (*i.e.*, $C_r = 5 \times 10^{-5}M$)

$E_{high} = 1.14$ V

$E_{low} = 1.15$ V

(3) with 0.1 ml of 0.025*M* indicator per 100 ml of titration solution (*i.e.*, $C_r = 2.5 \times 10^{-5}M$)

$E_{high} = 1.12$ V

E_{low} = undefined

(note that *m* and *m'* are experimental parameters which must be determined by the individual analyst).

These figures show that, at the sort of ferroin concentrations normally used (*i.e.*, $5 \times 10^{-5}M$ and $2.5 \times 10^{-5}M$) the predictions for E_{high} are in good agreement with experiment. The E_{low} values are also of interest: at ferroin concentration $5 \times 10^{-5}M$, E_{high} is lower than E_{low}, and this agrees with the experimental evidence, since at this concentration, the pink colour of the reduced form disappears, leaving a colourless solution, and the blue colour does not become visible until more titrant has been added. At the lower concentration of $2.5 \times 10^{-5}M$, the blue colour never becomes visible, which is in accord with the undefined nature of E_{low}.

At the very much higher concentration of $5 \times 10^{-4}M$, ferroin does indeed behave very much as an "ordinary" two-colour indicator, because both the colours are now quite intense. For this solution, therefore, the values found from the present treatment are in reasonable agreement with values calculated from Bishop's equation.

ΔE for a two-colour indicator is a function of *N*, and it is easy to see that increasing *N* to 15 would increase ΔE by 0.021 V, and decreasing *N* to 5 would decrease ΔE by 0.035 V, relative to the value for $N = 10$. Values of *N* in the range 8–12 would give ΔE values within the range $\Delta E_{(N=10)} \pm 0.01$.

The treatment can be extended to acid–base indicators by writing equations analogous to (1) and (7), but such a critical treatment is less important, because of the availability of a large number of indicators, covering the entire pH range. However, it is obvious that one-colour indicators are superior for obtaining an end-point at a desired potential, or pH, because the value of E_{low} (or pH_{low}) is concentration-dependent and so adjustable over a narrow range.

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A SELECTIVE SORBENT FOR CONCENTRATING NOBLE METALS

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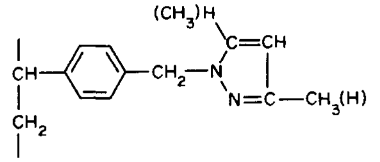
We have synthesized chelate sorbents containing pyrazole groups as substituent by aminating chloromethylated styrene–divinylbenzene copolymers with 3(5)-methylpyrazole. The structure of the chelate group of the sorbents may be depicted as



Sorbents with such groups possess selectivity with respect to noble metals in the presence of Cu, Fe, Co, Ni, *etc.* This is caused by the fact that the introduction of the aromatic system (polystyrene) into 3(5)-methylpyrazole as an *N*-substituent leads to a decrease in the reactivity of the pyrazole ligand.[2] The sorption of Fe, Cu and other elements becomes slight, whereas noble metals, which exhibit typical *b*-group behaviour, interact with the pyrazole groups of the sorbent. This difference allows such sorbents to be used for selective concentration of noble metals during the analysis of various materials.

In the present paper the synthesis of the sorbents is described, and their sorption capacity and selectivity for noble metals.

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3(5)-Methylpyrazol (98%, b.p. 204–5°, 90 ml) is added to 30 g of a chloromethylated styrene–divinylbenzene macroporous copolymer and kept for 3 hr for swelling. Then the mixture is heated to 60–70° and kept at this temperature for 8 hr, with careful stirring. The polymer is filtered off, washed with water and dried in air.

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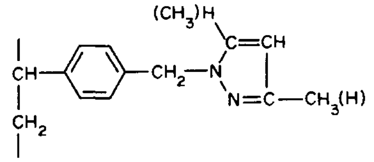

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In the present paper the synthesis of the sorbents is described, and their sorption capacity and selectivity for noble metals.

EXPERIMENTAL

Synthesis of the sorbents

3(5)-Methylpyrazol (98%, b.p. 204–5°, 90 ml) is added to 30 g of a chloromethylated styrene–divinylbenzene macroporous copolymer and kept for 3 hr for swelling. Then the mixture is heated to 60–70° and kept at this temperature for 8 hr, with careful stirring. The polymer is filtered off, washed with water and dried in air.

Table 1. Characteristics of sorbents based on 3(5)-methylpyrazole

Initial copolymer*		Sorbent N, %	Degree of chlorine substitution,† %	Sorption, *mg/g*		
				Ag(I)		Au(III), 1*M* HCl
DVB, %	Cl, %			pH ~ 7	1*M* HNO_3	
8	23	11.6	65	177	164	170
12	17	8.2	63	116	142	182
20	16	6.5	51	92	102	160
40	11	4.1	47	45	53	116
60	9	3.9	55	—	50	95

* Size of granules for all sorbents is 0.25–0.5 mm, except for 60% DVB (< 0.25 mm).
† Calculated according to nitrogen content.

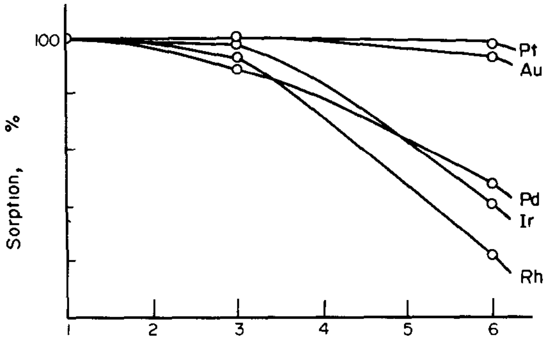

Fig. 1. Sorption of microgram amounts of noble metals from hydrochloric solutions. Solution volume 10 ml; 50 mg of sorbent (8% DVB); time of contact 2 hr; temperature ~100°.

Sorption

The sorption was studied under static conditions at room temperature and at 100°. The volume of solution was 10 ml, and the sorption time 2 hr. Standard solutions of the chloro-complexes were used: [Au(III)] = 1.02 mg/ml; [Pd(II)], [Pt(IV)] and [Rh(III)] = 10 μg/ml; [Ir(IV)] = 0.002–10 μg/ml. A 0.2*M* solution of silver nitrate was also used. The degree of sorption was estimated from the amount of metal found in the sorbent (after mineralization with acid). Silver was determined by titration, Au, Pd, Pt and Rh spectrophotometrically, and Ir radiometrically.

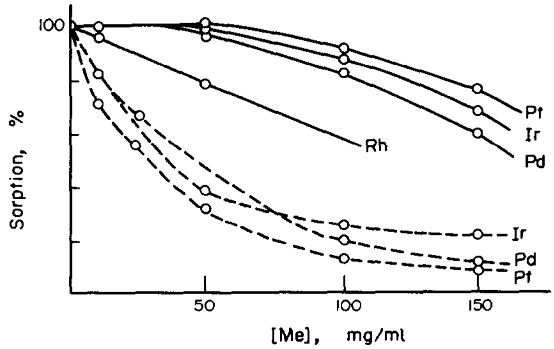

Fig. 2. Sorption of microgram amounts of noble metals in the presence of Cu (——) and Fe(III) (---) in 1 *M* HCl. Solution volume 10–20 ml; 50 mg of sorbent (8% DVB); time of contact 2 hr; temperature ~100°.

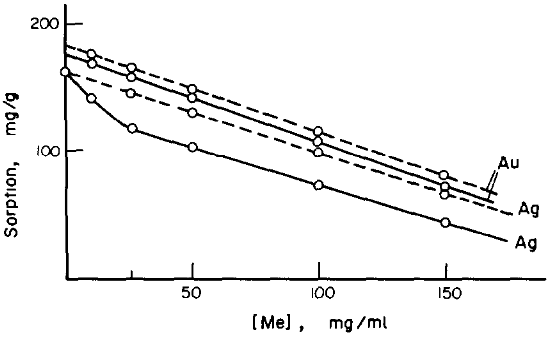

Fig. 3. Sorption of milligram amounts of Ag and Au in the presence of Cu (——) and Fe(III) (---) in 1*M* HCl. Solution volume 10–20 ml; 50 mg of sorbent (8% DVB); time of contact 2 hr; temperature 20°.

RESULTS AND DISCUSSION

The sorbents synthesized were based on styrene-divinylbenzene macroporous copolymers with different divinylbenzene(DVB) contents. The characteristics of the sorbents are given in Table 1.

As seen from the Table, the sorption properties are best for sorbents based on styrene copolymers with 8 and 12% DVB. The static capacity for the 8% DVB is 263 mg/g for Ag in 0.5*M* nitric acid and 660 mg/g for Au in 1*M* hydrochloric acid.

Sorption of the noble metals depends on the solution acidity and the concentration of other elements (Figs. 1–3). Microgram amounts of Pd, Rh and Ir are completely sorbed from solutions up to 3*M* in hydrochloric acid, and of Au and Pt from even more acid solutions. Sorption of Ag is maximal from 0.5*M* nitric acid.

The study of the noble metal sorption in the presence of Al, Ca, Co, Ni, Cu and Fe has shown that the extent of sorption depends on the concentration of the non-noble elements; they do not interfere in concentration below 50 mg/ml. Iron(III) has the largest effect (Fig. 3).

The selectivity for the noble metals is obviously due to the formation of Au, Pd, Pt, Rh and Ir co-ordination compounds with the functional analytical groups of sorbents. This may be confirmed by infrared spectroscopy. The appearance of absorption bands in the 200–400 cm^{-1} region in the spectra of the sorbents saturated with the metals indicates complexing of the metals with the nitrogen atom of the pyrazole group of the sorbent.[3] The low degree of sorption of Cu, Co and other elements is apparently because their complexes with the chelate groups of the sorbent have low stability.

This study has shown that these sorbents may be recommended for selective group concentration of noble metals in analysis of various materials. These sorbents may also be used for extraction of Au and Ag from solutions of salts of Cu, Fe and other elements (Fig. 3).

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Summary—New chelating sorbents have been synthesized by aminating chloromethylated styrene—divinylbenzene macroporous copolymers with 3(5)-methylpyrazole. The sorption of noble metals from acid solutions and the selectivity has been studied. The sorbents are of interest for selective concentration and extraction of the noble metals.

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DETERMINATION OF SOME ORGANIC THIO-COMPOUNDS BY PRECIPITATION OF MERCURIC SULPHIDE FROM MERCURY(II) AMMINE COMPLEXES—I.

DETERMINATION OF THIOACETAMIDE AND THIOACETANILIDE

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For the determination of thioacetamide (TAA), oxidimetric,[1,2] complexometric[3] and thiomercurimetric[4] methods have been developed. Among the instrumental methods, those based on the reaction of TAA with silver have been most widely used, including potentiometric,[5–8] amperometric[9] and coulometric[10] procedures. For the amperometric determination use has also been made of the reaction with copper(I).[11]

Mercury(II), in aqueous acid solution, forms with TAA a number of variously coloured precipitates. When boiled with potassium hydroxide solution these precipitates become converted into HgS.[12,13] Precipitation of HgS by TAA in an alkaline solution is made the basis for determination of mercury.[14–16]

The purpose of this paper is to describe an accurate and relatively rapid gravimetric method for determining thioacetamide and thioacetanilide at the concentrations conventionally employed in the quantitative precipitation of metallic sulphides. Thioacetanilide, a derivative of thioacetamide, can also be used for precipitating metallic sulphides from homogeneous solution.[17] The method for determining thioacetamide and thioacetanilide consists in precipitating HgS from solutions of ammino mercury complexes. When ammonia is added to a mercury(II) chloride or oxy-anion solution, mercury(II) ammine-chloride or a salt of Millon's base precipitates, respectively. If, however, the solution contains a high concentration of ammonium salts, the precipitates either dissolve or do not form. This is achieved by adding enough nitric acid (15 ml of conc. acid is usually enough) and ammonia (>30 ml of conc. solution) to prevent precipitation of mercury compounds other than the sulphide. Depending on the conditions, diammino or tetra-ammino mercury complexes are formed.[18–20]

These complexes have been utilized for separating iron from mercury[21,22] and bismuth from mercury.[22] Iron and bismuth are precipitated with ammonia, from a solution containing enough nitric acid to avoid formation of a transient precipitate of mercury compound.

EXPERIMENTAL

Reagents

Thioacetamide and thioacetanilide, repeatedly crystallized from ethanol, were used. The thioacetamide was analysed by Petri and Lipiec's gravimetric method.[5]

Procedure

Determination of thioacetamide. Concentrated nitric acid 15 ml, is added to V ml of $0.1M$ ($V = 0.2 \times$ number of mg of thioacetamide taken or 10 ml, whichever is the larger), then 100 ml of water and finally at least 30 ml of concentrated ammonia solution are added with stirring. The solution is heated to about 60° and the weighed sample of TAA dissolved in water is added to it. The solution is heated to boiling point, kept boiling for 3–5 min, and set aside. After the resulting precipitate has settled (a few minutes), it is collected on a porosity 4 or 5 sintered-glass crucible, washed with water and then several times with methanol, and dried for 15 min at 110°.

Determination of thioacetanilide. A weighed sample of thioacetanilide is dissolved in methanol and analysed as in the case of thioacetamide but with $V = 0.1 \times$ number of mg of thioacetanilide or 5 ml, whichever is the larger.

Table 1. Results

Compound	Taken, *mg*	Found, *mg*	Error, %
Thioacetamide	25.0	25.1	+0.4
	54.6	54.6	0.0
	104.0	104.4	+0.4
	150.2	150.0	−0.1
	203.8	203.8	0.0
Thioacetanilide	25.3	25.0	−1.2
	50.6	50.0	−1.2
	100.2	100.6	+0.4
	151.3	150.8	−0.3
	201.6	202.4	+0.4

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RESULTS

Results of determinations of thioacetamide and thioacetanilide are presented in Table 1.

A comparison of the amounts taken and found proves that the present method shows good accuracy.

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Summary—A gravimetric method based on precipitation of mercuric sulphide has been developed for determining thioacetamide and thioacetanilide. Concentrated nitric acid is added to $0.1M$ mercuric nitrate, the solution is made alkaline with concentrated ammonia solution, and thioacetamide (dissolved in water) or thioacetanilide (dissolved in alcohol) is added, and the mixture is boiled. The method has good accuracy, and takes about 40 min.

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CONSTANT-POTENTIAL ELECTROLYSIS: DETERMINATION OF DIFFUSION COEFFICIENTS OF THALLIUM BY USING A HANGING MERCURY DROP ELECTRODE

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For the determination of diffusion coefficients from measurements obtained in diffusion-controlled processes several methods have been used. Lingane and Loveridge[1] used conventional polarography, with the Ilkovič equation corrected for spherical electrodes. Other techniques used include alternating current techniques,[2] double galvanostatic pulse,[3] impedance measurements[4,5] and chronopotentiometry.[6]

Potentiostatic methods have been used for the determination of the rates and mechanisms of very fast electrode reactions that cannot be studied by polarographic methods.[7] The stationary mercury drop electrode has been used for this purpose, the electrode curvature being ignored; for this reason, electrolysis times of the order of μsec–msec were used and the equations for plane electrodes could be utilized.

Shain and co-workers[8–12] derived the theoretical equations for spherical diffusion conditions and used them for the determination of diffusion coefficients. There are no literature data on the diffusion coefficients of Tl(I) in sodium citrate–sodium hydroxide medium. For the diffusion coefficient of Tl in mercury, the value 0.99×10^{-5} cm^2/sec obtained by Cooper and Furman[13] by the polarographic method agrees with the value of 1.03×10^{-5} cm^{-2}/sec obtained by Wogau.[14] We have determined both coefficients by application of the potentiostatic method.

THEORY

The general equation of the I–t curves for processes controlled by spherical diffusion, deduced by Stevens and Shain[12] for systems where $D_o \neq D_r$, and valid for potentials more cathodic and more anodic than the standard potential of the system, is:

$$i = nFAD_0C_0^*\left[\frac{1}{(1+\gamma\sigma)(\pi D_0 t)^{1/2}} + \frac{1}{(1-\gamma^2\sigma)r_0} - \frac{\sigma(1+\gamma)^2 e^{\beta^2 t}\operatorname{erfc}\beta t^{1/2}}{r_0(1-\gamma^2\sigma)(\gamma\sigma+1)^2}\right] \quad (1)$$

where $\sigma = C_0/C_r = \exp[nF(E - E^0)/RT]$, C_0 and C_r are concentrations of the oxidized and reduced forms at the electrode surface, D_0 and D_r are the diffusion coefficients of the species, C_0^* is the bulk concentration of the oxidized form,

$$\gamma = \left(\frac{D_0}{D_r}\right)^{1/2}$$

and

$$\beta = \frac{1}{r_0}\left(\frac{\sigma D_0 - D_r}{\sigma D_0^{1/2} + D_r^{1/2}}\right).$$

Equation (1) can be reduced to simpler expressions for particular cases. Thus, for very cathodic potentials $\sigma \rightarrow 0$

RESULTS

Results of determinations of thioacetamide and thioacetanilide are presented in Table 1.

A comparison of the amounts taken and found proves that the present method shows good accuracy.

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where $\sigma = C_0/C_r = \exp[nF(E - E^0)/RT]$, C_0 and C_r are concentrations of the oxidized and reduced forms at the electrode surface, D_0 and D_r are the diffusion coefficients of the species, C_0^* is the bulk concentration of the oxidized form,

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and

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Equation (1) can be reduced to simpler expressions for particular cases. Thus, for very cathodic potentials $\sigma \rightarrow 0$

Table 1. Diffusion coefficient of Tl(I) in sodium citrate–sodium hydroxide medium (unmodified electrode)

	D_0, $10^{-5} cm^2/sec$					
	E −0.60 V Tl(I) = 2.58 × $10^{-3}M$		E −0.80 V Tl(I) = 2.58 × $10^{-3}M$		E −1.0 V Tl(I) = 1.80 × $10^{-3}M$	
r_0, mm	intercept	slope	intercept	slope	intercept	slope
0.432	0.58	0.80	0.44	0.66	0.69	0.70
0.484	0.33	0.81	0.52	0.72	0.63	0.71
0.523	0.31	0.81	0.56	0.74	0.61	0.72
0.559	0.44	0.81	0.65	0.73	0.58	0.77
0.599			0.64	0.72	0.64	0.76
0.632			0.65	0.72	0.69	0.75
0.658			0.70	0.72	0.72	0.78
0.685			0.73	0.73	0.74	0.76
0.708			0.73	0.73		

and equation (1) reduces to

$$i = nFAD_0C_0^*\left[\frac{1}{(\pi D_0 t)^{1/2}} + \frac{1}{r_0}\right] \qquad (2)$$

For very short times or for very large radius the term $1/r_0$ is negligible and the equation is transformed into the corresponding expression for plane electrodes.

Expression (1) can also be simplified when the term $\sigma = C_0/C_r$ is very large (working at potentials more anodic than the standard potential, E_0):

$$i = nFAD_0C_0^*\left[\frac{1}{\gamma\sigma(\pi D_0 t)^{1/2}} - \frac{1}{\gamma^2\sigma r_0}\right] \qquad (3)$$

At potentials near to E_0 it is necessary to utilize the complete equation (1).

Calculation of D_0

By means of electrolysis at constant potential, working with a stationary mercury drop electrode, and using sufficiently cathodic potentials, the I–t curves are obtained. From these curves, the I *vs.* $1/t^{1/2}$ plots are obtained, and are linear; from the slope, intercept and equation (2) it is possible to obtain D_0.

Calculation of D_r *from cathodic curves (indirect method)*

To calculate D_r it is necessary to work at sufficiently anodic potentials. From the I *vs.* $1/t^{1/2}$ plots straight lines are obtained of which the slopes (m) and intercepts (i_∞) are functions of $\gamma\sigma$ and $\gamma^2\sigma$ respectively.

$$m = \frac{nFAD_0C_0^*}{\gamma\sigma(\pi D_0)^{\frac{1}{2}}} \qquad -i_\infty = \frac{nFAD_0C_0^*}{r_0\gamma^2\sigma}$$

$$\gamma\sigma = \frac{nFAD_0C_0^*}{m(\pi D_0)^{\frac{1}{2}}} \qquad \gamma^2\sigma = -\frac{nFAD_0C_0^*}{i_\infty r_0}$$

From these expressions it is possible to calculate γ and D_r, because D_0 is already known.

Calculation of D$_r$ *from anodic curves (direct method)*

D_r can be calculated in a similar way to D_0. It is necessary to obtain an amalgam of known concentration and record the I–t curves; from these curves the I *vs.* $1/t^{1/2}$ graphs are plotted, and the D_r value is calculated from the slope and the intercept.

