Foreword

THE importance of chemical analysis in all branches of pure and applied chemistry has always been fully recognized, and has resulted in constant efforts to meet their increasing demands. However new analytical methods are not found by chance or empirically: they are the fruits of experimental research based on the principles of analytical chemistry: they are oriented to them. These principles are related to all branches of chemistry. It was, and sometimes still is, a widespread belief that analytical chemistry owes its advancement exclusively to the progress made in other fields of chemistry. The pertinent literature shows us how far this is from the truth. Analytical papers frequently include statements and observations whose importance may exceed their analytical interest, and these have often become the starting point for further investigations in specific branches of chemistry.

The present high standard of chemical and physical analysis could never have been achieved without research which, in respect of originality, intensity and utility, ranks as high as any research work carried out in other fields of chemistry. Evidence of this is shown by the enormous number of analytical papers dealing with new discoveries, with critical examinations of, and improvements in, previously described methods and, last but not least, with applications of appropriate methods of testing materials in biological and other sciences. This unending flow of new contributions will certainly continue and increase in the future. Existing journals are not sufficient to ensure the rapid publication which is demanded both by authors and readers. It is therefore highly opportune that TALANTA, this new international journal of analytical chemistry in its broadest sense, is being introduced. The high standards and the tradition of analytical chemistry in education and research in the United Kingdom fully justify this enterprise.

The roll of eminent colleagues from many countries who have agreed to act on the editorial and advisory boards shows clearly the enthusiastic echo which is to be found all over the world when international scientific collaboration is the goal.

Fritz Feigl

Talanta, 1958, Vol 1, pp 3-29, Pergamon Press Ltd , London

A CRITICAL EVALUATION OF THE GRAVIMETRIC METHODS FOR THE DETERMINATION OF THE PLATINUM METALS

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(*Received* 21 *January* 1958)

Summary—This paper is a review of quantitative gravimetric methods of analysis for the six platinum metals and covers the literature up to June, 1957. An attempt has been made to evaluate critically and relatively all of the acceptable methods. Although the complicated problems of *en masse* isolation from native sources are not considered, some attention is given to interferences arising from limited separations.

An appreciable amount of information pertinent to the analytical chemistry of the platinum metals lies more or less concealed in the vast volume of chemical literature which has accumulated over a period of a century and a half. To uncover, integrate, and evaluate this material would be a heavy burden for those who have had no specific and prolonged contact with this area of analytical chemistry. Consequently, for many analysts, the choice of an analytical method for a platinum metal is of necessity often somewhat of a least-resistance procedure. Evidence for this appears constantly in current literature. It is with the hope that long and varied experience will assist in the evaluation of the analytical data that the author presents the following review.

No attempt will be made here effectively to deal with the broad problem of the *en-masse* isolation of platinum metals or of detailed separations within the groups. However, one cannot avoid altogether the question of separation. The six platinum metals show strong chemical relationships which introduce potential interferences into every known method of separating and of determining a platinum metal. In general there are two principal approaches to the separation of platinum metals from associated base metals; the dissolution by dry fusion: and selective extractions by wet methods. The former, at the present time, is by far the more satisfactory.

Treatment of ores and concentrates by wet methods has been the subject of many publications. None are supported by data which can be accepted as proof of efficiency.

It is the author's opinion that, deficient as the fire assay can be, it will direct with reasonable safety the commercial discovery of significant platinum metal values. The recent methods of separation by ion exchange will find increasing applications of scientific and industrial value It is not at all improbable that these applications will involve some replacement of fire assay procedures and of some existing methods of refining.

For each of platinum metals an attempt will be made to deal with all usefully pertinent literature recorded prior to June 1957. Chronological order of discovery will be recognised in the description of each method only when some practical purpose is served.