EXPERIMENTAL

Reagents

Supporting electrolyte solutions of 1.0M sodium citrate and 0.1M sodium hydroxide. Tl(I) solutions obtained from hallium acetate and gravimetrically standardized by the Bashilova method.[15]

Apparatus

A Beckman Electroscan-30 with a three-electrode system was used; saturated calomel reference electrode; platinum auxiliary electrode separated from the solution by a sintered glass disc and agar-agar saturated KCl salt bridge; stationary hanging mercury drop working electrode. For more precise potential measurements a Metrohm E-510 potentiometer was used. To minimize convection the experiments were carried out on an antivibration table.

Procedure

The thermostatically controlled cell is put on the antivibration table and nitrogen is passed through the solution for 20 min to remove oxygen, then the solution is left for 3 min with no gas flow. The potential is applied and the cathodic or anodic I–t curve is scanned for 25 sec at 0.508 cm/sec. From these curves the I *vs.* $1/t^{1/2}$ diagrams are plotted. The slopes and intercepts are used to evaluate D_0. The Tl(0) amalgam is made by electrolysis of *ca.* $10^{-3}M$ Tl(I) solution at an applied potential of −0.80 V and then left long enough to become homogeneous. The amalgamated metal is dissolved electrolytically at −0.2 V to give the I–t curves. The electrode radius is evaluated by weighing 50 drops obtained under identical conditions.

RESULTS AND DISCUSSION

Determination of D$_0$ *from cathodic curves*

Influence of the applied potential. Table 1 shows that when potentials of −0.6, −0.8 and −1.0 V are used, the precision is poor and there is a great difference between the D_0 values obtained from the slope and the intercept of the I *vs.* $1/t^{1/2}$ graphs, except for values obtained with a large electrode radius, and the results obtained at the more negative potentials are superior. Though the poor precision was also caused, as can be seen later on, by the form and size of the electrode, −0.60 V is not sufficiently cathodic for the simplified equation to be valid.

Influence of convection. It was observed that convection had an effect when the time of electrolysis was very long or very short. With very long times, density gradients were produced in the cell, and vibrations causing current intensities higher than the theoretical. With very short times, higher current intensities than the theoretical were also obtained because the surface tension on the mercury drop changed, on application of the working potential; this effect caused the drop to fall if its radius was larger than 0.071 cm. An electrode of radius between 0.05 and 0.07

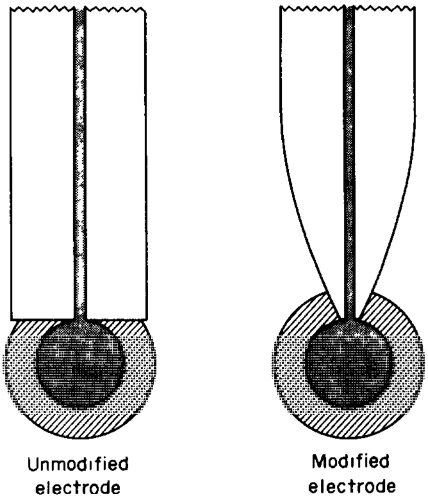

Fig. 1.

cm and electrolysis times between 5 and 25 sec were therefore used.

Influence of the electrode size. It was observed, for electrode radius smaller than 0.05 cm, that the D_0 values obtained from the intercept were smaller than those from the slope. This is probably due to the distortion of the limiting diffusion layer in the proximity of the capilary, causing smaller currents than the theoretical. The end of the capillary was therefore ground so that the orifice did not have a plane surface around it (Fig. 1). With this modified electrode agreeing values of D_0 were obtained by both methods over the radius range 0.05–0.07 cm (Table 2).

Table 3. Diffusion coefficient of Tl(0) in mercury (indirect method, modified electrode, Tl(I) = 1.29 × $10^{-3}M$)

	r_0 = 0.599 mm		r_0 = 0.632 mm	
E, mV	γ	D_r	γ	D_r
−424	0.90	0.96	0.91	0.94
−435	0.91	0.94	0.91	0.94
−457	0.93	0.90	0.94	0.88
−470	0.94	0.88	0.94	0.88
−478	0.94	0.88	0.94	0.88

Table 4. Diffusion coefficient of Tl(0) in mercury (direct method, Tl(I) = 1.29 × $10^{-3}M$, *E* −0.20 V *vs.* SCE)

	D_r, $10^{-5}cm^2/sec$	
r_0, *mm*	intercept	slope
0.484	1.31	1.29
0.523	1.24	1.19
0.559	1.12	1.09
0.599	0.99	0.99
0.632	1.00	0.99
0.658	0.98	0.98
0.685	0.98	0.97
0.708	0.96	0.98

Determination of D_r *from cathodic curves*

The diffusion coefficient for the reduced form in the mercury can be calculated from the cathodic or the anodic curves. The advantage of the cathodic method is that a known concentration of amalgam is not necessary. On the other hand, the precision is poor, because the current values are low and the values of i_∞ are calculated by extrapolation.[10]

With the modified electrode, drop radius of 0.0599 and 0.0632 cm and several potentials between −0.420 and −0.478 V, two series of experiments were carried out. From the results a value of 0.91 × 10^{-5} cm²/sec was obtained (Table 3), not too close to the value found by other authors.[13,14]

Direct determination of D_r

In this method an amalgam of known concentration is used. Under these conditions, with an electrode radius of 0.05–0.07 cm, a value of (0.98 ± 0.01) × 10^{-5} cm²/sec is obtained, in agreement with the values found by other authors.[13,14] For electrode radii <0.05 cm (Table 4), the precision is poor and the values from the intercept are greater than those from the slope, because the distortion of the limiting diffusion layer is then not negligible; the errors are of different sign according to whether the process is controlled by divergent diffusion (the anodic process) or convergent diffusion (the cathodic process).

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Table 2. Diffusion coefficient of Tl(I) in sodium citrate–sodium hydroxide medium (modified electrode)

	D_0, $10^{-5}cm^2/sec$					
	E −0.80 V Tl(I) = 1.38 × $10^{-3}M$		*E* −1.0 V Tl(I) = 1.38 × $10^{-3}M$		*E* −0.80 V Tl(I) = 2.58 × $10^{-3}M$	
r_0, mm	intercept	slope	intercept	slope	intercept	slope
0.432					0.55	0.60
0.484					0.63	0.72
0.523					0.67	0.74
0.559	0.77	0.73	0.73	0.73	0.74	0.78
0.599	0.76	0.74	0.73	0.74	0.77	0.76
0.632	0.77	0.76	0.77	0.76	0.78	0.78
0.658	0.79	0.77	0.79	0.77	0.78	0.78
0.685	0.78	0.78	0.79	0.79	0.78	0.82
0.708	0.77	0.78	0.81	0.79	0.79	0.82

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THE pH-DEPENDENCE OF ENTROPY CHANGES OF METAL–EDTA COMPLEX FORMATION

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Various methods for the determination of metal chelate stability constants have been developed, and reviewed.[1] The structure of metal chelate complexes in solution has been discussed on the basis of thermodynamic and spectroscopic data.[2] The chelate effect on the stability constant of the complex is of special interest.

The temperature-dependence of the stability constant is here studied at various pH values, and the pH-dependence of the entropy change of metal–EDTA complex formation is estimated and interpreted.

EXPERIMENTAL

The stability constants were determined by means of potentiometric measurements with a mercury electrode.[3] The concentrations of the mercury chelate, the metal ion and the metal chelate were 10^{-4}, 10^{-3} and $10^{-2}M$, respectively, and the metal ions studied were Ca^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+}. All chemicals were purified by recrystallization. Sodium perchlorate solution (0.1*M*) was used as the supporting electrolyte, and the ionic strength was kept at 0.11. The solution pH was controlled in the range 3–8 by adding perchloric acid. The method could not be applied outside this pH range because of the formation of HgHY^- in the acid region and $\mathrm{Hg(OH)Y}^{3-}$ in the alkaline region. The solution was deaerated with purified nitrogen before measurement. The temperatures were kept constant within ± 0.05°.

RESULTS AND DISCUSSION

The reaction between a bivalent metal ion and EDTA in acidic solution is represented by

$$\mathrm{M}^{2+} + 2\,\mathrm{Y}^{4-} + i\,\mathrm{H}^+ \rightleftharpoons \mathrm{MY}^{2-} + \mathrm{H}_i\mathrm{Y}^{i-4} \qquad (1)$$

The conditional stability constant of this reaction is defined as

$$K_{\mathrm{M'Y'}} = K_{\mathrm{MY}}/\alpha_{\mathrm{Y}} \qquad (2)$$

where K_{MY} and α_{Y} are the thermodynamic stability constant for the metal–EDTA complex and the side-reaction coefficient, respectively. α_{Y} is given by

$$\alpha_{\mathrm{Y}} = 1 + \sum[\mathrm{H}]^i\Pi K_{\mathrm{H,Y}}. \qquad (3)$$

According to the Schmid and Reilley methods[3] a combination of the Nernst equation for a mercury electrode with the equations for the stability constants of mercury–EDTA and metal–EDTA complexes gives the equation

$$E = E'^{0}_{\mathrm{Hg}} + RT/2F \ln [\mathrm{M}][\mathrm{HgY}]\,K_{\mathrm{MY}}/[\mathrm{MY}]K_{\mathrm{HgY}} \qquad (4)$$

where $E'^{0}_{\mathrm{Hg}} = 612$ mV (*vs.* SCE), and [M], [HgY] and [MY] are the concentrations of metal ion, mercury–EDTA and metal–EDTA complexes, respectively.

By substitution of equations (3) and (4) into (2), the conditional stability constant is given by

$$K_{\mathrm{M'Y'}} = [\mathrm{MY}]K_{\mathrm{HgY}}/[\mathrm{M}][\mathrm{HgY}] \times \left(1 + \sum_i [\mathrm{H}]^i\Pi K_{\mathrm{H,Y}}\right)\exp[2F(E - E'^{0}_{\mathrm{Hg}})/RT] \qquad (5)$$

From (5), $K_{\mathrm{M'Y'}}$ is obtained as a simple function of the potential of the mercury electrode, provided that the concentrations of the mercury–EDTA and metal–EDTA complexes, metal ion and hydrogen ion are kept constant, and hence, can be estimated from the experimental data and the stability constant for the mercury–EDTA complex.

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The conditional stability constant of this reaction is defined as

$$K_{M'Y'} = K_{MY}/\alpha_Y \qquad (2)$$

where K_{MY} and α_Y are the thermodynamic stability constant for the metal–EDTA complex and the side-reaction coefficient, respectively. α_Y is given by

$$\alpha_Y = 1 + \sum [H]^i \Pi K_{H_iY}. \qquad (3)$$

According to the Schmid and Reilley methods[3] a combination of the Nernst equation for a mercury electrode with the equations for the stability constants of mercury–EDTA and metal–EDTA complexes gives the equation

$$E = E'^{0}_{Hg} + RT/2F \ln [M][HgY]\,K_{MY}/[MY]K_{HgY} \qquad (4)$$

where $E'^{0}_{Hg} = 612$ mV (*vs.* SCE), and [M], [HgY] and [MY] are the concentrations of metal ion, mercury–EDTA and metal–EDTA complexes, respectively.

By substitution of equations (3) and (4) into (2), the conditional stability constant is given by

$$K_{M'Y'} = [MY]K_{HgY}/[M][HgY] \times \left(1 + \sum_i [H]^i \Pi K_{H_iY}\right) \exp[2F(E - E'^{0}_{Hg})/RT] \qquad (5)$$

From (5), $K_{M'Y'}$ is obtained as a simple function of the potential of the mercury electrode, provided that the concentrations of the mercury–EDTA and metal–EDTA complexes, metal ion and hydrogen ion are kept constant, and hence, can be estimated from the experimental data and the stability constant for the mercury–EDTA complex.

Table 1. Entropy changes of EDTA complex formation at various pH values

Cation	pH	ΔS°, $cal \cdot mole^{-1} \cdot deg^{-1}$
Ni^{2+}	3.71	21.0
	4.40	33.4
	4.90	41.1
	5.51	49.4
Pb^{2+}	3.00	16.3
	4.81	17.3
	5.10	18.1
	5.47	18.9
Mn^{2+}	3.00	29.9
	3.66	34.1
	5.86	34.6
	6.36	34.8
Ca^{2+}	4.10	13.0
	4.87	13.4
	6.31	13.5
	7.36	15.4

The standard free energy change for reaction (1) is related to the conditional stability constant by

$$K_{M'Y'} = \exp(-\Delta G^0/RT) \qquad (6)$$

From the temperature-dependence of $K_{M'Y'}$, the entropy change of reaction (1) can be calculated. The values found for the entropy change in formation of the complexes studied are shown in Table 1. The entropy changes for the Ca, Mn and Pb complex-formation reactions are practically independent of the pH, whereas for Ni there is a large change in ΔS with pH. The absorption spectra of the metal-EDTA complexes were measured at various pH-values, and the absorbances at the wavelength of maximum absorption are plotted against pH for each metal in Fig. 1. The absorbance of each metal complex decreases with pH. This decrease is ascribed to the side-reaction of EDTA with protons. However the drop in absorbance is much smaller for the Ni-EDTA complex, and this difference in behaviour must be related to the structure of this complex in solution. The Ni-EDTA complex should be octahedral, with two amino and four carboxylate groups co-ordinated to the central metal ion. This configuration may be sensitive to pH, since with decreasing pH the carboxylate group is prevented by protons from co-ordination with the metal ion, which would result in the formation of mixed-ligand (EDTA, water) complexes of nickel. Such a situation should lead to a decrease in the entropy change. Consideration of the log K and ΔH values for the complexes supplies an indication of the explanation. For the Ni, Ca and Mn complexes ΔH is comparatively small (-7.6, -6.5, -4.6 kcal/mole respectively) but the much bigger entropy change makes the nickel complex much the strongest of the three, and thus much less susceptible to the side-reactions of EDTA with protons. The lead complex has about the same stability as the nickel complex, but the ΔH is much more negative (-14.9 kcal/mole) and ΔS correspondingly less positive.

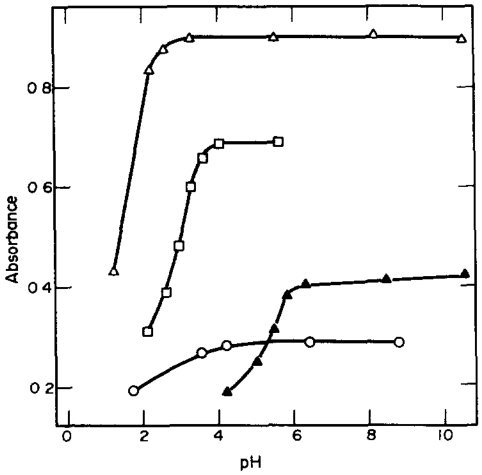

Fig. 1. The absorbance of the metal-EDTA complexes at λ_{max} *vs* pH. △: Pb–EDTA (0.1 m*M*), 242 nm; □, Mn–EDTA (0.5 m*M*), 210 nm; ▲, Ca–EDTA (0.5 m*M*), 210 nm; ○, Ni–EDTA (10 m*M*), 985 nm.

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Summary—The entropy changes of Ca^{2+}-, Mn^{2+}-, Ni^{2+}- and Pb^{2+}-EDTA complex-formation reactions were measured at various pH-values. The entropy changes for the Ca, Mn and Pb complexes were practically independent of pH, but that of the Ni complex decreased considerably with pH. It is suggested that mixed-ligand (EDTA, water) complexes of Ni are formed at low pH.

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DETECTION OF SOME NITROGEN COMPOUNDS AND THE SEMIQUANTITATIVE DETERMINATION OF DIPHENYLAMINE WITH *p*-DIMETHYLAMINOBENZALDEHYDE BY CAPILLARY SOLID-STATE SPOT-TESTS

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Interest in solid-state chemistry is growing.[1–5] Solid-state reactions have much to offer to chemists concerned with synthesis, reaction mechanism or the chemistry of natural processes. Feigl[6] has shown some possibilities of using solid-state reactions in qualitative organic analysis. These include hydrolytic and ammonolytic cleavages, and displacement, condensation and redox reactions that occur when organic compounds are melted or sintered with suitable reagents. *p*-Dimethylaminobenzaldehyde[7] (*p*-DAB) is a useful reagent in organic analysis. It gives coloured products and also produces fluorescent[8] compounds in solution. We earlier proposed *p*-DAB in the presence of hydrochloric acid for the specific detection of diphenylamine.[9] The mechanism and kinetics of this reaction in the solid state were investigated later.[10] It was found to be a diffusion-controlled reaction; a coloured boundary is formed at the junction of the two reactants and the diffusing species is $Ph_2NH_2^+Cl^-$.

It was therefore considered worthwhile to use the formation of a coloured boundary for the detection of organic compounds in the solid state. For this purpose a new technique for solid-state spot-tests, called capillary spot-tests, was devised. This technique is very simple and can be used for semiquantitative determinations as well. This report summarizes the results obtained. Diphenylamine was also semiquantitatively determined by this technique.

EXPERIMENTAL

Procedures

Solid-state detection. A well powdered and thoroughly mixed mixture of *p*-dimethylaminobenzaldehyde (*p*-DAB) and potassium hydrogen sulphate (PHS) in equimolar ratio was used as the reagent (*A*). A little of the solid was mixed in a micro test-tube with several mg of *A*. The colour developed at room temperature (31°) as well as on heating was recorded. For heating, the tube was placed for a few sec in a water-bath preheated to 100°. The limits of identification were determined by starting with known volumes of standard solutions of the compound concerned, evaporating to dryness at 100°, and mixing the solid residue with A.

Detection in solution. A drop of ethanolic test solution was mixed with 1 or 2 drops of a 1% solution of *A* in 50% aqueous ethanol. The colour developed at room temperature as well as in the hot solution was recorded.

Solid-state detection in capillaries. A capillary (1-mm bore) was part-filled with *A* by continuous tapping and then the solid test material was added at the open end. The colour and fluorescence of the product at the junction were recorded. The limits of identification were determined by starting with various synthetic mixtures of the solid test materials with starch.

Semiquantitative determination. Capillaries containing *A* and solid test material (various concentrations of diphenylamine) were kept at 50° in an oven for 5 hr, and the length of the coloured boundary formed at the junction was recorded. A plot of diphenylamine concentration *vs.* boundary length was linear but did not pass through the origin. The sensitivity is rather poor, 10% of diphenylamine giving a length of 1.0 mm, and 100% giving 3.5 mm.

Visual colorimetry. Capillaries containing *A* and solid test material (0.1–10% diphenylamine) were kept at room temperature for 2 hr or at 50° in an oven for 15 min, and the colour intensities were compared visually. Both procedures are equally good but it is faster, of course, to use heating. The colour intensity is proportional to the concentration of diphenylamine.

DISCUSSION

The results in Table 1 indicate that the solid-state reactions are sufficiently sensitive, and can be used to distinguish similar compounds by means of the colours obtained in the cold and on heating.

It is known[11] that many reactions which take place in solution are also observed in the reactions between the solids, particularly on trituration, where there is a close contact between the reacting substances. It is also known that many reactions between solids take place on simple contact of the reacting substances. This means that many compounds can be distinguished by solid-state contact reactions in a capillary, *cf.* Table 2.

Further, of the substances tested, only acridine, *p*-toluidine and semicarbazide hydrochloride form products with reagent *A* which give fluorescence in the capillary, the colours being OY, Y and Y respectively and the limits of identification 5, 20 and 100 μg.

However, the method is not specific for detection of nitrogen compounds. For example, aliphatic amides do not react, nor do uracil, uric acid, adenine, glycine, phthalimide, sarcosine, EDTA, thebaine, papaverine, purines, α-amino-acids and pyridine derivatives. On the other hand, some compounds react although they do not contain nitrogen, *e.g.*, Feigl[12] and van Urk[13] found various such colour reactions of *p*-DAB, and we found that santonin, resorcinol, phloroglucinol and hydroquinone react.