PLATINUM

The halogen–platinates

These methods are based on the slight solubility of the hexachloro- or hexabromoplatinates of ammonium, potassium, caesium, rubidium and univalent thallium[1] cations. Precipitation of platinum as the ammonium salt is a very old method for both commercial and analytical separation. Of the associated base metals few introduce interference; among the platinum metals there is some interference from iridium, rhodium, and palladium. The only serious objection to the method is the appreciable solubility of the salt although losses may be greatly reduced by the use of a small volume of excess ammonium chloride or the application of an alcohol medium for precipitation. Obviously, some of these techniques may increase the tendency toward co-precipitation. In any case, in the presence of associated platinum metals, re-precipitations are required. Schoeller[100] in his defence of the ammonium chloride reagent for platinum recorded a modified procedure to assist in the purification of the precipitate. The method, based on the assumption that the more serious contamination occurs in the later stages of the digestion, incorporates a two-stage precipitation. The first and major proportion of the chloroplatinate and iridate is separated and suspended in a boiling dilute solution of hydrochloric acid into which is conducted a stream of chlorine. Subsequently the platinum and iridium are again precipitated by ammonium chloride and ignited to metal. The minor proportions of the platinum and iridium are removed by ammonium chloride, the precipitate is converted to metal, leached with *aqua regia*, and together with the initial or major proportion of metals is alloyed with lead, treated with nitric etc. to isolate the iridium from which, by difference, the platinum content is obtained. Small losses of platinum are recovered by treatment of residual filtrates with zinc. Undoubtedly the method will yield acceptable results if the demands for accuracy are moderate, the samples to be analysed are large, and the analyst is efficient. Applied to amounts of platinum metals of the order of milligrams the method is not recommended. The author's various attempts to defend the procedure[98–100] deal only with the question of co-precipitation. There is the inference that under suitable conditions precipitation is complete and hence re-precipitation to remove impurities is the sole answer to the criticism of the method To the present author's knowledge Schoeller has provided no satisfactory data which permit an estimate of the accuracy of the method for either large or small samples. The statement[100] that "the final platinum results should, and generally do, agree within 0·001 gm" gives no satisfactory answer to the question of accuracy.

These criticisms are not intended to indicate that ammonium chloride, one of the oldest reagents, has ceased to be a useful tool in the industrial or even the analytical practice of the platinum metals. It is suggested that for the isolation of platinum from base metals or from other platinum metals, over the usual ranges of sample size, superior procedures are now available.

In addition to the precipitate formed with ammonium cation the hexahalogenplatinate anion forms precipitates with potassium, rubidium, caesium, univalent thallium, tetramethylphosphonium[3], and tetraphenylarsonium[15], and dimethylphenylbenzylammonium[93] cations. With the exception of the last two reagents the precipitates are useful largely for the determination of the respective cations.

Tetraphenylarsonium bromide was used by Bode[15] to produce, in the hot liquid, the orange-coloured precipitate $(C_6H_5)_4AsPtBr_6$. The mixture was cooled to room temperature, filtered, and washed with aqueous hydrobromic acid and a saturated solution of the precipitate, dried at 105–110°, and weighed. Complete removal of chloride ion from the sample was necessary but neutral solutions of the nitrate, required for dissolution of platinum, were not objectionable. The platinum metals and gold interfered; the effects of associated base metals were not discussed. For milligram amounts of platinum the same author recorded excellent recoveries However, Duval and co-workers[19] were unable to find evidence for a precipitate of constant composition although platinum could be removed quantitatively from solution. Until data are made available to corroborate Bode's contention the method cannot be recommended.

Dimethylphenylbenzylammonium chloride was used by Ryan[93] to produce the orange-coloured precipitate, $(C_{15}H_{18}N)_2PtBr_6$, which was dried at 110° and weighed. The results from platinic chloride solutions were low but by subsequent conversion to the bromide the author obtained excellent results on samples ranging from about 1–10 mg. Separation from most of the other platinum metals was necessary but the associated base metals such as Cu^{2+}, Fe^{3+}, Ni^{2+}, Cr^{3+} produced no interference; furthermore the presence of moderate amounts of lead was not detrimental. The reagent was readily prepared from dimethylaniline and benzyl chloride. This method has much in its favour and is worthy of further study.

Platinum sulphide

The platinum metals belong to the acid sulphide group and consequently sulphide ion is not selective. For quantitative purposes precipitation as sulphide is, in practice, applied extensively only to rhodium and platinum. For the latter metal it is one of the oldest recorded methods. It was used by Berzelius in 1826.[13] Over this long period little data have been given concerning the mechanism of the precipitation and to-day we have only an empirical approach to the problem of an accurate recovery of platinum sulphide. In 1896 Antony and Lucchesi[4] considered the precipitate obtained at 90° as pure PtS_2; at room temperature the mixed brown precipitate yielded H_2S on heating, and at 200° PtS_2 was produced. Some two decades earlier von Meyer[73] considered the precipitated sulphide as a loose compound of platinum disulphide and hydrogen sulphide. In 1950 Jackson and Beamish[61] provided some evidence for the latter hypothesis. These authors formed the sulphide by adding to hexachloroplatinic acid a saturated aqueous solution of hydrogen sulphide 0·1 molar in hydrochloric acid. The precipitate was washed consecutively with water, ethanol, pyridine, and ether, and was dried at 100°. The composition of the precipitate was $PtS_2 \cdot H_2S$; when heated in nitrogen between 150° and 250°, it evolved hydrogen sulphide. The thermogram of platinum sulphide published by Champ, Fauconnier and Duval[19] failed to indicate the above composition, although the procedure used to produce the sulphide was the usual "gassing procedure".

One may arrive at certain tentative opinions concerning the character of the precipitation by an examination of the polemical discussion provided by Feigl[31] and by Kolthoff[66] To account for the contamination of copper sulphide by zinc sulphide the latter rejected Feigl's suggestion that the mass law was inoperative and that the explanation lay in the production of co-ordinated compounds. Kolthoff provided evidence to support the view that solubility equilibrium was involved and that supersaturation of zinc sulphide was more or less slowly reduced, partly by the selective adsorption of hydrogen sulphide at the surface of the copper sulphide precipitate. The mechanism of this adsorption is not explained, but by analogy with Jackson's data[61] one may entertain the conception that these associations of hydrogen sulphide are not always simple adsorption phenomena.

Early literature contains a variety of procedures for the precipitation of platinum sulphide[43,55,113] some of which are characterised by unacceptable techniques and unnecessarily complicated procedures[37,60]. An interesting example of the homogeneous precipitation of the sulphide recorded some thirty years ago by Doht[26] involved the production of hydrogen sulphide by the addition to the hydrochloric acid solution of platinum of dihydrogen sodium phosphite and sulphurous acid. The reaction resulted in the formation of some sulphur.

The essential features of most of the early procedures are incorporated into three very similar standard methods.[43,55,113] It has been the author's experience that the application of each of these procedures to solutions of platinum which in their preparation were evaporated in the presence of sodium chloride yielded high results. As a result of a critical examination of these methods, Jackson and Beamish[61] reported that the positive error could be avoided by the addition of ammonium chloride to sodium chloride solutions of platinum prior to the evaporation required for the removal of nitric acid. Furthermore, it was found that the requirement of prolonged gassing with H_2S was unnecessary. Complete and easy recovery was effected by the addition of hydrochloric acid solutions saturated with hydrogen sulphide. Furthermore, contrary to some opinions, the positive error usually encountered was not due entirely to the retention of sulphur by the platinum; the contribution made toward this positive error by the presence of sodium chloride was probably the result of some type of co-precipitation by a complex platinum constituent, and its elimination by proper treatment with ammonium chloride was presumably a kind of replacement phenomenon. In any case the authors were able with their procedure to obtain acceptably accurate results.

A new approach to the sulphide precipitation of platinum metals, which must yet undergo further examination, was proposed by Taimni and Salaria.[108] The method for platinum appears simple and useful. The solution of platinum chloride is treated with sodium hydroxide and sodium sulphide to produce the soluble thiosalt. On the addition of acetic acid and ammonium acetate, a subsequent heating treatment, washing with water, alcohol and ether, and drying *in vacuo*, the precipitate of $PtS_2 \cdot 5H_2O$ could be weighed in a sintered-glass crucible. The experimental data indicated remarkable accuracy and precision.