Table 1. Detection of various nitrogen compounds with reagent *A*

	Solid-state reaction			Solution reaction		
	Colour		Identification limit, μg	Colour		Identification limit, μg
Compound	Hot	Cold		Hot	Cold	
Diphenylamine	Y	G	1	—	Y	10^4
N-Phenyl-1-naphthylamine	Y	G	0.2	—	—	—
N-Phenyl-2-naphthylamine	Y	G	0.2	—	Y	10^4
α-Naphthylamine	Y	G	1	Y	Y	2.5
β-Naphthylamine	Y	G	0.2	Y	Y	1
o-Tolidine	O	O	0.5	Y	Y	2
p-Toluidine	Y	G	1(4)	Y	Y	2(2)
o-Phenylenediamine	Y	G	2	Y	Y	2.5
p-Phenylenediamine	RY	G	0.2	Y	Y	0.5
o-Nitrobenzoic acid	Y	Y	40(30)	Y	Y	10^4 (5×10^3)
m-Nitrobenzoic acid	Y	Y	30(25)	Y	Y	10^4 (5×10^3)
p-Nitrobenzoic acid	Y	Y	20(15)	Y	Y	10^4 (5×10^3)
o-Nitrophenol	Y	YG	300(200)	—	—	—
p-Nitrophenol	Y	Y	250(100)	—	—	—
o-Nitroaniline	Y	Y	8	Y	Y	60
m-Nitroaniline	Y	Y	4	Y	Y	40
p-Nitroaniline	Y	Y	2	Y	Y	10
Urea	RY	RY	10	Y	Y	10^3
Phenylurea	Y	YG	10	Y	Y	5×10^3
N-Methylurea	Y	YG	10	Y	Y	10^4
Thiourea	Y	Y	10	Y	Y	10^3
Phenylthiourea	Y	YG	10	Y	Y	10^3
Allylthiourea	Y	RY	10	—	—	—
1,3-Dibutylthiourea	Y	Y	15	—	—	—
sym-Di-*o*-tolylthiourea	Y	Y	10	Y	Y	2.5×10^3
Benzamide	Y	Y	50	—	—	—
Salicylamide	Y	Y	250	—	—	—
Nicotinamide	Y	YG	5×10^3	—	—	—
Nicotinic acid	Y	YG	10^4	—	—	—
α-Picolinic acid	Y	YG	5×10^3	—	—	—
L-Proline	Y	Y	5×10^3	—	—	—
Cystine	Y	Y	—	PY	PY	—
Caffein	Y	Y	10^3	—	—	—
Benzidine	R(Y)	R(Y)	0.01(50)	Y(Y)	Y(Y)	10^4 (5×10^3)
Acridine	Y	Y	10	Y	Y	15
Diphenylcarbazide	Y	Y	5	—	—	—
Indolyl-3-acetic acid	Y	B	50	Y(after 20 min)		—
Indoxyl acetate	B	B	60	—	—	—
Indole	V	V	20	—	—	—
DL-Tryptophan	Y	Y	30	Y	Y	0.5×10^3
8-Hydroxyquinoline	Y	YG	125	Y	Y	0.25×10^3
Barbituric acid	O(O)	O(O)	0.2(1)	Y(Y)	Y(Y)	1 (10)
Thiobarbituric acid	LV(Pink)	V(Pink)	0.2(1)	Pink(Pink)	Pink(Pink)	0.8(10)

L-Glutamine, DL-serine, L-valine, L-tyrosine, DL-alanine, DL-methionine, DL-citrullin, taurine and glutamic acid all give yellow colours in the solid-state tests, and DL-aspartic acid and L-leucine give yellow in the cold and yellow-green in the hot.

L-Histidine monohydrochloride gives yellow in all four tests, and cystine gives yellow in the solid-state tests and pale yellow in the solution reactions. Y = yellow, O = orange, G = green, R = red, V = violet, B = brown, L = light, P = pale.

Information in brackets refers to direct reaction with *p*-DAB.

Table 2. Contact reaction results in capillaries with reagent *A* at 50°C

Compound	Colour for 2% concentration	Colour for 10% concentration
Diphenylamine	*Y–O	O–O
p-Toluidine	Y–O	Y–O
o-Tolidine	Y–O	O–O
α-Naphthylamine	Y–DY	O–O
β-Naphthylamine	O–G	G–G
N-Phenyl-1-naphthylamine	Y–O	—
N-Phenyl-2-naphthylamine	Y–O	—
o-Phenylenediamine	Y–O	O–O
p-Phenylenediamine	O–R	R–R
Indolyl-3-acetic acid	V	—
Indole	V	—
DL-Tryptophan	V	—
Benzidine	LR	—
o-Nitrobenzoic acid	—	LG–LG
m-Nitrobenzoic acid	—	Y–Y
p-Nitrobenzoic acid	—	Y–Y
o-Nitrophenol	—	Y–B
p-Nitrophenol	—	O–R

*The first letter refers to the initial colour and the second to that after 48 hr.

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APPLICATION OF TRIETHYLENETETRAMINE TO THE SEPARATION OF METAL IONS ON SELECTIVE EXCHANGE RESIN CHELEX 100

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(*Received* 13 *January* 1976. *Accepted* 23 *April* 1976)

Separation of metal ions on the selective exchange resin Chelex 100 often requires the use of specially chosen complexing agents.[1–8] We have found triethylenetetramine (TETA) is a particularly useful complexing agent in this connection. The copper(II) complex is particularly stable,[9] which enables copper to be removed from the resin by elution with small quantities of TETA solution although the affinity of the resin for copper is high. In this paper the utility of TETA is illustrated by its application to the separation of Cu^{2+} from Ni^{2+} and of Pb^{2+} from Cu^{2+}. The problem of separation of these ions arises in the analysis of some natural raw materials. Mineral acids have been used to separate alkaline earth metals from others on the basis of the differences in stability of the metals complexes with the iminodiacetate functional groups of Chelex 100.[10–15]

EXPERIMENTAL

Reagents

Exchange resin. Chelex 100 (Bio-Rad Laboratories), 100–200 mesh, with maximum exchange capacity 3.0 mmole/g of the dry resin in Na^+-form and 3.48 mmole/g of the resin in H^+-form, and Dowex A-1, (Serva Entwicklungslabor, Heidelberg), capacity 2.4 mmole/g, were used. The capacity was determined from the sorption of $Cu(NH_3)_4^{2+}$,[16] and confirmed by elemental analysis

Standard solutions. These were prepared by dissolving enough of the appropriate nitrates for the concentrations of the metal ions to be: Ca^{2+} 24 mg/ml, Mg^{2+} 24 mg/ml, Cu^{2+} 1.2 mg/ml, Ni^{2+} 0.6 mg/ml, Pb^{2+} 1.0 mg/ml. The solutions were then standardized complexometrically.

The distribution coefficients

The batch method[16] was used. Weighed portions (0.2833 g) of Chelex 100 were placed in special vessels containing 0.085 mmole of Me^{2+} in 25 ml of solution in one series and 0.085 mmole of Me^{2+} and 0.85 mmole of TETA in 25 ml of solution in a second series. The pH was measured, then the solutions were shaken mechanically for 12 hr. After equilibrium was reached the aqueous phase was analysed for Me^{2+}. Ca^{2+} and Mg^{2+} were titrated with EDTA or determined by atomic absorption. Cu^{2+}, Ni^{2+} and Pb^{2+} were determined by atomic absorption.

Table 2. Contact reaction results in capillaries with reagent *A* at 50°C

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β-Naphthylamine	O–G	G–G
N-Phenyl-1-naphthylamine	Y–O	—
N-Phenyl-2-naphthylamine	Y–O	—
o-Phenylenediamine	Y–O	O–O
p-Phenylenediamine	O–R	R–R
Indolyl-3-acetic acid	V	—
Indole	V	—
DL-Tryptophan	V	—
Benzidine	LR	—
o-Nitrobenzoic acid	—	LG–LG
m-Nitrobenzoic acid	—	Y–Y
p-Nitrobenzoic acid	—	Y–Y
o-Nitrophenol	—	Y–B
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Separation of metal ions on the selective exchange resin Chelex 100 often requires the use of specially chosen complexing agents.[1–8] We have found triethylenetetramine (TETA) is a particularly useful complexing agent in this connection. The copper(II) complex is particularly stable,[9] which enables copper to be removed from the resin by elution with small quantities of TETA solution although the affinity of the resin for copper is high. In this paper the utility of TETA is illustrated by its application to the separation of Cu^{2+} from Ni^{2+} and of Pb^{2+} from Cu^{2+}. The problem of separation of these ions arises in the analysis of some natural raw materials. Mineral acids have been used to separate alkaline earth metals from others on the basis of the differences in stability of the metals complexes with the iminodiacetate functional groups of Chelex 100.[10–15]

EXPERIMENTAL

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Standard solutions. These were prepared by dissolving enough of the appropriate nitrates for the concentrations of the metal ions to be: Ca^{2+} 24 mg/ml, Mg^{2+} 24 mg/ml, Cu^{2+} 1.2 mg/ml, Ni^{2+} 0.6 mg/ml, Pb^{2+} 1.0 mg/ml. The solutions were then standardized complexometrically.

The distribution coefficients

The batch method[16] was used. Weighed portions (0.2833 g) of Chelex 100 were placed in special vessels containing 0.085 mmole of Me^{2+} in 25 ml of solution in one series and 0.085 mmole of Me^{2+} and 0.85 mmole of TETA in 25 ml of solution in a second series. The pH was measured, then the solutions were shaken mechanically for 12 hr. After equilibrium was reached the aqueous phase was analysed for Me^{2+}. Ca^{2+} and Mg^{2+} were titrated with EDTA or determined by atomic absorption. Cu^{2+}, Ni^{2+} and Pb^{2+} were determined by atomic absorption.

Table 1. Distribution coefficients and degrees of adsorption of Ca^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} on Chelex 100, as a function of pH

Ca^{2+}			Cu^{2+}			Ni^{2+}			Pb^{2+}		
pH	K_d	Bound to resin, %	pH	K_d	Bound to resin, %	pH	K_d	Bound to resin, %	pH	K_d	Bound to resin, %
1.6	0.16	0	1.85	4.0×10^2	82.1	1.6	14.6	6.3	2.0	2.43×10^2	49.3
1.9	0.41	0.3	1.99	6.75×10^2	86.8	2.6	8.8×10^2	77.7	4.5	$>6 \times 10^4$	100
2.8	33	21.3	2.35	7.45×10^3	98.8	4.3	2.9×10^4	99.1	7.0	$>6 \times 10^5$	100
4.5	6.84×10^3	98.3	3.0	3.0×10^4	99.6	6.5	$>10^5$	100	3.0	99.0×10^3	97.4
5.0	1.38×10^4	99.1	4.0	1.7×10^5	100	8.3	$>10^5$	100			

K_d was calculated from

$$K_d = \frac{\text{mmole of Me}^{2+}/\text{g of resin}}{\text{mmole of Me}^{2+}/\text{ml of solution}}$$

Separation procedures

Weighed portions (1.5 g) of Chelex 100, (Na^+-form) for separation I, or of Dowex A-1 (H^+-form, 2.0 g) for separation II, were placed in special flasks containing 25 ml of 0.1 *M* sodium hydroxide and shaken mechanically for 30 min until the pH of the solution in equilibrium with the resin was 5. The slurry thus prepared was poured into a column (12 mm bore), the bed being 13.5 cm high. A 10-ml sample, containing 120 mg of Ca^{2+}, 1.2 mg of Cu^{2+} and 1.2 mg of Ni^{2+}, or 120 mg of Mg^{2+}, 1.2 mg of Cu^{2+} and 1.0 mg of Pb^{2+}, was placed on the top of the column and allowed to percolate at a fixed flow-rate of about 2.5 ml/min.

Separation I. Ca^{2+} was washed out from the column with 200 ml of 0.5 *M* potassium nitrate, pH 2.5, Cu^{2+} with 100 ml of 0.17 *M* TETA at pH 5.0, and Ni^{2+} with 200 ml of 0.17 *M* TETA at pH 9.0.

Separation II. Mg^{2+} was eluted with 100 ml of 0.5 *M* potassium nitrate, pH 2.5, Cu^{2+} with 100 ml of 0.17 *M* TETA at pH 5.0 and Pb^{2+} with 100 ml of 0.5 *M* nitric acid.

The effluents from the column were collected in fractions either with an automatic fraction collector (at 2-min intervals), or in standard flasks, and analysed by titration or atomic absorption.

RESULTS AND DISCUSSION

Table 1 gives the distribution coefficients and degrees of adsorption of Chelex 100, as a function of pH.

The distribution coefficients increase regularly with increasing pH. The affinity of the cations for the resin is $Ca^{2+} < Ni^{2+} < Pb^{2+} < Cu^{2+}$.[10] Table 2 shows the corresponding data when TETA is also present.

The TETA greatly increases the selectivity of Chelex 100, and the variation in adsorption with pH indicates some possible separations. The remarkable increase in K_d at high pH may be due to formation of mixed complexes and is being further investigated. The best pH values for elution of Cu^{2+} and Ni^{2+} were found to be 5.0 and 9.0 respectively. In Table 3 the results of Ca^{2+}, Cu^{2+}, Ni^{2+} separation on Chelex 100 are given. The elution curves are presented in Fig. 1. The fractions were analysed by atomic absorption.

The elution of Cu^{2+} with TETA seems of practical interest because of difficulties recorded elsewhere.[10] This elu-

Table 2. Distribution coefficients and adsorption of Cu^{2+}, Ni^{2+}, Pb^{2+} ions in % on Chelex 100 with TETA

Cu^{2+}			Ni^{2+}			Pb^{2+}		
pH	K_d	Bound to resin, %	pH	K_d	Bound to resin, %	pH	K_d	Bound to resin, %
1.7	4.20×10^2	82.6	1.7	0.26	0.2	2.0	6.54×10^2	73.2
2.3	2.03×10^3	95.8	4.25	2.77×10^3	96.9	4.0	5.89×10^3	95.9
3.45	1.73×10^3	95.1	7.5	51.3	36.7	6.9	1.61×10^4	98.5
3.97	1.73×10	61.5	9.0	6.4	6.7	8.7	7.94×10^3	96.9
6.0	1.6	1.2	11.0	2.84×10^3	97	10.6	9.31×10^4	99.7
9.0	1.3	1.2						
11.0	1.73×10^3	5.1						

Table 3. Separation of 120 mg of Ca^{2+}, 1.2 mg of Cu^{2+} and 1.2 mg of Ni^{2+} on Chelex 100

Column	Ca^{2+}	Cu^{2+}	Ni^{2+}
1	100	98	100
2	99	97	94
3	100	100	94
4	100	100	100
5	98	100	100

Table 4. Separation of 120 mg of Mg^{2+}, 1.2 mg of Cu^{2+} and 1.0 mg of Pb^{2+} on Dowex A-1

Column	Recovery, % Mg^{2+}	Cu^{2+}	Pb^{2+}
1	99	100	103
2	99.3	100	110
3	98.6	104	104
4	98.4	100	105
5	100	102	103
6	100	100	110

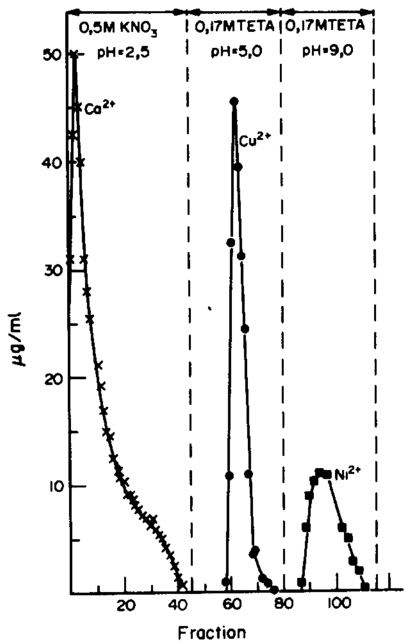

Fig. 1. Elution curves of Ca^{2+}, Cu^{2+} and Ni^{2+} on Chelex 100. Ca^{2+} solutions were 10-fold diluted for the determination.

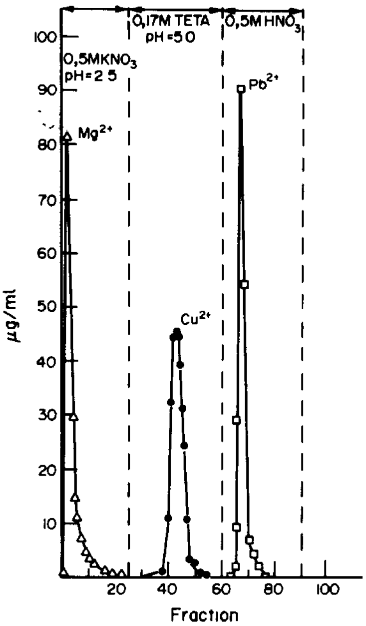

Fig. 2. Elution curves of Mg^{2+}, Cu^{2+}, Pb^{2+} on Dowex A-1. Mg^{2+} solutions were 100-fold diluted for the determination.

tion is quick and quantitative. There is a even a possibility of visual estimation of Cu^{2+} during the elution as the sharp sapphire-blue layer of Cu^{2+}–TETA complex moves along the column. Results for separation of Mg^{2+}, Cu^{2+} and Pb^{2+} on Dowex A-1 are given in Table 4. The elution curves are shown in Fig. 2.

Possible applications include determination of heavy metal ions in fertilizers or water.

Acknowledgement—The authors wish to express their appreciation of the experimental help given by Mrs Teresa Sokołowska.

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Summary—The distribution coefficients of Ca^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+} on Chelex 100 in the presence and absence of triethylenetetramine have been determined. Ca^{2+}, Cu^{2+}, Ni^{2+} and Mg^{2+}, Cu^{2+}, Pb^{2+} mixtures have been separated on Chelex 100 and Dowex A-1 respectively.

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ION-EXCHANGE SEPARATION AND ATOMIC-ABSORPTION DETERMINATION OF FIFTEEN MAJOR, MINOR AND TRACE ELEMENTS IN SILICATES*

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In geochemical analysis, it is often necessary to separate single elements (especially minor and trace elements) to avoid matrix interference in the subsequent quantitative determinations. Moreover, the development of analytical schemes to include as many major, minor and trace elements as possible, is important if it is desired to use only one or two portions of sample.

Generally speaking, especially in geochemistry, it is very important to develop standardized analytical methods which give selective separations and then quantitative determination of the elements in individual pure solutions.

Separation schemes have been extensively investigated, and the results have been examined in detail by Strelow in a recent review.[1] The same author and his collaborators[2] have described a scheme in which Fe(III), Al, Ti, Zr, V(V) and Mo(VI) are retained on an anion-exchanger in oxalic and hydrochloric acid media, and Na, K, Mn(II), Mg and Ca, which pass through the anion-exchange column, are retained on a cation-exchanger. The elements are then eluted selectively. Recently Strelow *et al.*[3] have presented an accurate determination of Al, Fe(III), Ti, Ca, Mg, Mn(II), Na, K, V(V) and Zr in silicate rocks, based on separation on a single cation-exchange resin, employing different acid mixtures. Govindaraju[4] has proposed a method of silicate analysis based mainly on ion-exchange dissolution and emission spectrometry; Al, Fe(III), Mg, Ca, Mn(II), Ti, Ba, Co(II), Cr(III), Cu, Ni, Sr and V(V) were accurately determined. Szlaurová *et al.*[5] have proposed an analytical scheme for fifteen radionuclides, Zr, Nb, Mo(VI), Sr, Ba, Y, Ce(III), Sc, Cs, Eu, Mn(II), Cu, Co(II), Fe(III), Zn, employing seven cation- and anion-exchangers.

In a previous work[6] we presented a method for separation of eighteen cations Li, Na, K, Mg, Ca, Sr, Ba, Al, Ti, Mn(II), Cu, Ni, Co(II), Fe(III), Zn, Hg(II), Sb(III) and Bi by means of cation- and anion-exchange resins. Mn(II), Cu, Fe(III), Zn, Hg(II), Sb(III) and Bi were absorbed after passage of the sample, dissolved in 7*M* hydrochloric acid in methanol, through a borosilicate glass tube filled with anion-exchange resin. The other ions were absorbed on a cation-exchanger before concentration of the sample. All the ions (0.1 meq of each) were then selectively eluted from the two columns with hydrochloric acid of concentration ranging from 0.05 to 12*M*.

In the present work we have examined the possibility of applying such a scheme to silicate materials, because of its simplicity and the large number of ions separated. We left Sb, Hg and Bi out of consideration because, although their separation is good, they are not easily determined owing to their extremely low concentration (< 1 ppm) in common silicate materials.

In the original work,[6] the eluted elements were determined by complexometric titration (Mg, Sr and Ba), flame photometry (Li, Na and K) and colorimetry the rest. In the present application atomic-absorption spectrophotometry (AAS) was used for all the elements except titanium (determined colorimetrically with Tiron[7,8]), in order to achieve maximum speed of analysis.

The necessity for separation of these elements, even though AAS is widely (but mistakenly) regarded as highly selective, is confirmed by the following reports: barium suffers interference from calcium, aluminium and alkali metals[9,10] and so does strontium;[11,12] Ca, Mg, Al, Na, Fe, Ti, Li and K are highly active as interfering agents;[13–16] Mn and Zn suffer from matrix interference.[14] Although no comparable data are available for Cu and Ni, we think it best to separate these elements from the silicate matrix for their concentration from trace levels.

EXPERIMENTAL

Ion-exchange

Dowex 50W X8 and Dowex 1 X8, both 200–400 mesh, were used. The cation-exchanger was converted into the H^+ form with 3*M* hydrochloric acid and washed with demineralized water. The anion-exchanger was treated first with 12*M* hydrochloric acid, then with 4% sodium hydroxide solution, and converted into the Cl^- form with 3*M* hydrochloric acid and washed with demineralized water. Borosilicate glass tubes (12-mm bore) were packed with 100- and 180-mm beds of the anion- and cation-exchanger respectively. Elutions were effected at 380 mmHg overpressure. An automatic fraction-collector was used.

Method

Weigh out 100 mg of finely powdered sample (120-mesh) in a PTFE dish. Moisten the powder with water to avoid spattering. Add 10 ml of 40% hydrofluoric acid and 10 ml of 70% perchloric acid, mixing with a platinum or PTFE rod. Allow to stand overnight in the fume-cupboard and then heat to dryness. Add 10 ml of hydrofluoric acid and 10 ml of perchloric acid and heat to dryness. Add 5 ml of perchloric acid and heat to dryness. Add 50 ml of a 7*M* solution of hydrochloric acid in methanol. Pass the sample solution through the anion-exchanger, pretreated with 20 ml of the 7*M* hydrochloric acid in methanol, at a flow-rate of 2.5 ± 0.3 ml/min. This column sorbs Mn(II), Co(II), Fe(III), Cu and Zn, which are later eluted as shown in Fig. 1. Wash the column with 30 ml of 7*M*

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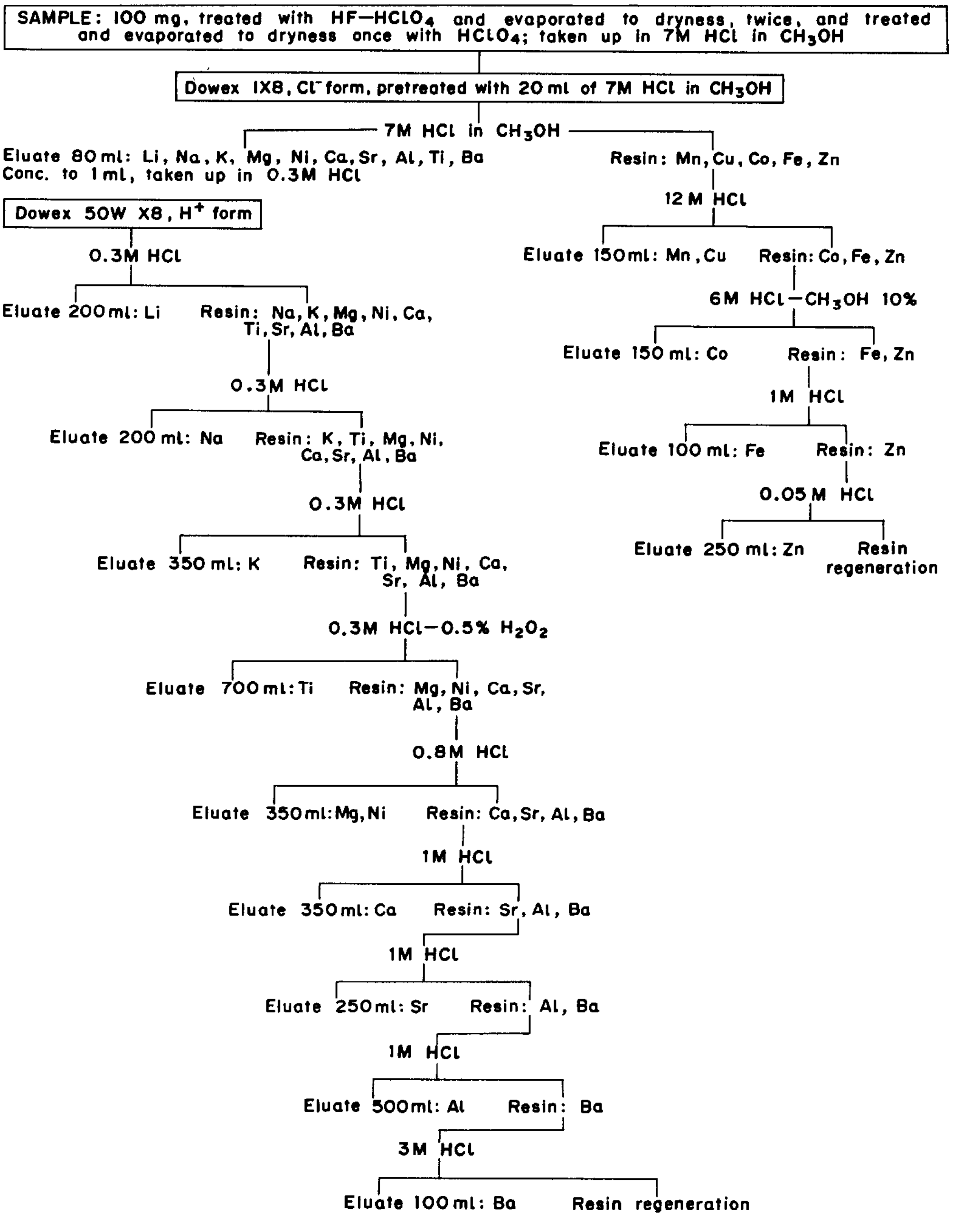

Fig. 1.

hydrochloric acid in methanol, evaporate the combined effluent to 1 ml, and add 50 ml of 0.3*M* hydrochloric acid. Pass this sample through the cation-exchanger, which sorbs Li, Na, K, Mg, Ca, Sr, Ba, Ni, Al and Ti, which are then eluted as described in Fig. 1. The columns are finally regenerated by the treatment described for preparation of the exchange-resins.

The ions are evaluated quantitatively by the methods given in Table 1. The calibration curves have been obtained by direct use of standard solutions of the element concerned.

RESULTS AND CONCLUSION

The scheme described earlier[6] referred to mixtures containing the same number of equivalents of each ion present. To evaluate the effectiveness of the scheme in silicate analysis, we prepared a synthetic sample containing these ions in the ratios found in common geological samples (Table 1).

Aliquots of this solution, containing the fifteen elements in the amounts corresponding to 100 mg of a common silicate sample, were treated according to Fig. 1 and the elements were collected in 10-ml fractions to determine the elution curves. Quantitative analyses were done, in order to test the reproducibility of the method. In the earlier scheme,[6] Mn and Cu were further separated on a third column filled with Amberlite CG 400, Cl⁻ form. These two elements show no interaction in AAS, so we prefer to determine them in the same solution instead of using the third column. The same applies to Mg and Ni.

Table 1. Analytical methods used in the separation scheme and composition of synthetic standard

Species	Content	Methods	Wavelength, *nm*	Flame
Al_2O_3	10.20 %	AAS K as ionization suppressor[8]	309.3	NA
Fe_2O_3	6.76 %	AAS[7]	248.3	AA
CaO	13.28 %	AAS La as releasing agent[7]	422.7	AA
MgO	13.80 %	AAS La as releasing agent[7]	285.2	AA
Na_2O	3.05 %	AAS Cs as ionization buffer[8]	589.0	AA
K_2O	1.40 %	AAS Cs as ionization buffer[8]	766.5	AA
TiO_2	2.60 %	COL Tiron as complexing agent[7]	580	—
MnO	0.20 %	AAS La as releasing agent[7]	279.5	AA
Ba	1050 ppm	AAS K as ionization suppressor[9]	553.6	NA
Co	50 ppm	AAS[14]	240.7	AA
Cu	70 ppm	AAS[14]	324.8	AA
Li	9 ppm	AAS Cs as ionization buffer[14]	670.8	AA
Ni	270 ppm	AAS[14]	232.0	AA
Sr	1350 ppm	AAS La as releasing agent[14]	460.7	NA
Zn	160 ppm	AAS La as releasing agent[14]	213.9	AA

Note. K and La were added because the ionization effect is independent of the separation. NA = nitrous oxide–acetylene flame; AA = air–acetylene flame.

Table 2. Synthetic solution analytical data

Species	Taken, *mg*	Found, *mg*	Final volume after sepn., *ml*	Concentration ratio	Dilution ratio	Relative concentration, *ppm*
Al_2O_3	20.0	20.5	500	—	—	40
Fe_2O_3	13.0	12.8	100	—	2	65
CaO	27.0	27.1	350	—	10	7.7
MgO	26.0	26.0	350	—	10	7.4
Na_2O	6.0	5.8	200	—	10	3
K_2O	3.0	3.0	350	—	—	8.5
TiO_2	5.6	5.7	700	—	10	0.8
MnO	0.40	0.35	150	—	—	2.6
Ba	0.20	0.20	100	4	—	8
Co	0.01	0.01	150	10	—	0.6
Cu	0.01	0.01	150	10	—	0.6
Li	0.002	0.002	200	8	—	0.08
Ni	0.04	0.04	350	14	—	1.6
Sr	0.20	0.18	250	10	—	2
Zn	0.30	0.31	250	—	—	1.2

Note. Before AAS the solution is concentrated or diluted by the factors indicate in the columns headed concentration and dilution ratios.

Table 3. Analysis of standard samples

	Major and minor components, %															
	Al_2O_3		Fe_2O_3		CaO		MgO		Na_2O		K_2O		TiO_2		MnO	
Samples	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
W-1[19]	15.08	15.00	11.11	11.09	10.88	10.96	6.55	6.62	2.15	2.15	0.70	0.64	1.09	1.07	0.20	0.17
G-2[19]	15.33	15.40	2.77	2.65	1.99	1.94	0.78	0.76	4.16	4.07	4.51	4.51	0.52	0.50	0.04	0.034
BCR-1[19]	13.68	13.61	13.49	13.40	7.00	6.92	3.30	3.46	3.30	3.27	1.70	1.70	2.24	2.20	0.18	0.18
UB-N[17]	3.01	2.93	8.47	8.35	1.08	1.17	35.01	35.00	0.10	0.10	0.02	0.02	0.15	0.12	0.12	0.12
DR-N[17]	17.40	17.52	9.60	9.67	7.10	7.07	4.51	4.46	2.89	2.99	1.80	1.73	1.10	1.10	0.25	0.21
VS-N[18]	13.25	13.39	4.05	4.11	4.51	4.48	4.51	4.51	6.00	5.94	8.10	8.12	1.10	1.06	0.12	0.10
GA[19]	14.39	14.50	2.88	2.83	2.45	2.45	1.00	0.95	3.60	3.55	4.10	4.03	0.05	0.04	0.20	0.20
GOG-1[21]	19.25	19.73	4.83	4.75	9.40	9.15	12.25	13.27	1.80	1.90	0.045	0.043	0.092	0.082	0.053	0.065
G[20]*	21.20	21.13	2.10	2.01	2.01	0.55	0.53	0.82	0.82	0.28	0.29	2.55	2.53	0.90	0.87	0.01
K[20]*	25.00	25.02	2.80	2.76	0.70	0.67	0.51	0.46	0.15	0.12	0.51	0.47	0.90	0.92	0.02	0.02

Table 3.—*contd.*

	Trace elements, *ppm*													
	Ba		Co		Cu		Li		Ni		Sr		Zn	
Samples	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
W-1[19]	172	160	55	47	115	110	20	14.5	85	76	180	190	95	86
G-2[19]	2100	1870	6	5.5	20	11.7	38	34.8	15	5.1	490	479	90	85
BCR-1[19]	690	675	40	38	25	18.4	15	12.8	25	15.8	350	330	120	120
UB-N[17]	53	40	105	110	27	30	30	30	1860	2000	16	10	80	85
DR-N[17]	377	380	32	35	50	52	42	45	30	22	385	400	150	150
VS-N[18]	970	1010	731	724	805	796	487	495	823	815	758	747	805	790
GA[19]	795	850	8	5	20	14	105	100	12	7	321	305	88	75
GOG-1[21]	138	—	50	53	51	46	2	1.8	465	411	180	166	—	—
G[20]	765	759	26	—	22	18.2	460	470	30	24	80	72	—	—
K[20]	155	147	20	—	7	5.4	285	275	30	22	25	19	—	—

(a) = Value found; (b) = recommended or mean value; * = Mediaeval pottery.

Table 2 shows that the separation scheme provides quantitative results. We have also analysed some international rock, mineral and ceramic standards (Table 3). The results show good accuracy for major, minor and trace elements in the usual ranges found in silicate analyses.

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Summary—A scheme of ion-exchange separation of fifteen elements (major, minor and trace) determined mainly by atomic-absorption spectrophotometry (Ti by colorimetry) is applied to rock, mineral and ceramic analysis. Mn, Cu, Co, Fe and Zn are separated on an anion-exchanger and Li, Na, K, Mg, Ca, Sr, Ti, Al, Ni and Ba on a cation-exchanger. The method has been tested by analysis of a synthetic mixture of the fifteen ions in the ratios in common rock samples, and of various international standards (100-mg samples).

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LETTER TO THE EDITOR

SELECTIVITY INDEX

Sir,

Several years ago I pointed out that some system was needed to grade degrees of selectivity and I suggested that the term "Selectivity Index" might be used. I had discussed this matter at some length with Dr. Betteridge, who proposed a further scheme which provided considerably more detailed information. We arranged to publish our observations simultaneously.[1] The Selectivity Index was included in Dr. Betteridge's system.

Some interest was shown at the time[2] and later we submitted a further letter, covering the suggestions and criticisms which had been raised.[3] Since that time nothing further has been published.

Later, when I was Chairman of the Nomenclature Commission of the Analytical Chemistry Division of IUPAC, I included this subject in our general programme. A working party was formed, but more urgent matters had to take precedence and very little headway was made. The project was eventually abandoned. I believe that little progress is likely to be made until more opinions have been collected and the objectives have been clarified. The purpose of this letter is to attempt to stimulate further interest in this problem and to obtain some written or verbal contributions. Undoubtedly, this step is essential before the topic is suitable for Committee deliberation.

I believe that there are several reasons why little progress has been made.

1. When I first made this proposal, I deliberately avoided giving detailed conditions in the expectation that a discussion would be provoked which would cover all aspects. From the discussions I have since had with the Commission's working groups, it seems that it was this lack of precise definition which has provided a stumbling block to further progress.

2. My purpose was to provide a simple means of expressing by spoken word the reaction behaviour of a particular ion. I wanted a description that did not necessitate the use of a blackboard or pencil and paper to illustrate it. Dr. Betteridge's idea was intended for tabulation and thus would cover much more ground. Unfortunately, although Dr. Betteridge's scheme included my Selectivity Index, the whole issue has become confused. Before Dr. Betteridge's scheme could be implemented it would be necessary to agree on some form of my *original* proposal as to what is meant by Selectivity Index.

3. I used the term "index" in its general sense. Because of the system recommended by Dr. Betteridge, which uses indices in a different manner, it would perhaps be better to use the term Selectivity Number.

4. It seems that one of the main problems is whether the Selectivity Index should refer to the "natural" selectivity of a particular ion or the selectivity under the most favourable conditions, *i.e.*, the optimal pH; in the presence of masking agents; suitable oxidation state, *etc*.

This might be overcome by the use of two numbers, the one indicating the normal selectivity and the other the value under the most favourable conditions. For example, suppose that reagent X gives a reaction with six different ions under normal conditions. Under the most favourable conditions only two ions give the reaction. Then the selectivity numbers would be 6/2. Such an expression could provide all the information required completely verbally; it would also indicate the improvement in selectivity produced by the most favourable conditions. It is true that there are two selectivities, the "natural" (for want of a better term) and the most favourable selectivity. The latter could be called the "optimal" selectivity, but there may be better terms which could be used. Of course, a lot of complications can be introduced, as I have discovered from the many discussions. One popular question is "how to refer to the reaction of a trace of material in the presence of a large bulk of another". If it is kept in mind that one is only attempting to give a general description, then these special cases can be ignored. If an attempt is made to cover every special case, it would probably need a computer to analyse the systems. When one knows approximately the reaction behaviour in the presence of moderate amounts of other ions, it is sufficient for the purpose I have in mind. For special conditions one would need to look up the necessary reference books. As I have repeatedly emphasized, I am only seeking an expression which can be given verbally and which can convey an approximate idea of reaction behaviour. If a classification of this kind could be devised, the way would then be clear for preparing the more detailed information provided by Dr. Betteridge's system.

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16 June 1976

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PRELIMINARY COMMUNICATIONS

THE ANALYTICAL POTENTIAL OF GAS-PHASE MOLECULAR ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF ANIONS IN SOLUTION

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We have recently demonstrated[1] that nitrogen may be determined by conversion into ammonia in solution and subsequent measurement of the absorption in the ultraviolet region by the ammonia gas displaced from the alkaline sample solutions by a current of air. The selectivity, sensitivity, and precision of the method were found to compare favourably with the corresponding parameters for possible alternative methods of analysis, and the method has been applied to the determination of nitrogen in soil and plant samples. Factors influencing the sensitivity of the method for the determination of ammonium-N have been investigated in detail,[2] using the standard absorption-tube cell from a Shandon-Southern A 3490 Arsenic/Selenium Detection Unit, and a hydrogen hollow-cathode lamp. Subsequent work has shown that the method may also be applied to the determination of nitrate, if the latter is first reduced to ammonia with titanous sulphate solution.[3]

Because of the simplicity of these methods, the speed with which analyses may be completed, and the relative ease with which the methods could be fully automated, it seemed worthwhile to investigate the feasibility of determining other species by similar procedures. Sulphur dioxide, hydrogen sulphide, and the nitrogen dioxide-dinitrogen tetroxide system all absorb strongly in the analytically-useful (non-vacuum) region of the ultraviolet spectrum. These gases may be readily prepared at room temperature by the addition of dilute acid to solutions of sulphite, sulphide, and nitrite respectively. The absorption spectra obtained by adding 5-ml aliquots of 6M hydrochloric acid to 100 mg portions of the sodium salts of these anions in 100-ml volumetric flasks fitted with rubber septa are shown in Figs. 1 (S^{2-} and SO_3^{2-}) and 2 (NO_2^-): 0.05 - 0.2-ml aliquots of the gas evolved were injected into the 10-mm silica sample cell, which was also fitted with a rubber septum. All reactions and cell-filling operations were performed in a nitrogen atmosphere in a dry-box, so that spectra could be plotted down to 185 nm against an appropriate blank, with a Cary-Varian model 118 double-beam solution spectro-

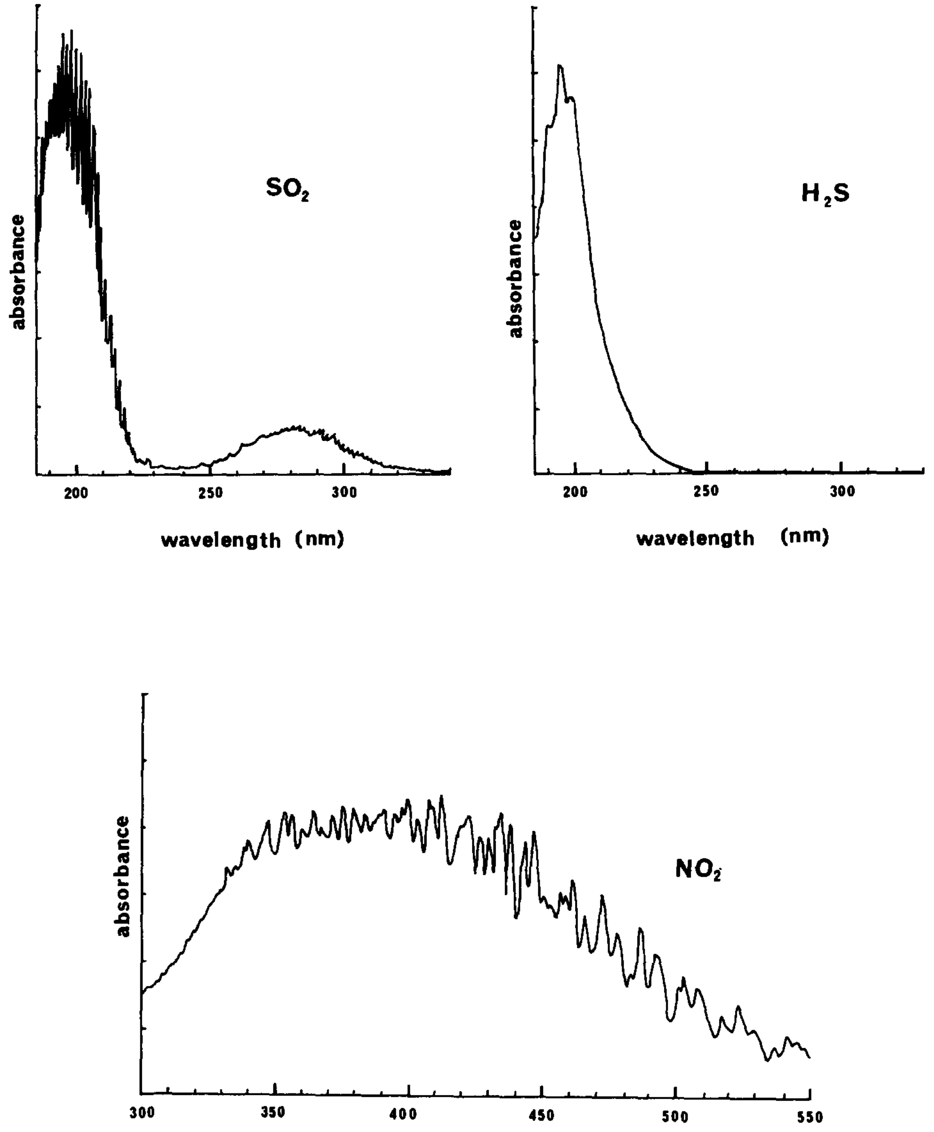

Fig. 1. Absorption spectra of sulphur dioxide, hydrogen sulphide, and nitrogen dioxide

photometer purged with dry nitrogen.