Because this approach to sulphide precipitation has been extended by the author to include all of the platinum metals except osmium and because the data supplied in each case indicates a rather high degree of accuracy and precision it seemed desirable to evaluate experimentally the proposed procedures. Obviously an examination of this type is not a matter of a few experiments, involving as it does all of the platinum metals, and subjecting to question data indicating an efficiency beyond that obtained for most gravimetric reagents for the platinum metals. The results here recorded should be accepted only as an interim report and must not be construed as generally adverse criticism.

These various attempts to corroborate the results obtained by Taimni and

Salaria[108] resulted in difficulties with the simultaneous precipitation of sulphur which was only partially removed by the various solvents recommended in the original procedure. High blanks of poor precision were encountered and precipitates adhered tenaciously to the beaker wall. It is most unfortunate that the papers in question dealt perfunctorily and inadequately with the most important problem of the preparation of the reagents and with the probability of significant and variable blanks. However, subsequent to the appearance of the methods of analysis, the authors recorded an important contribution concerning the stability of the sulphide reagent and provided a detailed description of the method of preparation.[109] Attempts to apply this more recently recorded procedure to the determination of platinum have not encouraged confidence in this new method of sulphide precipitation. While the positive errors were of reduced magnitude, they remained significant and there was little indication of the high accuracy and precision reported by the authors. It can be hoped that those who have acquired experience with these sulphide procedures will not fail to report their findings.

Other, somewhat casual, attempts to precipitate platinum sulphide and at the same time avoid the disadvantages of gaseous hydrogen sulphide have been recorded. Thioformamide[35] was used in dilute sulphuric or a solution of sulphuric and hydrochloric acids. Hydrochloric acid alone introduced filtering difficulties. Thioacetic acid was recommended by Atterberg[5] for small amounts of platinum. Ray[88] discussed the reactions with thioacetamide. While this precipitant has become a widely used substitute for hydrogen sulphide, little application to the precipitation of platinum is recorded. One must not conclude that these organic thio salts are merely reagents for the homogeneous production of nascent hydrogen sulphide. The assumption that these reagents hydrolyse rapidly and quantitatively under precipitating conditions and can be substituted for H_2S without modification of procedure is invalid. Gagliardi and Pietsch[35] found that with palladium an intermediate compound was formed. Recent work on the mechanism of the reaction of thioacetamide with the acid sulphide metals[107] has indicated various instances of the formation of intermediate compounds. The data accumulated indicate that in certain cases the reactions involved in the use of thioacetamide are complicated by mechanisms which change with the acidity of the solution.

Platinum-organic sulphide precipitates

Literature dealing with the chemistry of organic sulphides contains many references to the use of platinum chloride for the purpose of isolating organic compounds. Thus Mazourevitch[72] applied this approach to the production of 1:2:4-triazoles. There seems little doubt that a careful examination of these publications would reveal a variety of satisfactory precipitating reagents for platinum. However, only the following three organic sulphide compounds have been recommended for the quantitative precipitation of platinum: phenylthiosemicarbazide, mercaptobenzylthiazole, and thiophenol. The reactions of platinum chloride with these and analogous organic compounds can be quite complicated. Indications of the complexities are recorded by Tschugaev and co-workers[114,115]. Furthermore the precipitates are rarely pure substances and only in the case of thiophenol is the dried precipitate used as a weighing form. These reagents are in general even less selective than is hydrogen sulphide.

Phenylthiosemicarbazide was used by Naito and co-workers[75,76]. An ethanol solution of the reagent precipitated a blue compound at pH 6–7 which was subsequently ignited to metal.

2-Mercaptobenzothiazole was proposed as a reagent by Ubaldini and Nebbia[116–118] for the precipitation of platinum, palladium and rhodium. The latter two metals in contrast to platinum could be precipitated in solutions of potassium hydroxide. Without considerable modification it is unlikely that this separation will find general use.