The results clearly indicate that gas-phase molecular absorption spectrometry (GPMAS) may be used for the sensitive determination of sulphide, sulphite and nitrite in solution, and that is is unnecessary to employ a nitrogen-purged monochromator. This has been confirmed for nitrite, using identical apparatus to that employed for the determination of ammonia,[2] but with 6M hydrochloric acid in place of the 40% sodium hydroxide solution used in the latter determination. The selectivity of the methods ultimately developed will depend upon the gas-generation system used. Thus, for example, the sensitivity of the nitrite determination deteriorates 100-fold if 6M sulphuric acid is employed in place of hydrochloric acid, and this could perhaps be used to improve the selectivity of the determination of sulphide or sulphite by GPMAS. Alternatively, suitable scrubbing solutions or solid absorbents or thermal decomposition techniques may be necessary to improve selectivity. No detectable absorbance was found for relatively large amounts of hydrogen selenide or hydrogen telluride, when these were prepared by reduction of selenite and tellurite salts with sodium borohydride in acid solution, so that selenide and telluride should cause no spectral interference in the determination of sulphide.

The absorption spectra of sulphur dioxide and hydrogen sulphide are relatively simple, and require no further comment here. The absorption spectrum obtained from the reaction between sodium nitrite and hydrochloric acid is more complex, however. The

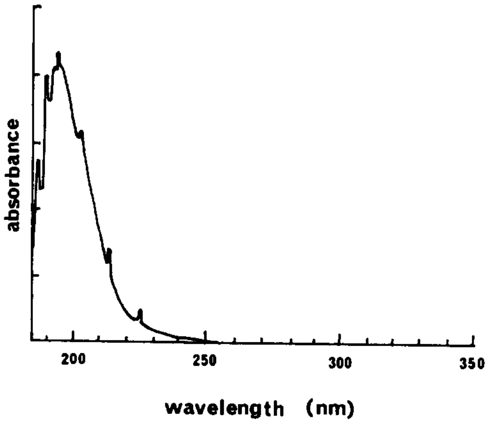

Fig. 2. Absorption spectrum of the undried products of the reaction between sodium nitrite and hydrochloric acid

structure which appears on the most sensitive band centred at 195 nm for this system is no longer observed if the gas mixture is dried with calcium chloride. The absorption spectrum might be expected to correspond to that of a relatively complex mixture of NO, NO_2, N_2O_4, N_2O_3 and HNO_2,[4-6] and possibly even NOCl.[7] The well-characterized part of the absorption spectrum of the NO_2-N_2O_4 system,[8] the lower spectrum in Fig. 1, is observable only at considerably higher gas mixture concentrations, and is of less interest from the analyst's viewpoint, because of the poorer sensitivity.

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ÜBER CHEMOLUMINESZENZERSCHEINUNGEN BEI DER REAKTION ZWISCHEN SULFID UND HYPOHALOGENIT IN WÄSSRIGER LÖSUNG

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Werden bei einer chemischen Reaktion Moleküle in elektronisch angeregten Zuständen gebildet, so ist die dabei oft auftretende Lumineszenz eine empfindlich meßbare physikalische Größe, mit deren Hilfe man den Verlauf einer Reaktion verfolgen bzw. einzelne Reaktionspartner quantitativ bestimmen kann.[1-4] Zum Zwecke der Sulfidbestimmung untersuchten wir deshalb die durch Sulfid katalysierte Reaktion zwischen Jod und Azid[5] auf eine eventuell durch Radikalreaktion auftretende Lumineszenz.

Wir fanden eine schwache Lumineszenz, deren Intensität von der Jod- und der Sulfidkonzentration abhängig war, ohne daß das Azid hierauf einen Einfluß ausgeübt hätte. Das bedeutet, daß die Lumineszenz die Oxidation des Sulfids durch Jod, eine Nebenreaktion der Jod-Azid - Reaktion, begleitet.

Die Lumineszenz trat nur im alkalischen Bereich auf ($pH > 8.0$), in welchem Jod bereits als Hypojodit vorliegt. Da das Jod als starker Quencher wirkte, durfte seine Konzentration nicht zu hoch sein. Mit Sulfidlösungen im $10^{-6}\underline{M}$ Bereich konnte ein Lumineszenzoptimum bei einer Jodkonzentration von $5 \cdot 10^{-6}\underline{M}$ beobachtet werden.

Wie weitere Untersuchungen zeigten, können außer Jod auch Brom bzw. Chlor[6] als Oxidationsmittel dienen. Die Lichtausbeute war sowohl bei Brom als auch bei Chlor um den Faktor 5 größer als bei Jod. Mit anderen Oxidationsmitteln [Hexacyanoferrat(III), Wasserstoffperoxid, Kaliumjodat] konnte keine Lumineszenz beobachtet werden. Sauerstoff[7] hat keinen meßbaren Einfluß auf die Reaktion zwischen Sulfid und Hypohalogenit, wie die Verwendung von Lösungen zeigte, welche vor und während der Messung gründlich mit Stickstoff gespült wurden.

Bei Anwendung höherer Konzentrationen an Brom wurde ebenfalls ein Quencheffekt beobachtet. Die besten Lichtausbeuten erhielten wir im Bereich $10^{-5} - 5 \cdot 10^{-5}\underline{M}$ Br_2. Die pH-Abhängigkeit der Reaktion (Abb. 1, Kurve a) weist auf Hypobromit als aktives Oxidationsmittel hin. Im weiteren Verlauf der Untersuchungen wurde wegen der höheren Lichtausbeute und des geringeren Quencheffektes nur Brom als Oxidationsmittel verwendet.

Zur Photonenzählung benutzten wir ein Flüssigkeitsszintillationsspektrometer (Intertechnique SL 30, Zählung bei ausgeschalteter Koinzidenzstufe und ganz geöffneten Fenstern). Die Lösungen wurden mittels einer Peristaltikpumpe durch ein Strömungssystem gefördert. In einer Mischzelle unmittelbar vor der Zählkammer wurde coulometrisch Brom aus einer $10^{-3}\underline{M}$ Kaliumbromidlösung produziert (Lösung I) und dort sofort mit einer Pufferlösung von geeignetem pH (Lösung II) vermischt. Dieser Reagenslösung wurde in der Durchflußzelle, die in die Zählkammer des Szintillationszählers eingesetzt war, das Sulfid in einer $10^{-4}\underline{M}$ Natriumhydroxidlösung (Lösung III) zudosiert.

Eine Erhöhung der Lichtausbeute um den Faktor 2 - 10 kann durch Zusatz von fluoreszierenden Substanzen erreicht werden, die zwischen 500 und 650 nm absorbieren. Es erwies sich dabei im pH-Bereich 9-11 Methylenblau als sehr günstig, da es mit keinem der untersuchten Oxidationsmittel allein zu einer nennenswerten Lumineszenz führte. Wie Abb. 1, Kurve b zeigt, erbrachte die Verwendung von Methylenblau als Sensibilisator eine beträchtliche Erhöhung der Lichtausbeute.

Eine Aussage über die angeregte Spezies, die bei dieser Reaktion entsteht, ist noch nicht möglich. Zwar beobachtet man im Szintillationszähler mit seiner sehr günstigen Zählgeometrie bei Zusatz von Methylenblau Zählraten von $5 \cdot 10^4 - 10^6$ cpm, doch ergibt die hieraus vorgenommene Abschätzung der Lumineszenzausbeute, bezogen auf die eingesetzte Sulfidmenge, Werte von nur $10^{-8} - 10^{-10}$. Deshalb gelang es bisher nicht, mit einer Anordnung aus Monochromator und Photonenzählgerät ein Spektrum der primär emittierten, d.h. aus der Reaktion zwischen Hypobromit und Sulfid herrührenden, Strahlung zu erhalten. Lediglich bei Verwendung von Methylenblau als Sensibilisator war ein Signal im Bereich der Fluoreszenzstrahlung dieses Farbstoffes zu beobachten.*

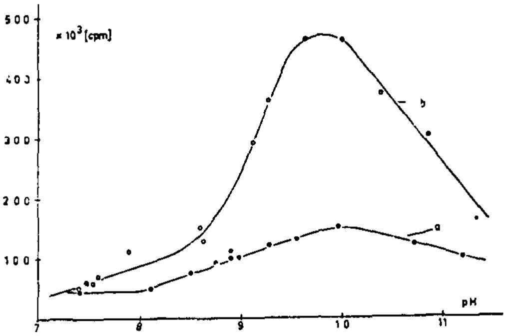

Abb. 1. pH-Abhängigkeit der Lumineszenz

Kurve a: ohne Sensibilisator
Lösung I: $5 \cdot 10^{-5}\underline{M}$ Br_2 in $10^{-3}\underline{M}$ KBr
Lösung II: HCl- bzw. NaOH-Lösung verschiedener Konzentration zur Einstellung der gewünschten pH-Wertes
Lösung III: $3 \cdot 10^{-5}\underline{M}$ Na_2S in $10^{-4}\underline{M}$ NaOH

Kurve b: mit Sensibilisator
Lösung I: $10^{-5}\underline{M}$ Br_2 in $10^{-3}\underline{M}$ KBr
Lösung II: wie bei a, jedoch mit jeweils $5 \cdot 10^{-5}\underline{M}$ Methylenblau
Lösung III: $10^{-6}\underline{M}$ Na_2S in $10^{-4}\underline{M}$ NaOH

Im Hinblick auf eine analytische Anwendung der Reaktion zur Sulfidbestimmung wurde die Abhängigkeit der Lumineszenz von der Sulfidkonzentration unter folgenden Bedingungen ermittelt:

Lösung I: $10^{-5}\underline{M}$ Br_2, coulometrische erzeugt in $10^{-3}\underline{M}$ Kaliumbromidlösung;
Lösung II: $5 \cdot 10^{-5}\underline{M}$ Methylenblau in $10^{-3}\underline{M}$ Boratpuffer vom pH 9;
Lösung III: Natriumsulfid in $10^{-4}\underline{M}$ Natriumhydroxidlösung;
Pumpgeschwindigkeit für jede Lösung: 2,2 ml/min.

Es ergab sich eine annähernd lineare Eichkurve im Bereich $10^{-7} - 5 \cdot 10^{-6}\underline{M}$ Sulfid.

Andere Reduktionsmittel (Thiosulfat, Sulfit, Äthylmercaptan) stören nicht durch eine Lumineszenz sondern durch Verbrauch an Oxidationsmittel.

Gegenwärtig wird versucht, das System zu einem empfindlichen Verfahren zur Sulfidbestimmung auszubauen. Hierbei steht das bislang nur unzureichend gelöste Problem der Erfassung von Schwefelwasserstoffspuren in der Atmosphäre unter Reinluft- und "background"-Bedingungen im Vordergrund.

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EDITORIAL

For the last two years "card index summaries" of the papers in *Talanta* have been published in English, French and German as a separate part of each issue, the intention being to provide copies that could be cut out and pasted onto cards. This arrangement, however, is only of use to the first person having access to a copy and using it (always assuming that in the case of library copies the librarian has not mistaken the summaries for advertising matter and thrown them away). It therefore seems likely that demand for the service is low, and in view of its relatively high cost it is felt that readers would probably prefer to do without the card index summaries and have the savings used to stabilize the subscription rate, especially in these days of high inflation. This issue will therefore carry the last set of card index summaries. We shall, of course, continue to print summaries along with the papers themselves, and these will be in the same language as the paper, with an English translation for papers written in French or German.

Talanta, Vol. 23, p. 1 Pergamon Press. 1976 Printed in Great Britain

PAPERS RECEIVED

Ferricyanide as an indicator in cerimetry: L. M. Bharadwaj, D. N. Sharma, P. D. Sharma and Y. K. Gupta. (8 *June* 1976)

Stability constants of rhodizonic acid complexes in solution: Srikumar Mukerjee and Narendra S. Rawat. (10 *June* 1976)

Determination of thiourea and its organic derivatives with iodine trichloride: Sameer Bose, M. P. Sahasrabuddhey and Krishna K. Verma. (11 *June* 1976)

Einflüsse dritter Partner bei der Losungspektralanalyse nach dem Zerstäuberverfahren—II: Einflüsse organischer Lösungsmittel: Gerhard Ackermann and Manfred Münx. (24 *May* 1976)

Determination of cadmium in soils by neutron-activation analysis: E. Steinnes. (15 *June* 1976)

Selektivitätssteigerung katalytischer Bestimmungsverfahren—extraktionskatalymetrische Molybdänbestimmung: Matthias Otto and Helmut Müller. (24 *May* 1976)

Separation of Cr(III) from numerous metal ions on stannic arsenate in DMSO–HCl systems: M. Qureshi, K. G. Varshney and N. Fatima. (17 *June* 1976)

2,2′-Diaminodiphenyldisulphide—a new sensitive spectrophotometric reagent for platinum: Saswati P. Bag and Susil K. Chakrabarti. (17 *June* 1976)

Selectivity index: R. Belcher. (21 *June* 1976)

Formation constants of metal complexes with Semi-Glycinecresol Red: Takashi Yoshino, Sadaaki Murakami and Osamu Ushimaru. (21 *June* 1976)

Properties of two-step redox titrations: Robert L. Epstein and James A. Goldman. (7 *June* 1976)

Analytical studies using iodine–luminol chemiluminescence: William M. Hardy, W. Rudolf Seitz and David M. Hercules. (1 *June* 1976)

Determination of mercury in manganese nodules and crusts: J. R. Toth and J. D. Ingle, Jr. (1 *June* 1976)

Simultaneous determination of oxygen and cadmium in cadmium and cadmium compounds: Kazuo Imaeda, Takeo Kuriki, Keiko Ohsawa and Yoshiaki Ishii. (22 *June* 1976)

Bromamine-T as a new oxidimetric titrant in aqueous medium—direct titrations employing potentiometry and visual indicators: C. G. R. Nair, R. Lalithakumari and P. Indrasenan. (29 *June* 1976)

All-*cis*-1,2,3,4-cyclopentanetetracarboxylic acid: a reagent for the estimation of zirconium: G. A. Rama Rao and K. Srinivasulu. (30 *June* 1976)

Chemical separation and spectrographic estimation of rare earths in PuO_2 and $(U,Pu)O_2$: A. G. I. Dalvi, C. S. Deodhar and B. D. Joshi. (30 *June* 1976)

Extractive spectrophotometric determination of codeine, narcotine, papaverine and thebaine with Solochrome Green V 150: N. V. Rama Rao and S. N. Tandon.

A simple expression for the buffer index of a polyprotic weak acid: Rolf Hesse and Åke Olin. (1 *July* 1976)

Talanta, Vol. 23, p. I. Pergamon Press, 1976. Printed in Great Britain

OBITUARY

PROFESSOR F. E. BEAMISH

Frederick E. Beamish, FCIC, Professor Emeritus, University of Toronto, died on 8 April 1976 at Guelph, Ontario. It is impossible to catalogue adequately the accomplishments of a man of his stature. He was simply the world's number one authority on the analytical chemistry of the noble metals, having to his credit over 150 publications in this field, including 3 books (one in press) and 20 critical review articles.

Those who knew him only as a renowned scientist knew only a fraction of the man. Dr. Beamish was a loving husband and father and leaves his wife Dorothy and sons Dr. Dick and Dr. Bill Beamish. Perhaps first of all he was a teacher of chemistry and the research process and by example the purveyor of the best values in life. A dedicated gardener and naturalist, he treated the often miniscule problems of his students and his friends in the same delicate and loving way he worked with his favourite begonias and ferns. Beamish was a very religious man with an infectious sense of humour, these attributes often becoming the strength, during troubled times, of those with whom he had close associations.

Dr. Fred Beamish was born in Hanover, Ontario in 1901. He completed his M.A. at McMaster in 1929. He was appointed lecturer at the University of Toronto in 1931, associate professor in 1935 and full professor in 1946. He was accorded the title of Professor Emeritus, University of Toronto, in 1969, but he never really retired, continuing his writings until in 1974 a serious illness terminated his work.

Dr. Beamish was a tireless researcher, often spending 12 hours a day, 6 days a week at his desk and in the laboratory. He expected the same dedication and honesty of approach from his students. To have been a Beamish student was to have lived among the chosen few. Dr. Beamish left an indelible mark on those whom he taught, as is evidenced by the success of his students in government, industry and universities.

Among his other accomplishments Dr. Beamish was the first chairman of the Analytical Chemistry Division of the CIC, Canadian representative on the Analytical Section of IUPAC and on the advisory or editorial boards of the journals *Talanta*, *Analytical Letters* and *Analytical Chemistry*. He received an honorary D.Sc. from McMaster University in 1962, won the Fisher Award for Analytical Chemistry in 1970 and was appointed Fellow of the Royal Society of Canada in 1958.

Fred Beamish's devotion to hard work, clean living and complete honesty is an example to all. In this respect, Fred lives on amongst that large group of people who knew him well.

Talanta, Vol 23, p i Pergamon Press. 1976 Printed in Great Britain

PAPERS RECEIVED

A new selective reagent for the spectrophotometric determination of palladium: F. Corigliano, S. Di Pasquale and A. Ranieri. (22 *March* 1976)

Polarographic behaviour of some *o*-hydroxyketoximes: R. P. Singh, K. B. Pandeya and Asha Kapahi. (24 *March* 1976)

Coulometric determination of ascorbic acid with electrogenerated octacyanomolybdate(V): R. Cordova-Orellana and F. Lucena-Conde. (24 *March* 1976)

Determination of strontium in human tooth enamel by flameless atomic-absorption spectrometry: Christine A. Helsby. (26 *March* 1976)

Potentiometric determination of hydrogen peroxide and sodium perborate with potassium dichromate: N. Krishna Murty and K. Rama Rao. (29 *March* 1976)

Titrimetric estimation of phosphate, molybdate, tungstate and sulphate with lead(II) nitrate solution, using 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid (NQS-4S) and 1,2-naphthoquinone-2-thiosemicarbazone-4-sulphonic acid (NQTS-4S) as visual indicators: Shanthi Kesavan, B. S. Garg and R. P. Singh. (30 *March* 1976)

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Development of the differential refractometer: J. R. Majer. (31 *March* 1976)

An application of the Zeeman effect to analytical atomic spectroscopy—III: The extension of calibration curves: D. E. Veinot and R. Stephens. (31 *March* 1976)

Induced reduction of thallium(III) by hydrogen peroxide: P. D. Sharma and Y. K. Gupta. (2 *April* 1976)

Limit of detection and selectivity coefficients of liquid membrane electrode: Naoki Kamo, Norio Hazemoto and Yonosuke Kobatake. (5 *April* 1976)

The determination of selenium and other impurities in high-purity copper by flameless atomic-absorption spectrophotometry: J. D. Mullen. (5 *April* 1976)

Acid-base titrations by stepwise additions of equal volumes of titrant, with special reference to automatic titrations—I: Theory, discussion of the Gran functions, the Hofstee method and two proposed methods for calculating equivalence volumes: Lennart Pehrsson, Folke Ingman and Azel Johansson. (5 *April* 1976)

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An improved turbidimetric procedure for the determination of sulphate in plants and soils: Balbir C. Verma, K. Swaminathan and K. C. Sud. (6 *April* 1976)

Dalzin as an analytical reagent and its application in analysis: M. R. Navaratna and C. S. P. Iyer. (6 *April* 1976)

Polarographic studies on cadmium(II) and lead(II) complexes of 2-amino-3-hydroxypyridine: R. S. Sindhu, K. B. Pandeya and R. P. Singh. (6 *April* 1976)

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Accuracy of steel analysis by using spark-source mass-spectrometry with electrical detection: E. Van Hoye, F. Adams and R. Gijbels. (12 *April* 1976)

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PAPERS RECEIVED

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Electroreduction of molybdenum(VI) at a prehydrogenated platinum electrode: P. ZANELLO, G. RASPI and A. CINQUANTINI. (15 *January* 1976)

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Analytical applications of complex formation in non-aqueous solutions—I. Complexes of bismuth(III) with potassium diphenyldiselenophosphate in organic solvents: N. T. YATISIMIRSKAYA, ARAIN RAFEE and A. I. BUSEV. (15 *January* 1976)

Application of zone melting technique to metal chelate systems—X. Zone refining of bis(acetylacetonato)beryllium(II), tris(acetylacetonato)aluminium(III) and bis(di-isovalerylmethanato)copper(II): ISAO YOSHIDA, HIROSHI KOBAYASHI and KEIHEI UENO. (27 *January* 1976)

Application of zone melting technique to metal chelate systems—XI. Refining of tetrakis(dipropionylmethanato)zirconium(IV) from hafnium and trace amounts of some other metals: ISAO YOSHIDA, HIROSHI KOBAYASHI and KEIHEI UENO. (27 *January* 1976)

Spectrophotometric determination of pyrrole derivatives: J. P. SHARMA, A. K. DUBEY and V. K. S. SHUKLA. (28 *January* 1976)

Dynamic surface tension measurements for the assessment of potable water quality: G. LOGLIO, U. TESEI, A. FICALBI and R. CINI. (28 *January* 1976)

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Detection of some nitrogen compounds and the semi-quantitative determination of diphenylamine with *p*-dimethylaminobenzaldehyde by capillary solid-state spot tests: M. QURESHI, H. S. RATHORE and ALI MOHAMMED. (3 *February* 1976)

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Extraction behaviour and selective determination of arsenic(III) and arsenic(V) with ammonium pyrrolidinedithiocarbamate, sodium diethyldithiocarbamate and dithizone by means of flameless atomic-absorption spectrophotometry with a carbon-tube atomizer: TOSHIHIKO KAMADA. (3 *February* 1976)

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Electrolysis at constant potential. Determination of diffusion coefficients of thallium by using a hanging mercury drop electrode: J. HERNÁNDEZ MÉNDEZ and R. CARABIAS MARTÍNEZ. (11 *February* 1976)

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EDITORIAL

In this issue we present the first article in our new feature in which critical reviews are given of the development of particular types of instrument and of the equipment currently available. This first paper is on the mass filter, used in mass spectrometry. For the feature to become a success it is vital that we have the co-operation of our readers both in identifying the areas in which such reviews would be topical and useful, and in contributing to the feature. Anyone interested should write in the first instance to Dr. J. R. Majer, Chemistry Department, The University, P.O. Box 363, Birmingham 15, U.K., who will be responsible for this section, and who has written the first contribution to it.

Talanta, Vol. 23, p. i. Pergamon Press, 1976, Printed in Great Britain

PAPERS RECEIVED

Iron(II)-induced oxidation of hypophosphite by peroxydiphosphate in acid medium: SURINDER KAPOOR and Y. K. GUPTA. (11 *December* 1975)

The use of long chain alkylamines for preconcentration and determination of traces of molybdenum, tungsten and rhenium by atomic absorption spectroscopy—III. Tungsten in geological samples: C. H. KIM, P. W. ALEXANDER and L. E. SMYTHE. (15 *December* 1975)

Gravimetric estimation of palladium with *m*-(mercaptoacetamido)phenol: GEETHA PARAMESWARAN. (15 *December* 1975)

The application of ternary complexes to spectrofluorometric analysis: P. R. HADDAD. (18 *December* 1975)

Studies on some metal hydrous oxide sols, using electrocapillary curves: WAHID U. MALIK, RAMESH BEMBI, AJAY K. JAIN and J. S. TYAGI. (22 *December* 1975)

Interpretation of selectivity coefficients of solid-state ion-selective electrodes by means of the diffusion layer model: ADAM HULANICKI and ANDRZEJ LEWENSTAM. (22 *December* 1975)

Catalytic ion-exchange method for detection of microgram amount of amino-acids: SAIDUL ZAFAR QURESHI and IZZATULLAH. (22 *December* 1975)

Controlled-potential iodometric determination of iron after extraction with di-isopropyl ether: RONALD KARLSSON and LO GORTON. (23 *December* 1975)

Dosage du cuivre, plomb, cadmium, zinc dans l'eau de mer par redissolution anodique en utilisant un standard interne: PHILIPPE GOUT. (23 *December* 1975)

Determination of some trace impurities, indium, manganese, arsenic and antimony in different samples of zinc metal by neutron-activation analysis: M. DERMELJ, V. RAVNIK, L. KOSTA, A. R. BYRNE and A. VAKSELJ. (23 *December* 1975)

A study of the simultaneous determination of lead and barium as chromates by amperometric titration: B. PIHLAR and L. KOSTA. (23 *December* 1975)

Precipitation of zinc ammonium phosphate from homogeneous solution: G. SIVA REDDY and Y. KRISHNA REDDY. (24 *December* 1975)

A coulometric method for the assay of some easily oxidized organic substances with iodine as an oxidizing agent: L. E. EDHOLM. (29 *December* 1975)

Determination of 14 trace elements in cobalt by instrumental proton activation analysis: V. KRIVAN. (31 *December* 1975)

Talanta, Vol. 23, p. I. Pergamon Press. 1976. Printed in Great Britain

TALANTA ADVISORY BOARD

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

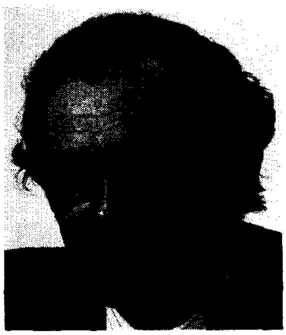
J. K. Foreman
H. V. Malmstadt
H. M. Ortner

They also wish to record their sincere thanks for the help given by

D. M. W. Anderson
F. E. Beamish
H. B. Mark Jr.

who retire from the Advisory Board.

Since graduating from London University Mr. Foreman's career has been largely divided between the Windscale Works of the United Kingdom Atomic Energy Authority and the Laboratory of the Government Chemist in London; he has been Deputy Government Chemist since 1970. His principle analytical interests have been in the field of radiochemistry, physical methods of analysis, separation techniques and automation of analytical techniques for both laboratory and chemical plant use. He is co-author of a recently published book entitled *Automatic Chemical Analysis*.



Professor Malmstadt was educated in chemistry at the University of Wisconsin and in electronics at Princeton and MIT during the war, when he was a Radar Officer in the U.S. Navy. He is now Professor at the University of Illinois and is kept busy by teaching, research, consultancy work, designing instruments, writing (8 books and over 120 research papers), lecturing throughout the world, and serving on numerous advisory boards. He has received several awards for his outstanding contributions to instrumentation and analytical chemistry.

Dr. Ortner was trained at the home of microanalysis, Graz, and since 1970 has worked at the chemical laboratory of Metallwerk Plansee, in Austria, and is now head of this laboratory. His work has ranged over a variety of topics, from clinical trace analysis to work on the refractory metals and their alloys. His current interests include X-ray fluorescence analysis, bulk and topochemical trace analysis of Mo, W, Nb, Ta and their alloys, and gel chromatography, especially the behaviour of isopoly and heteropoly acids. For several years he was Secretary of the Austrian Society for Microchemistry and Analytical Chemistry, and is now a member of several working groups dealing with standardization of methods.

Talanta, Vol. 23, p. i. Pergamon Press, 1976. Printed in Great Britain

PAPERS RECEIVED

Synthesis and evaluation of some pyridyl-substituted pyrimidines as copper-specific chromogenic reagents: A. A. Schilt, J. F. Wu and F. H. Case. (13 *November* 1975)

Concentration and separation of trace metals with an arsonic acid resin: J. S. Fritz and E. M. Moyers. (10 *November* 1975)

Zero-current bipotentiometric end-point indication with pretreated electrodes—IV. Use of pretreated silver electrodes: L. Kékedy and M. Serban. (26 *November* 1975)

A study on compounds of Cr(NCS)$_6^{3-}$ with Tl(I) and Ag(I): Alessandro de Robertis, Athos Bellomo and Domenico de Marco. (26 *November* 1975)

Use of Zeo-karb 226 and Dowex A-1 in the analysis of high purity zinc and zinc-base alloys for Tl and In: S. Ganapathy Iyer, P. K. Padmanabhan, L. D. Nair and Ch. Venkateswarlu. (26 *November* 1975)

Spectrophotometric determination of osmium with prochlorperazine maleate: H. Sanke Gowda and P. G. Ramappa. (27 *November* 1975)

Acid–base equilibria in ethylene glycol—III. Selection of titration conditions in ethylene glycol medium, and protolysis constants of alkaloids in ethylene glycol and its mixtures: P. Zikolov, T. Zikolova and O. Budevsky. (27 *November* 1975)

Some comments on the progress of analytical chemistry 1910–1970: T. Braun. (28 *November* 1975)

Synergic uranium extraction from phosphoric acid media with di(2-ethylhexyl)phosphoric acid and tri-n-octylphosphine oxide: Florin T. Bunus and Victoria C. Domocos. (1 *December* 1975)

Construction and analytical evaluation of a mercury(I)-sensitive extractive membrane electrode: G. E. Baiulescu and N. Ciocan. (2 *December* 1975)

Derivation of the sampling constant equation: C. O. Ingamells. (3 *December* 1975)

Physical studies on the compound of zirconium with tartrazine: A. Pogorevici Papandopol, D. Todor, S. Badilescu and G. E. Baiulescu. (8 *December* 1975)

Fitting equations to parabolic graphs: V. Rozenblum. (8 *December* 1975)

Interference by hypophosphite, pyrophosphate and phosphate in cerimetry and its removal: Surinder Kapoor and Y. K. Gupta. (9 *December* 1975)

Redox reactions in non-aqueous media. Determination of organotrithiocarbonates with iodine and iodine halides: Balbir Chand Verma and Swatantar Kumar. (9 *December* 1975)

Polarographic behaviour of chromium(VI) at various pH values: I. M. Issa, M. Tharwat, M. G. Allam and M. Ismail. (10 *December* 1975)

Thin-layer chromatographic separation of alkaline earth metals on microcrystalline cellulose: Koji Ishida, Fuyuki Oryu and Tomoshige Morita. (10 *December* 1975)

Talanta, Vol 23, pp i–ii Pergamon Press, 1976 Printed in Great Britain

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Mixed-ligand complexes of lead(II) with dicarboxylic acids: S. C. BAGHEL, K. K. CHOUDHARY and J. N. GAUR. (14 *April* 1976)

Extraction chromatography of chloride complexes of osmium(III, IV and VI) on paper treated with tributyl phosphate and Amberlite LA-1 hydrochloride: S. PRZESZLAKOWSKI and A. FLIEGER. (20 *April* 1976)

The analysis of tungsten carbides by X-ray fluorescence spectrometry: K. KINSON, A. C. KNOTT and C. B. BELCHER (20 *April* 1976)

A new electrochemical analyser for nitric oxide and nitrogen dioxide: J. M. SEDLAK and K. F. BLURTON. (20 *April* 1976)

Structural effects in partition chromatography of amino derivatives of acridine in ion-association systems with HDEHP: EDWARD SOCZEWIŃSKI and DANUTA RATAJEWICZ. (21 *April* 1976)

A selective gravimetric method for simultaneous determinations of copper(II) and palladium(II) in presence of other ions with 3-(*o*-carboxyphenyl)-1-phenyltriazene *N*-oxide and application of the copper determination method to copper ore and alloys: S. C. SAHA, P. K. CHAKRABORTY and D. CHAKRABORTI. (21 *April* 1976)

Dissociation and homoconjugation equilibria of some acids and bases in *N,N*-dimethylformamide: EZIO ROLETTO and ADRIANO VANNI. (22 *April* 1976)

Determination of calcium in urine by titration with EDTA: BYRON KRATOCHVIL and PETER G. JEREMY. (22 *April* 1976)

Analytical application of *o*-hydroxymercuribenzoic acid, dithiofluorescein and mercurated fluorescein: MIECZYSLAW WROŃSKI. (22 *April* 1976)

Thermodynamic examination of galvanic cell measurements: BJØRN BERGTHORSSON. (26 *April* 1976)

Spectrophotometric determination of titanium in ores with cyclopentanone-2-carboxyanilide: SANAT KUMAR MANDAL and JYOTIRMOY DAS. (27 *April* 1976)

Equilibria of iron(III) complex formation with Methylthymol Blue and Xylenol Orange: TAKASHI YOSHINO. (28 *April* 1976)

Room temperature phosphorescence of several polyaromatic hydrocarbons: T. VO DINH, E. LUE YEN and J. D. WINEFORDNER. (3 *May* 1976)

Determination of aspirin and alkali metal salts of salicylic acid in complex mixtures: L. SZEKERES and J. A. JOSEPH (4 *May* 1976)

Titrimetric determination of ferrocyanide with zinc(II) sulphate solution, using heterocyclic azo-dyes as visual indicators: J. P. GUPTA, B. S. GARG and R. P. SINGH. (6 *May* 1976)

Determination of certain hydrocarbons by photometric titration with permanganate in non-aqueous medium: CZESLAW WYGANOWSKI. (7 *May* 1976)

Spectral and pH studies on some azo compounds: MAMDOUH S MASOUD, T. M. SALEM and M. ELHENAWI. (11 *May* 1976)

Investigation of phase growth kinetics during interaction of silicon single crystals and molybdenum thin films: B. I. FOMIN, A. E. GERSHINSKII and E. I. CHEREPOV. (12 *May* 1976)

Spectrophotometric determination of tellurium in concentrates and brasses by chloroform extraction of the tellurium(IV) hexabromide–diantipyrylmethane complex after separations by iron collection and xanthate extraction: ELSIE M. DONALDSON (13 *May* 1976)

Characteristic of the specificity of analytical methods—I: Non-specificity coefficients: LEON PSZONICKI (17 *May* 1976)

Use of hydroxylamine hydrochloride in the complexometric determination of manganese in pyrolusite: B. P. CHATTERJEE and S. K. MUKHOPADHYAY. (18 *May* 1976)

Equipment stability in IR spectrometry: A statistical approach by serial correlation: CANDIN LITEANU and IOANA ILEANA PANOVICI. (18 *May* 1976)

A compilation of nuclear data relevant to thermal-neutron activation analysis: T. D. MACMAHON. (21 *May* 1976)

Evolution des solutions aqueuses de niobates alcalins: existence de hauts polymères: ALINE GOIFFON and BERNARD SPINNER. (21 *May* 1976)

Photometrische Bestimmung von Quecksilber(II) im Nanogrammbereich mit Thio-Michlers-Keton: GERHARD ACKERMANN and HEINO RODER. (6 *May* 1976)

Study of mixed chelates by solvent extraction: Mixed chelates of indium with *β*-diketones in carbon tetrachloride and xylene media: M. SUDERSANAN and A K. SUNDARAM. (24 *May* 1976)

Matrix problems in the determination of lithium by flameless atomic-absorption spectrometry and their solution: AMITAL KATZ and NURIT TAITEL. (25 *May* 1976)

On the errors in acid-base determination by titration to preset pH values: ÅKE OLIN and BO WALLÉN. (26 *May* 1976)

L'acide phosphomolibdyque réactif pour la détermination spectrophotométrique de quelques dérivés de phénothiazine des produits pharmaceutiques: MARIA STAN, V. DORNEANU and GH. GHIMICESCU (27 *May* 1976)

2-Carboxy-2′-hydroxy-3′,5′-dimethylazobenzene-4-sulphonic acid (CHDMAS) as a spectrophotometric reagent for the simultaneous determination of nickel(II) and cobalt(II): B. K. Deshmukh, V. M. Parate and R. B. Kharat. (27 *May* 1976)

Microdetermination of thiourea and phenylurea with tervalent gold as oxidizing agent in alkaline medium: S. J. Rai, R P. Chamoli, G. C. Mishra and P. C. Gupta. (28 *May* 1976)

A new analytical procedure for quantitative determination of Al^{3+} in the presence of Fe^{3+}: Mansour Abedini. (28 *May* 1976)

Estimation of methionine and its metal complexes by oxidation with chloramine-T and dichloramine-T: N. M. M. Gowda and D. S. Mahadevappa. (3 *June* 1976)

Determination of aminocresol isomers by high-speed liquid chromatography: H. Sakurai and M. Kito. (3 *June* 1976)

Luminescence characteristics of several classes of drugs affecting the central nervous system: L. A. Gifford, J. N. Miller, J. W. Bridges and D. T. Burns. (4 *June* 1976)

Oxidations with ammonium hexanitratocerate(IV)—I: Milligram determination of polycyclic hydrocarbons: Q. S. Usmani, M. M. Beg and I. C. Shukla. (6 *June* 1976)

A modified oxidative microcoulometric method for determination of sulphur in hydrocarbons containing large amounts of chlorine: Anders Cedergren. (6 *June* 1976)

Talanta Vol 23, pp i-ii Pergamon Press 1976 Printed in Great Britain

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Polarographic determination of titanium in presence of iron: malonate complexes of titanium: J. P. Srivastava. (12 *February* 1976)

Semimicro determination of mercaptans with copper(II): Sameer Bose, M. P. Sahasrabuddhey and Krishna K. Verma. (17 *February* 1976)

Study of thermal decomposition of analytical-grade thiocyanatobismuthates(III): Andrzej Cygański. (17 *February* 1976)

Determination of some organic thio-compounds by precipitation of mercuric sulphide from mercury(II) amine complexes—I. Determination of thioacetamide and thioacetanilide: Andrzej Cygański. (17 *February* 1976)

3-Benzoyl-4-hydroxycoumarin as a complexing agent for the estimation of Th(IV), U(VI) and Ce(IV), and their separation from one another and lanthanum: Devender Singh and H. B. Singh. (18 *February* 1976)

The use of chelating resin column for preconcentration of trace elements from sea-water in their determination by neutron-activation analysis: Chul Lee, Nak Bae Kim, Ihn Chong Lee and Koo Soon Chung. (18 *February* 1976)

A selective sorbent for concentrating noble metals: G. V. Myasoedova, I. I. Antokolskaya, O. P. Shvoeva, L. I. Bolshakova and S. B. Savvin. (20 *February* 1976)

Ion-selective electrodes in organic functional group analysis: Microdetermination of nitrates and nitramines, using the iodide electrode: Saad S. M. Hassan. (20 *February* 1976)

The effect of low-temperature ashing on the structure and composition of mineral components: Y. Michotte, D. L. Massart and J. Pelsmaekers (20 *February* 1976)

The gas chromatography of ternary complexes of manganese(II), iron(II), cobalt(II) and nickel(II) with hexafluoroacetylacetonate and di-n-butylsulphoxide: Thomas P. O'Brien and Jerome W. O'Laughlin. (11 *February* 1976)

Non-destructive radiochemical method for determining carbon concentrations in thin sheet 3% Si–Fe: W M. Swift and K. W. Guardipee (24 *February* 1976)

Ein neues Reagenz von Typus EDTA, Komplexsalze der 4,4′-Diaminodiphenylmethandiessigsäure mit verschiedenen Metallionen: Const. Gh. Macarovici and Eugen Chis (24 *February* 1976)

Resorcinol-1,8-naphthalein and tetrabromoresorcinol-1,8-naphthalein as indicators in the neutralization of weak acids with a strong base: E. Singh (26 *February* 1976)

Fluorine-19 magnetic resonance. Thermodynamics of the reaction of *o*-alkylphenols with hexafluoroacetone: Floyd F. L. Ho. (23 *February* 1976)

Application of differential electrolytic potentiometry to the titration of iodate ion with ferrous ion in different acid solutions: N B. Mazumdar, K. Chatterjee and S. N. Das. (1 *March* 1976)