Beamish and co-workers were able to effect complete precipitation of platinum with a wide variety of organic sulphides but only one reagent proved suitable for quantitative purposes. In general there existed a marked tendency toward positive errors and these were not removed by the usual methods of reducing co-precipitation. Thiophenol[22] produced acceptable accuracy with 10–25-mg samples provided ignition was carefully controlled. However the reagent has an objectionable odour and is unstable, requiring storage in a nitrogen atmosphere. Thermograms for this platinum phenolate[19] suggested that at 230 to 300° the pure substance $Pt(C_6H_5S)_2$ was attained and thus could be used as a weighing form. The authors made no reference to the problem of removing excess reagent Presumably no effort was made to accomplish this with solvents. The present author was unable to find a suitable washing medium; but it would appear that the recommended temperature range assured volatilisation of the excess reagent prescribed by the original recipe. In any case very acceptable results can be obtained.

Other organic platinum precipitants

It has been recorded that dimethylglyoxime may be used for the quantitative determination of platinum. This erroneous opinion may have found its origin initially in a publication by Cooper[21] who described the platinum-dimethylglyoxime precipitate and stated that it could be collected and dried in a Gooch crucible for weighing as $Pt{\cdot}C_8H_{11}N_4O_4$. However, no data were given to prove its elementary composition or to indicate the completeness of precipitation. Later work[112] has shown the precipitation to be significantly incomplete. In any case the precipitated dimethylglyoxime complex is not amenable to either direct weighing or to ignition. The latter process is usually accompanied by rather violent explosions.

α-Furildioxime was used by Ogburn[77] to isolate platinum as part of a scheme of semi-quantitative separations of the platinum metals. The complex was ignited to the metal weighing form. Duval and associates[19] recorded a thermogram for the precipitate and reported that while recovery of platinum was complete there was no evidence of an organic weighing form. Presumably Ogburn was not unaware of the impurity of the precipitate since ignition was used, and in the light of the fact that no quantitative superiority was claimed the method merely retains its classification as a means of separation.

Precipitation of platinum as metal

The most commonly used reagents for the reduction to the platinum metal weighing form are formic acid, zinc and magnesium. Of these reagents formic acid is the most widely accepted. It is recommended by chemists who have had wide experience in the analytical chemistry of the platinum metals and procedures for its use are included in most of the text books of good repute. The present author's experience with it on the macro scale has been reasonably satisfactory but for milligram amounts of platinum the reagent is not recommended. It is only fair to record that here there exists a difference of opinion among those with experience in this work Blackmore *et al.*[14] reported that "the average recovery of 10-mg samples was good, but the poor precision indicates a compensation of errors. Both the precision and the accuracy of the recovery of 5-mg samples were poor. Furthermore, without any discernible cause, significant amounts of platinum sometimes appeared in the filtrate. Washing the precipitate with a dilute solution of an electrolyte instead of water did not prevent the occurrence of this phenomenon." It was noted that while strict adherence to recommended procedures usually resulted in clear supernatant liquids occasional samples did not coagulate well; furthermore precipitates which presumably were well coagulated sometimes gave evidence of dispersion upon washing. It was concluded "that the precision obtained by formic acid precipitations is not sufficient to justify its use in gravimetric determinations of small amounts of platinum". Furthermore, it should be stated that precipitations of platinum by formic acid are particularly subject to contamination by metals such as copper, etc.

Precipitation of platinum by zinc is not usually recommended for gravimetric purposes. Frequently separations from base metals have thus been accomplished but attempts by the author to use these procedures for the separation and the determination of platinum resulted in errors as large as ten per cent Blackmore *et al*[14] attempted to ascertain the cause of this error and were able to suggest a procedure capable of producing good accuracy for 10-milligram samples Of some practical significance was the finding that when platinum is precipitated by zinc in the presence of copper, contamination of the precipitate by copper prevented leaching the precipitate with acid solutions. This process, previously recommended by various authors, presumably results in electrolytic dissolution of platinum through action on a platinum–copper couple. In any case considerable platinum was found in the leach liquid Thus, in preference to leaching, Blackmore reduced the zinc content of the precipitate by roasting in hydrogen to encourage volatilisation. With excessive contamination there resulted a permanent resistance to volatilisation apparently because of the incorporation of zinc with platinum to form alloys In the application of zinc for analytical purposes there must be recognition of two factors, excess of mechanically mixed zinc in the final precipitate may result in high values irrespective of the process of purification, and the absence of zinc in the acid solution upon the completion of the precipitation can result in re-dissolution of platinum particularly if heating is continued. Since analytical recovery is only feasible when the final liquid is acid there results serious limitations to the application of the method. However, when there is knowledge of the approximate platinum content the method recommended by Blackmore is capable of yielding very satisfactory accuracy.