Application of secondary electron capture negative ion (SECNI) mass spectrometry to the analysis of metal–organic compounds: Dainis R. Dakternieks, Ian W. Fraser, John L. Garnett and Ian K. Gregor. (1 *March* 1976)

Candoluminescence—new flame technique for trace analysis—II. Determination of ng amounts of manganese: R. Belcher, S. Karpel and Alan Townshend. (1 *March* 1976)

Radiochemical separation of selenium from hydrochloric or hydrobromic acid into toluene: S. Landsberger and G. G. J. Boswell. (1 *March* 1976)

Extractive separation of tungsten as phosphotungstate: V. Yatirajam and Sudershan Dhamija. (10 *March* 1976)

Quadrivalent manganese as an oxidimetric reagent in sulphuric acid solutions: S. K. Mandal and B. R Sant. (11 *March* 1976)

The determination of glycerol in water by flow-injection analysis—a novel way of measuring viscosity: D. Betteridge and J. Růžička. (12 *March* 1976)

Effects of auxiliary complex-forming agents on the rate of metallochromic indicator colour change—IV: Mechanism of the colour change of Xylenol Orange in copper(II)–EDTA titrations: Hiroko Wada, Tomosuke Ishizuki and Genkichi Nakagawa. (12 *March* 1976)

Radiotracer studies on calcium ion-selective electrode membranes based on poly(vinyl chloride) matrices: A. Craggs, G J Moody and J. D. R. Thomas. (15 *March* 1976)

Optimization of silicate rock decomposition and determination of major elements by atomic-absorption spectrophotometry: F. Bea Barredo and L. Polo Diez (15 *March* 1976)

Indirect determination of fluoride ion by EDTA back-titration of lanthanum: Kunio Murase, Naosuke Shiraishi, Genkichi Nakagawa and Kazunobu Kodama. (16 *March* 1976)

Behaviour of trace impurities during chemical dissolution of a metal: Platinum elements in aluminium and nickel: A A. Samadi, R. Grynszpan and M. Fedoroff. (16 *March* 1976)

Determination of americium and curium by using ion-exchange in nitric acid–methanol medium for environmental analysis: E. Holm and R. Fukai. (16 *March* 1976)

Optimization of the conditions for emission–spectral determination of mercury by the use of an iron electrode cell: S. Alexandrov, Z. Milenova and V. Simeonov. (16 *March* 1976)

Dissociation of the ammonium ion in water–urea and water–tert.butyl alcohol mixtures: YVON POINTUD, HENRI GILLET and JEAN JUILLARD. (17 *March* 1976)

Extraction studies of palladium with 4-*S*-benzyl-1-*p*-chlorophenyl-5-phenyl-2,4-isodithiobiuret: B. K. DESHMUKH and R. B KHARAT (17 *March* 1976)

A critical investigation of some triphenylmethane dyes as redox indicators in the titration of antimony(III) with cerium(IV) sulphate: G. GOPAL RAO and S. G. VISWANATH. (17 *March* 1976)

Talanta. Vol. 23, pp. i–ii. Pergamon Press, 1976. Printed in Great Britain

PUBLICATIONS RECEIVED

Flame Emission and Atomic Absorption Spectrometry, Vol. 3—**Elements and Matrices**: JOHN A. DEAN and THEODORE C. RAINS (Eds.). Dekker, New York, 1975. Pp. xii + 674. $49.50.

At last the third and final part of this treatise has arrived, and it has been worth waiting for. Fourteen chapters by many well-known authorities selectively review the literature on the determination of some 80 elements, making comparisons between the emission, absorption and fluorescence modes when possible, and covering choice of wavelength, solvent, flame, and so on. Interferences and ways of dealing with them also receive due attention. A further eleven chapters cover specific applications where the methods have been found useful—analysis of biological fluids, food, petroleum products, glass, cement, metals (ferrous and non-ferrous) rocks, water, and air. Recent up-dating has ensured uniform coverage of the literature up to mid-1974. The volume is adequately indexed, and even without the first two volumes will prove a very useful reference work for most laboratories.

Chromatographic Analysis of the Environment: ROBERT L. GROB (Ed.). Dekker, 1975. Pp. x + 752. $49.50.

This book is too long—the organization into sections dealing with air pollution, soils, water pollution, and waste, each divided into chapters on gas-, liquid-, paper-, and thin-layer chromatography has resulted in too much overlap and in the subject matter being too widely dispersed (*e.g.*, pesticides are discussed in at least eight different places). It seems scarcely necessary to devote over 70 pages to the theory of chromatography when this is already covered in so many other texts. The law of propagation of errors is illustrated in an all too common way in the quotation "average error ranging from 0·6716 to 2·9190 g/ml"—apparently neither editor nor the original writer has stopped to consider whether such figures are meaningful or not. But to be fair, one must admit that the volume represents a detailed review of a large section of the literature of analytical chemistry, albeit very much a western view, and with few references later than 1971.

Power Sources, 5—Research and Development in Non-mechanical Electrical Power Sources: D. H. COLLINS (Ed.). Academic Press, London, 1975. Pp. xii + 740. £21.00; $54.00.

The texts of 47 papers presented at the 9th International Symposium in Brighton, 1974, are presented in this volume. Most papers deal with aspects of electrochemical cells or the individual electrodes. Edited discussions of the papers are also included. The contents will be of interest to those involved in development work on electrochemical cells.

Trace Element Analysis: VLADO VALKOVIĆ. Taylor & Francis, London, 1975. Pp. x + 229. £7.00.

This nicely produced little book gives a succinct account of a very wide field indeed, ranging from theories of the origin of the elements to the latest methods for finding and determining minute traces of the elements and their compounds. There is a lot of compression, of course, and sometimes one feels that other source books might have been mentioned in the text, since some of those given are a little out of date, but the book has pace, and can be dipped into almost anywhere with profit to the reader. At the price it is a good buy.

A Handbook of Organic Analysis, 5th Ed.: H. T. CLARKE, revised by B. HAYNES. Arnold, London, 1975. Pp. x + 291. £12.00, boards, or £4.95, paper.

There are already so many undergraduate texts on organic analysis that one wonders whether this book can possibly hope to corner a share of the market. However, it has been nicely produced on good quality paper, and the price of the paperback edition is not much greater than those of other comparable texts. The usual topics—preliminary tests, examination for functional groups, separation of mixtures, preparation of derivatives, and determination of physical properties—are covered thoroughly but succinctly, although the language does sometimes give away the fact that the first edition of this book appeared in 1911. A small section on spectroscopic methods is included, but this is not really adequate for a chemistry degree course nowadays. Like most similar texts, this book includes a number of classified tables of organic compounds, but these tables are more extensive than usual, since they include a large number of structural formulae, and much detailed information about the particular reactions of each individual compound. Another unusual feature of this book is the inclusion of two chapters on quantitative organic analysis—one on elemental analysis and the other on functional group analysis. The choice of methods is generally satisfactory, although some may prefer not to ask a student to carry out a digestion with sulphuric–perchloric acid mixture. The procedures are sometimes discussed in too much detail, particularly when such details refer only to a particular model of the apparatus concerned. Inclusion of some references to the original literature would also be an improvement. However, these chapters offer a sound and thorough introduction to quantitative organic analysis, and it is to be hoped that future organic chemists who have used this book will have a much greater understanding of the intricacies and problems of organic microanalysis.

Chemical Analysis of Organometallic Compounds, Vol. 4: T. R. CROMPTON, Academic Press, London, 1975. Pp. x + 302, £9.40.

Volume 4 of this series covers the elements phosphorus (244 pages), arsenic (23 pages), antimony (2 pages) and bismuth (2 pages), and also mentions that no references have been found to the analytical chemistry of organometallic compounds of vanadium, niobium, tantalum or palladium, although it is difficult to see why palladium is included as a Group VA element. As in previous volumes, methods are given for determination of elements, functional groups, and the compounds themselves. Procedures are given in detail, so the methods can be used without reference to the original literature. The literature is covered only to 1970.

Radioactivity and Atomic Theory: FREDERICK SODDY, edited with commentary by THADDEUS J. TRENN. Taylor & Francis, London, 1975. Pp. xvii + 518. £12.00.

This volume consists of facsimiles of Soddy's Annual Progress Reports on Radioactivity, over the period 1904–1920, together with an annotated review and a biographic sketch. It will be a handy acquisition for those libraries that do not possess the originals.

Scandium: Its Occurrence, Physics, Chemistry, Metallurgy, Biology and Technology: C. T. HOROVITZ (editor), K. A. GSCHNEIDNER JR., G. A. MELSON, D. H. YOUNGBLOOD and H. H. SCHOCK. Academic Press. New York, 1975. Pp. xvi + 598. £16.00, $42.25.

From eka-boron to 1974, all one might wish to know about scandium, nicely printed and reasonably priced for these days. The interdisciplinary approach gives several books for the price of one.

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PAPERS RECEIVED

Assay of *p*-aminobenzenesulfonamides with chloramine-T: Norman M. Trieff, V. M. Sadagopa Ramanujam and G. Cantelli Forti. (8 *June* 1976)

Juglone and lawsone as acid–base indicators: Krishna C. Joshi, P. Singh and Girraj Singh. (8 *July* 1976)

Colorimetric and volumetric determination of some penicillins with ammonium vanadate: E.-Sebai A. Ibrahim, Y. A. Beltagy and M. M. Abe El-Khalek. (8 *July* 1976)

Spectrophotometric studies on complex formation of niobium(V) with 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid: A. Salaam A'Azmi and G. C. Shivahare. (13 *July* 1976)

Determination of 30 elements in coal and fly-ash by thermal and epithermal neutron activation analysis: J. J. Rowe and E. Steinnes. (13 *July* 1976)

Thermodynamic parameters and stability constants of Cu(II), Ni(II), Co(II), Zn(II), Pd(II), Rh(III) and Pt(IV) complexes with diaminoacetylurea: P. C. Srivastava, S. K. Adhya and B. K. Banerjee. (13 *July* 1976)

Ultraviolet-absorption spectra of colourless molybdate complexes of phosphorus compounds—I. Formation of pentamolybdodiphosphate complex and its absorption spectra: Toshitaka Hori. (13 *July* 1976)

Ultraviolet absorption spectra of colourless molybdate complexes of phosphorus compounds—II. Formation of pentamolybdodiphosphite complex and its absorption spectra: (13 *July* 1976)

Chromazurol S ion-selective electrode for chelatometric titration: M. Kataoka, M. Shin and T. Kambara. (13 *July* 1976)

Organic phase species in the extraction of molybdenum(VI) by Aliquat 336: A. S. Vieux, N. Rutagengwa, L. Basolila and C. Mulenga. (13 *July* 1976)

An abbreviated fire-assay/atomic-absorption method for the determination of gold and silver in ores and concentrates: P. E. Moloughney. (13 *July* 1976)

Homogenitätskriterien für festkörperanalytische Untersuchungen: Klaus Danzer and Ludwig Küchler. (13 *July* 1976)

Etude à l'aide d'une microsonde électronique de trouvailles archéologiques gauloises: C. Triché, G. Fouet and G. Saves. (4 *June* 1976)

Optimization of the synergic extraction of iron(II) from water into cyclohexane with hexafluoroacetylacetone and tri-n-butyl phosphate: Michael L H. Turoff and Stanley N. Deming. (16 *July* 1976)

Behaviour of lead(II) in stripping voltammetry from a stationary, flat, thin-layer mercury electrode: A. E. Charola and R. J. Manuele. (8 *July* 1976)

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PUBLICATIONS RECEIVED

Handbook of Enzyme Technology: A. WISEMAN, editor. Ellis Horwood, Chichester, 1975. pp. 275. $15.00.

There have been considerable developments in the biochemistry of enzymes, stemming largely from fundamental studies on their large scale application in the food and pharmaceutical industries. Professor Wiseman, especially in his annual "Summer Schools" on fermentation, has done much to establish a bridge between academic and industrial research. This book is a further contribution to this liaison. In a short volume but with a high information density, it offers a particularly complete overall view of the problems posed by preparation and use of enzymes in all their forms. After a brief theoretical survey of the nature, mode of action, kinetics and analysis of enzymes, the book deals with culture of micro-organisms, sources, methods of extraction, and purification of enzymes, methods of fixing them on insoluble supports, methods of conferring new properties on enzymes, and finally a panoramic view of the applications of enzymes in industry and research. A very stimulating aspect of this last chapter is its suggestions of new applications. The balance between theory and practice is excellent throughout. The contributors' personal experience is well illustrated by their justifiably severe criticism of manufacturers who supply insufficient information or use peculiar activity units. The chapter on transfer coefficients and scale-up problems in fermentation is admirably clear and concise. Other notable features are the fullness of the bibliography and the list of suppliers of equipment and enzymes. The only criticism is that though the book is nominally divided into two parts—theory and practice—both aspects occur in both halves, and the reader needs to go back and forth to find all the information on a particular point, but this is a minor drawback in an outstandingly useful book that fully justifies the name of handbook.

ICP Information Newsletter: RAMON M. BARNES, editor. University of Massachusetts. $30.00 per annum (12 issues). $3.00 for individual issues.

This new publication is intended to serve as a vehicle for information and opinions on use of inductively coupled plasma discharge sources in spectrochemical analysis. It includes contributed papers, abstracts, information about equipment commercially available, news of conferences, etc. Further information is obtainable from Dr. Barnes, Department of Chemistry, GRC Tower I, University of Massachusetts, Amherst, Massachusetts 01002.

Chemical Information Systems: J. E. ASH and E. HYDE, Ellis Horwood, Chichester, 1975. pp. x + 309. £12.00.

This book is an admirable introduction to a complex subject, and it should be read by anyone contemplating making use of modern information systems. The first chapters discuss in general terms the nature and development of chemical information systems, methods of organizing information for efficient retrieval by computer, and the cost-effectiveness and cost-benefits of these complex systems. Later chapters cover in some detail the methods which are used to represent chemical structures (mainly organic) in information systems, with particular reference to the Wiswesser Line-Formula Notation, the Dyson-IUPAC notation, and the use of connection tables. Two industrial systems (Hoechst's GREMAS and I.C.I.'s CROSSBOW) are discussed in some detail, to illustrate the wide range of techniques involved in a complete system. Methods of file-screening, and the problems of indexing chemical reactions are also discussed. The final chapter, Information Science in Relation to the Chemist's Needs, discusses the needs and problems of inorganic, physical, organic, engineering and macromolecular chemistry: readers of *Talanta* will be disappointed that analytical chemistry is not mentioned.

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PUBLICATIONS RECEIVED

Spectrophotometric Determination of Elements: ZYGMUNT MARCZENKO, Horwood, Chichester, 1976. Pp. xi + 643. £19.50.

All of those associated with the translation and revision of this book from the Polish (1968) and Russian (1971) are to be congratulated. It is all that the analyst could desire for a one-volume manual and reference text on spectrophotometry. The first hundred pages discuss the principles of the method, the principal organic reagents and procedures for preconcentration and separation. The rest of the book describes for each element two or three tested methods of determination and reviews suitable separation procedures and alternative methods of determination. The presentation is extremely clear. The judgements of alternative methods are both comprehensive and fair, whilst the accounts of the selective procedures are full of the practical details necessary for their application. The layout is similar to Sandell's well known text, but this is a very individual work. Professor Marczenko has achieved the remarkable feat of extracting the essence of 7000 references and distilling from them an invaluable, judicious and readable book, which should be within easy reach of all who use spectrophotometric methods. The publisher has co-operated by providing a good typographical layout and binding which allows the book to be handled comfortably and to be laid open on the bench.

Handbook of Organic Reagents in Inorganic Analysis: Z. HOLZBECHER, L. DIVIŠ, M. KRÁL, L. ŠŮCHA and F. VLÁČIL, Horwood, Chichester, 1976. Pp. 734. £19.50.

Organic reagents play a very important part in inorganic analysis, as this monograph illustrates very comprehensively. The earlier chapters give a critical account of theoretical aspects of the structure and properties of organic reagents and their compounds with metals, covering such varied topics as the nature of the bonds in complexes, absorption spectra of reagents and their complexes, and methods of investigating structures of complexes. In the treatment of solution equilibria which follows, the topics discussed include thermodynamics and kinetics of complexation reactions, redox reactions, partition and precipitation equilibria, and masking. Also included is an account of the applications of organic reagents in separations, distillation, extraction, chromatography, ion-exchange, spot tests, gravimetry, titrimetry, photometry, kinetic methods and ion-selective electrodes. This section of the book could well serve as a general text for students of analytical chemistry. The later chapters of the book describe practical applications of organic reagents. In chapter 5, for each element (or group of closely related elements) the most useful reagents are tabulated, with, for each, the method of use, the relevant conditions, and the range of application. The final chapter is a selective compilation of currently-used organic reagents: in addition to the reagents for spectrophotometry, fluorimetry, gravimetry and spot tests which frequently appear in lists like this, it includes numerous examples of masking agents, buffers, indicators (acid-base, redox, metallochromic, adsorption), complexing titrants, extractants and ion-exchangers. The comprehensive index and extensive cross-referencing between chapters and sections add greatly to the practical utility of this part of the book.

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XXth COLLOQUIUM SPECTROSCOPICUM INTERNATIONALE
7th INTERNATIONAL CONFERENCE ON ATOMIC SPECTROSCOPY

The XXth Colloquium Spectroscopicum Internationale and the 7th International Conference on Atomic Spectroscopy will be held jointly at Prague, Czechoslovakia, from August 30, to September 7, 1977.

The meeting will cover all branches of atomic and molecular spectroscopy. The official languages are English, French, German and Russian.

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The Fourth SAC Conference of the Analytical Division of the Chemical Society will be held in the University of Birmingham, England, 17–22 July 1977. Plenary lectures will be given by Professors R. Belcher, V. A. Fassel and Yu. A. Zolotov among others. The scientific programme will also contain invited lectures on topics of major current interest, contributed papers, and group discussion sessions. An extensive social programme is also planned.

Further information can be obtained from The Secretary, Analytical Division, Chemical Society, Burlington House, London W.1. Intending delegates who wish to offer papers should contact the Secretary as soon as possible. Abstracts (about 200 words) must be submitted before 31 December 1976.

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In Fig. 4 (on p. 236) in the paper by Takayoshi Yoshimori and Noriyuki Sakaguchi, *Talanta*, 1975, **22**, 233, the numbers on the ordinate should be 25, 50, 75 and 100 ppm of water, not 50, 100, 150, 200.

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PUBLICATIONS RECEIVED

Operational Amplifiers in Chemical Instrumentation: Robert Kalvoda. Horwood, Chichester, 1975. Pp. 178. £7.50.

Too many chemists refuse to give even a moment's thought to what goes on inside their many "black boxes", while some who do are baffled rather than helped by textbooks on electronics. For such people this book is written—by the expert, himself a chemist, for other chemists. The treatment of circuit theory and the concept of the operational amplifier (OA) as a design element is thorough but also clear and readable, with numerical examples used frequently to illustrate the points being made. Some fifteen basic types of circuits built round OA's are discussed in detail (such as followers, differentiator, integrator, log-converter, active filter, regulator *etc.*). The measurement and significance of the most important parameters of an OA are outlined in another chapter. A substantial section of the book is devoted to applications of OA's in the basic circuits combined to form complete instruments, *e.g.*, for measurement of temperature, potential, current, light intensity or absorbance, and in equipment for polarography and coulometry. This book can be strongly recommended both as interesting reading and as a working manual.

Encyclopedia of Electrochemistry of the Elements, Vol. IV: Allen J. Bard (Ed.). Dekker, New York, 1975. Pp. 488, $79.50.

As successive volumes of this series appear it becomes increasingly evident that it is likely to constitute the leading work of reference in the field of electrochemistry for many years to come. A firm editorial hand has ensured that all contributors work to the same format so that one quickly gets to know where to look for any specific piece of information. The group of authors in this volume is quite international (USA, UK, Poland, USSR) and the standard of the English is consistently high with the result that the reviewer could enjoy reading several chapters and comparing the chemistry of the elements dealt with. The elements in this volume are Au, F, Po, S, Sb, Se, Sn, Te and Tl.

Thermodynamics of Fluids: K. C. Chao and R. A. Greenkorn. Dekker, New York, 1975. Pp. xi + 553. $29.75.

The subtitle of this book "An Introduction to Equilibrium Theory" defines the scope of the treatment. The fundamentals of classical thermodynamics are summarized in the first chapter. This is followed by a development of the concepts of partition functions and the role of intermolecular forces. Chapter 3 deals with the thermodynamic properties of gases and gas mixtures and introduces the ideas of fugacity and energy functions. The text continues with the definition of ideal solutions and theory is then applied to real solutions. The book ends with a study of phase equilibria including chemical and vapor–liquid equilibria and adsorption. The book is written from the point of view of the process engineer and it includes at the end of each chapter useful lists of data, problems and references.

Aldehydes—Photometric Analysis, Vols. 1 and 2: Eugene Sawicki and Carole R. Sawicki. Academic Press, London, 1975. Pp. xxviii + 283 and xiv + 344. £10.50 and £10.80.

These are the first two volumes of an exhaustive treatise on the analysis of aldehydes written by the acknowledged experts in the field. Each aldehyde is discussed in a separate chapter unless the treatment can be applied to a similar group of compounds. Each chapter gives the physical properties of the aldehyde or group of aldehydes and outlines the spectral characteristics. Details of suitable methods of assay are then provided together with a list of the relevant references. Each volume has a separate author and subject index.

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PUBLICATIONS RECEIVED

Gas and Liquid Chromatography Abstracts Cumulative Indexes 1969–1973: Compiled and edited by C. E. H. KNAPMAN, Applied Science Publishers Ltd., Barking, 1976. Pp. 381. £16.00.

The dust-jacket of this book says that to obtain maximum benefit from the publication it is advisable to have the bound volumes of *Gas and Liquid Chromatography Abstracts*. The reader (unless an avid reader of telephone directories as a hobby) is more likely to think that the book is of very little use at all *unless* the abstracts themselves are readily available. Except for the umlaut and accents on French names, no notice is taken of diacritical marks in spelling authors' names, which seems somewhat impolite. The subject index is arranged in seven sections dealing with subjects such as apparatus and technique; sample type; applications and specialized separations. The sections are themselves subdivided into narrower categories, within which there is an alphabetical listing of the subjects of the abstracts. The index is therefore arranged in a way that involves a two-step process for finding a particular bit of information. It would have been helpful if the running headlines had given the section numbers and/or names instead of the uninformative "Author Index" or "Subject Index". One look at the page makes it obvious which is which!

Principles and Practice of Analytical Chemistry: F. W. FIFIELD and D. KEALEY, International Textbook Co., London, 1976. Pp. vi + 378. £4.50 limp, £8.50 cased.

According to the back cover, the purpose of this book is to provide the non-specialist with a broad understanding of the principles of modern analytical chemistry. To a large extent it succeeds in its aim, especially when it is dealing with instrumental methods, but there are some surprising omissions and oversimplified statements, which may prove misleading. For example, the statement "When the reduction potentials of two species differ by 0.1 V or more, the resulting redox reaction will proceed rapidly and stoichiometrically so that it may be used as the basis for a titrimetric procedure". Apart from the false logic caused by the English, there are at least two bits of wrong information in this statement, one of which is put right (by implication) on the following page. Older readers will deplore the use of the term "strong hydrochloric acid", and the slavish devotion to SI units when the use of "*M*" instead of "mol dm^{-3}" would have saved a great deal of type, paper and reading strain. On the whole, in spite of the numerous blemishes, the book is a useful survey of the subject, though much the stronger on the instrumental side. It must be stressed, however, that the class of reader for whom the book is intended will not usually be well enough informed to identify and correct the errors.

New Developments in Separation Methods: edited by ELI GRUSHKA, Dekker, New York, 1976. Pp. viii + 246. $23.50.

This is a selection of papers from Volumes 9 and 10 of *Separation Science*, covering some of the less widely known modern separation techniques and the newer applications of old ones. Topics covered include the logistics of separation, liquid membrane technique, clathrates, electrochemical methods, foam technique, and ultracentrifugation.

Chelates in Analytical Chemistry, Volume 5: edited by H. A. FLASCHKA and A. J. BARNARD, JR., Dekker, New York, 1976. Pp. xiii + 328. $36.50.

With its two articles, one on polyaminocarboxylic acids as colorimetric reagents, the other on *o*-dihydroxy compounds as reagents, this volume brings the series to a close. The present volume keeps up the standards set and will be useful to all who are interested in the applications of chelation in analysis.

Chemical Analysis, Second Edition: H. A. LAITINEN and W. E. HARRIS, McGraw-Hill, New York, 1975. Pp. xix + 611. £12.95.

This book, like its predecessor, should be prescribed reading for anyone aspiring to call himself an Analytical Chemist. Once again, the emphasis of the text is on the "processes occurring in sampling, separation and measurement, emphasizing the chemistry, rather than the physics, of analysis", because "knowledge of chemical reactions is important, first because it is needed for direct application to classical methods, and second because it is essential in instrumental methods where chemical reactions are involved in operations preceding the use of an instrument in the final measurement." The immediate overall impression of this new edition is that of greater maturity: the authors have been better able to stand back from the subject, enabling them to explain it better to the uninitiated. Despite new chapters on chemical standards, ion-selective electrodes, liquid–liquid extraction, separations, and two on chromatography, the total number of chapters, and (surely by coincidence!) the number of pages remain the same as in the first edition. To make room for the new material, the section on precipitations has been reduced from eight chapters to four, and the section on redox reactions has been shortened by omitting some of the less important applications. Some chapters, such as those on equilibrium and activity and sampling, remain essentially unchanged, but others, like those on complexation equilibria, reaction rates, and statistics, have been almost completely rewritten Usually, rewriting was necessary to allow incorporation of new ideas and material, but with the statistics chapter, the content is largely unchanged, but it is presented in a much more comprehensible style. As before, many important references to the original literature are included: in this edition, the literature is covered to the end of 1973. Undoubtedly, many previous devotees will find that their favourite topics have been omitted, and will wish to retain their copies of the first edition—but they should definitely give high priority to the acquisition of the second edition as a "companion volume". To those previously unacquainted with "Laitinen", this book is even more heartily recommended.

Inorganic Chemistry: R. B. HESLOP and K. JONES, Elsevier, Amsterdam, 1976. Pp. viii + 830. Dfl. 49.00, $17.95.

This is the successor to "Heslop and Robinson", so well known that it was hardly ever referred to by its title. Like its predecessor, this is a welcome blend of traditional "descriptive" inorganic chemistry with modern "theoretical" inorganic chemistry, clearly set out and easily understood. It also manages to instil a good deal of common sense appraisal into its treatment of current fashions and ideas, and utters appropriate warning notes where confusion may arise in the mind of the unwary. Thus at a time when the use of equivalents is decried on the grounds that the term equivalent is not unequivocal, it is pleasant to see a clear warning that the sacred animal the "mole" needs exactly the same kind of qualification as the equivalent does (specification of what the quantity refers to). However, most good things have a flaw somewhere, and here it takes a particularly unfortunate form, namely the use of "p" as an operator to mean $-\log X$ in one context, and $+\log X$ in another, especially as the latter use is accompanied by the statement that it is frequently used for the particular purpose. The use of SI units in the shape of "kmol m^{-3}" will stop most analysts dead in their tracks, and the amount of effort needed to translate SI units *into each other* (not to mention writing them out) is sufficient condemnation of the "prohibition" of well known, universally used, and readily understood units such as mole/litre (*M* for short). The use of pm for units in dealing with atomic radii also comes as rather a shock to the older reader. About a fifth of the problems are analytical in nature, although analysis itself seems to manage to escape mention. The index is comparatively poor.

Advances in Chromatography, Vol. 13: J. C. GIDDINGS, E. GRUSHKA, R. A. KELLER and J. CAZES (Eds.) Dekker, New York, 1975. Pp. 374. $28.50.

Two more editors have been added to give increased breadth to the subject matter of the series. Volume 13 is nevertheless, cast very much in the style of its predecessors. Some of the articles are very theoretical, but practicalities are discussed by Gouw and Jentoft (Supercritical fluid chromatography), Algelt and Gouw (Chromatography of heavy petroleum fractions) and Leathard (Qualitative analysis by GC). All of these are interesting and of sufficient generality to be read with pleasure and interest by the non-specialist.

Ultra-violet and Visible Spectroscopy, 3rd Edition: C. N. R. RAO, Butterworths, London, 1975. Pp. VII + 242. £4.90.

This new edition of a standard work is updated by the inclusion of photoelectron spectroscopy, circular dichroism and liquid crystals, and by a revision of all the chapters. A few references from 1972 are given but most are pre-1970. It remains a compact and useful companion and source book to those engaged with ultraviolet–visible spectroscopy.

Analisis por Activacion Neutronica: Teoria, practica y aplicaciores: A. TRAVESI, J. E. N., Madrid, 1975. Pp. XVIII + 717. Pesetas 1500.

It is a pleasure to handle again a book which is beautifully laid out, has clear illustrations and tables, has an attractive cover and may be placed open on the table or bench without either cracking or shutting. It comprehensively surveys activation analysis up to *ca.* 1970. The text starts with neutrons and nuclear reactions and concludes with a reveiw of industrial applications. In between lies all that is relevant to activation analysis and the basic tables of nuclear properties are included as appendices. It is certain to become a standard work.

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NOTICES

SHORT SUMMER COURSE IN X-RAY SPECTROMETRY

A two-week short course in modern X-ray spectrometry will be offered at the State University of New York at Albany from 7 to 18 June, 1976. The course will be instructional and will develop the basic theory and techniques starting from elementary principles. No previous knowledge or experience are required. The first week will cover basic principles and techniques and the second week will continue with further fundamentals and practical applications. Both weeks will illustrate and employ the wavelength-dispersive and energy-dispersive methods. Emphasis in the second week will be placed on advanced principles and techniques, absorption-enhancement corrections by several procedures including mathematical methods and computer automation of modern X-ray spectrometers. Equal time will be devoted to lectures and laboratory-problem solving sessions. Registration may be made for either week at a registration fee of $375.00 or for the entire two-week session at a registration fee of $700.00, payable in advance. For further information and to register please communicate with:

Professor Henry Chessin,
State University of New York at Albany,
Department of Physics,
1400 Washington Avenue,
Albany, New York 12222,
U.S.A.

SHORT SUMMER COURSE IN X-RAY POWDER DIFFRACTION

A two-week short course in modern X-ray powder diffraction will be offered at the State University of New York at Albany from 21 June to 2 July, 1976. The course will be tutorial in nature and will develop the basic principles and practical applications starting from elementary considerations. No previous knowledge or experience are required. The first week will cover principles and practice of instrumentation, specimen preparation, identification of powder patterns including complex phase identification, practical considerations on the use of the several indices with emphasis on computer retrieval and computer-assisted identification. The second week will cover qualitative identification of powder patterns in greater depth, computer-assisted search for correct powder identification, quantitative analysis of polycrystalline mixtures of two or more phases, automated powder diffractometers and other topics in depth. Equal time will be devoted to lectures, laboratories and problem-solving sessions. A suitable amount of time will be set aside for discussion of individual problems. The registration fee is $375.00 for either week, or $700.00 for the entire two-week session, payable in advance. For further information and to register please communicate with:

Professor Henry Chessin,
State University of New York at Albany,
Department of Physics,
1400 Washington Avenue,
Albany, New York 12222,
U.S.A.

TRACE ANALYSIS OF ENVIRONMENTAL MATERIALS
TARC INTERNATIONAL SYMPOSIUM III

The third of a continuing series of international conferences on analytical chemistry will be held from 4 to 6 August, 1976 at Dalhousie University, Halifax, Nova Scotia. The conference is co-sponsored by the Chemical Institute of Canada and the Trace Analysis Research Centre at Dalhousie University. Papers on all aspects of trace analysis of environmental samples will be presented. Information on the conference may be obtained by writing to:

Professor D. E. Ryan,
Trace Analysis Research Centre,
Dalhousie University,
Halifax, Nova Scotia, B3H 4J1, Canada

FOURIER TRANSFORM NMR SPECTROSCOPY

University of East Anglia: 13–17 September 1976

A Residential School of the Chemical Society's Education and Training Board

During the past five years advances in NMR have been particularly characterized by the utilization of Fourier transform methods. These have resulted in the merging of techniques associated with pulsed NMR and continuous wave NMR. Most chemical spectroscopists have been more familiar with the latter than with the former and there is, therefore, a need for a Residential School dealing with the relevant aspects of pulsed NMR and spin relaxation processes, leading to a full discussion of Fourier transform NMR techniques and applications. The subject matter will be taught at a level suitable for spectroscopists with a working knowledge of continuous wave ^{1}H NMR but with little or no previous knowledge of Fourier transform techniques or relaxation concepts. The aim is to provide a working knowledge of Fourier Transform NMR and its applications (for instance, in organic and inorganic structure determination, in biochemistry and polymer chemistry).

For full details and application form please contact:

Miss M. Virginia Auguste,
The Chemical Society,
Burlington House,
Piccadilly,
London W1V 0BN.

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January December

SUBJECT INDEX

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ERRATA

In the paper by P. R. Haddad, P. W. Alexander and L. E. Smythe, *Talanta*, 1975, **22**, 61, the following corrections should be made.

Page 62, 10 lines up from foot of page, for "10*M* sulphuric acid" read "10*N* sulphuric acid"

Page 66, line 12 of text, for "1.8*N* sulphuric acid" read "1.6*N* sulphuric acid"

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PUBLICATIONS RECEIVED

The Determination of Sulphur-containing Groups, Vol. 2: M. R. F. Ashworth, Academic Press, London, 1976. Pp. xi + 288. £9.80.

The subject of the second volume of this series is the analysis of compounds containing the —SH group. The large number of methods which have been described in the literature are collected together under general headings which identify the dominant feature of the method. Chapter 1 is concerned with the most important of the chemical methods, that is the oxidation of the thiol group and the chapter has some 54 subsections each dealing with a specific oxidant. Subsequent chapters describe other chemical methods such as the formation of mercaptides, addition to double bonds, reactions with acyl or alkyl halides and reduction. There are also chapters dealing with physical methods, such as polarography or chromatography. The style of the book is that of a critical review, experimental details being kept to a minimum in order to permit coverage of the very wide field. The readers are referred to the original literature for precise information and each separate chapter is provided with its own bibliography.

Detectors in Gas Chromatography: Jiři Ševčik, Elsevier, Amsterdam, 1976. Pp. 192. S23.25.

This book is the fourth volume in a series devoted to various aspects of chromatography, entitled the *Journal of Chromatography Library*. It is surprising that so much effort and ingenuity has been expended in the design and development of gas chromatography detector systems that it is now possible to devote a whole book to their description. Further, it is interesting to see that some detectors, which in their day had good performance and characteristics, have now become obsolete and do not merit even a mention in the text. The thrust and argument of this present work is that the behaviour of the detector is all-important in determining the ultimate efficiency of the gas chromatographic analyser. The detectors considered are those based on thermal conductivity, ionization, electron-capture and solution properties or reactions. The characteristics of each system are outlined and special attention is paid to the effects of detector geometry and experimental conditions on the ultimate performance. As a result this book will be of considerable value, not only to those involved directly in research, but also to those using gas chromatography as a routine analytical tool and to those analysts who may contemplate its use in the future.

Analytical application of Complex Equilibria: J. Inczédy, Ellis Horwood, Chichester, 1976. Pp. 415. £17.50.

Chemical systems used routinely by the analyst have always been complex, and with the spread of organic reagents, instrumental methods and trace analysis, they have become even more complicated. It is possible to find the optimum conditions for any reaction by purely empirical means, but intelligent use of equilibrium constants make the selection more rapid and certain. Ringbom showed how the concept of the conditional constant enables complex equilibria to be easily handled. His approach illuminates the workings of many analytical systems. This is illustrated by this book which first reviews methods for measuring equilibrium constants and then shows how Ringbom's methods can be applied to gravimetry, titrimetry, polarography, spectrophotometry, solvent extraction and ion-exchange separations. It is an eminently practical book with 82 worked examples, which show how calculations can be made for many important systems. There is also a useful collection of constants for common analytical reagents. It is not bedside reading, but it is strongly recommended as a laboratory manual and a teaching aid, on account of the breadth of examples selected and the clarity of the presentation.

Handbook of Analysis of Organic Solvents: V. Šedivec and J. Flek, Ellis Horwood, Chichester, 1976 Pp. 455. £18.00.

This is essentially a reference book of organic solvents containing an incredible amount of information. There are tables of the important physical constants, the boiling points of 1662 azeotropic mixtures, the densities and vapour pressures of many solvents, all in ascending order of magnitude. The common impurities for each solvent are noted and trade and trivial names given. Chemical tests for the solvents and some of the impurities are given. It is to be regretted that no account is taken of the common spectroscopic methods. The inclusion of spectra in discussion of the solvents and spectral data in the Tables would have improved the book. Nevertheless, it still remains a very valuable and convenient reference book for all users of organic solvents.

Aldehydes—Photometric Analysis, Vol. 3: Eugene Sawicki and Carole R. Sawicki, Academic Press, London, 1976. Pp. xiii + 341. £10.80.

This book is a further volume in the series which provides a comprehensive treatise on the analysis of aldehydes by optical methods. It is the first of five volumes which are to be devoted to the analysis of aldehyde precursors. These substances are first converted into the appropriate aldehyde before determination by methods which have been described in earlier volumes in the series. Each aldehyde is dealt with in a separate chapter and where it has more than one precursor these are described in order in the appropriate subsections. Very full experimental details are given and there is a very wide range of precursors covered, many of which are of biochemical or medical importance. Although the treatment is restricted to determinations by absorption or emission methods it is suggested that many of the isolations and conversions described could be followed by determinations using other physical techniques. There is a full list of references given at the end of each chapter and author and subject indexes are provided at the end of the book.

Nukleare Analysenverfahren: T. BRAUN and E. BUJDOSO (Eds.), Akadémiai Kiadó, Budapest, 1976. Pp. 269. £13.90.

This is a collection of 27 papers presented at a Conference in Dresden from 12 to 16 May, 1975 and concerned with analytical methods based on the properties of nuclei. The papers are written in French, German and English and are provided with summaries in English. They are collected together under three separate headings and form part of Volume 28 of the Journal of Radioanalytical Chemistry. The first section deals with methods based on heavy particle bombardment and has papers on Rutherford back-scattering, ion generators and X-ray emission. The second section contains eleven papers dealing with aspects of radiochemical assay including substoichiometry and automation. The final section comprises nine papers which deal with activation analysis, including both gamma-ray and charged-particle methods. It should be noted that the items in the contents list entitled "Bibliography Section" and "Index to Volume 28" do not appear in the book.

Biological Separations in Iodinated Density Gradient Media: D. RICKWOOD (Ed.), Information Retrieval Ltd., London, 1976. Pp. 205. £5.50.

This is a collection of research communications delivered at a colloquium recently held at the University of Glasgow (1975). It is therefore of direct interest to biologists currently using centrifugation technology. This collection of papers illustrates the wide range of biological problems which can be studied by employing ultracentrifugation techniques involving iodinated density gradient media, particularly the non-ionic compound given the trivial name "Metrizamide". For example, such gradients have been used to study nucleic acid–protein interactions, and to fractionate chromatin and other nucleoprotein complexes such as ribonucleoprotein particles and virus particles. Enzymes differing only in buoyant density, because some of them have been synthesised from deuterated amino-acid precursors, can be separated without loss of biological activity. The successful separation of cultured mammalian cells has been achieved, and the potential of such gradients for separating subcellular components is considered. This book also provides an ideal introduction for research workers who are interested in, but as yet unfamiliar with, the special qualities of iodinated density gradient media. For example the first article deals with the physicochemical properties of such media and discusses some of their advantages over the well-established media such as sucrose and caesium salt solutions.

Nitrogen Metabolism in Plants: LEONARD BEEVERS, Arnold, London, 1976. Pp. x + 333. £14.00 (Boards), £6.95 (Paper).

This book in the Contemporary Biology series, though not of direct concern to analytical chemists, does contain a great deal of chemistry and could give researchers who are stuck for a problem some new ideas on fruitful areas for investigation. The author has undoubtedly succeeded in bringing together a very wide range of material from scattered sources and welding it into readable and useful form.

Biochemical Fluorescence: Concepts, Vol. 2: RAYMOND F. CHEN and HAROLD EDELHOCH (Eds.), Dekker, New York, 1976. Pp. xv + 536. SFr. 133.00.

This is the second half of a book for biochemists on the principles and applications of fluorescence spectroscopy, with sixteen chapters on various applications, the first volume having contained seven chapters on the theoretical principles. The pages in this volume are numbered from 409 to 944, and the last 44 are the cumulative indexes for the two halves. This state of affairs is presumably due to the book's being reproduced from typescript, and one wonders whether the publishers would not have been better advised to have it printed in a single volume selling at the price of this half. The object of the book is to show that it is not enough merely to collect spectroscopic data, and that interpretation is necessary if the techniques are to be of real use. The contributors were asked to indicate future trends in application and seem to have been quite good at gazing into the future.