To the best of the author's knowledge there are no proved data on the application of magnesium as a reducing reagent Leidé and Quennessen[68], and others, used both magnesium and aluminium for reducing various platinum metals. It is accepted that with magnesium the degree of contamination of the platinum is less than that experienced with zinc. Since methods of determining platinum are not numerous and since none of those recommended is free of faults it would seem that a detailed examination of the magnesium reduction method would be of value.

As one would expect there exist a considerable number of reagents capable of producing platinum metal as a precipitate. Some of these are aluminium, mercury, titanium^{III} chloride, tellurium, hydrogen, etc. The last is used widely for the recovery of platinum from residues obtained in the determination of potassium, etc

In connection with the ignition of platinum precipitates the chemist should not ignore a phenomenon which becomes more apparent with the higher temperatures. Ignition under these conditions in the presence of oxygen will result in a loss of weight, the explanation for which has not been recorded. One would like to think of the formation of volatile oxides comparable to those formed with osmium and ruthenium. The thermodynamic data for the known oxides discourage this hypothesis. Evidence for the existence of a slight gain in weight of an ignited platinum residue has been recorded by Duval[19,28]. The explanation that there was developed from 538° to 607° a layer of PtO is not acceptable without confirming data. Recent researches on the chemisorption of oxygen on platinum between 0° and 800° suggest the formation of a non-stoichiometric oxide. There is here a problem in research which would prove of scientific interest and of practical value.

PALLADIUM

Of the six platinum metals the methods for the determination of palladium, both classical and instrumental, are relatively numerous. The deficiency of precipitating reagents for the remaining four metals is due in part to their tendency toward tervalency and to the facility with which they form a variety of complex dissolved constituents. Furthermore the ease with which one may find precipitating reagents seems to be a strong motivating force with the analytical researcher. This suggestion is supported by the preponderance of methods for the determinations of other bivalent cations such as copper, zinc and cadmium. To choose from the voluminous literature the most suitable reagent for these metals is a frustrating experience. In some instances, where the question of superiority is not ignored entirely, the claims are trivial, inadmissible, inapplicable or exaggerated While specific knowledge of the large number of reagents is potentially useful for the study of mechanisms and theories of precipitation, there is little justification for multiplicity of analytical procedures. In the case of palladium there exists a variety of efficient precipitating reagents. To compare the efficiency, or to evaluate critically, all of the existing procedures would serve little purpose. However, the effort will be made for those methods which are clearly advantageous and a reference will be made to all reagents recorded in the literature, of which there are some two dozen.

Oxime precipitants

Undoubtedly the most important type of precipitating reagent for palladium contains the oxime group. The application of dimethylglyoxime to quantitative analysis was first recorded by Duparc[27] and by Wunder and Thuringer[126–128] who found that the reagent quantitatively precipitated palladium and nickel; the former from acid media and the latter in alkaline media. The precipitation was carried out in the cold and the reagent was dissolved in dilute hydrochloric acid. The palladium complex was ignited to metal. In one paper[127] the authors recorded procedures for the consecutive precipitation of gold and palladium by first heating the solution in the presence of excess reagents to precipitate gold and subsequently treating the filtrate to remove palladium. Mixtures of palladium and platinum were separated by isolation of the latter with ammonium chloride. Reference was also made to the separation of rhodium and of iridium from palladium. Some of these methods of separation could not have been quantitative. The authors also dealt with the separation of palladium from iron and copper.[127] A few years later Gutbier and co-workers, continuing their interest in the determination of palladium, used dimethylglyoxime to separate palladium and tin.[47] Davis[25] thus separated palladium and platinum with no contamination by the latter. Gol'Braikh[44] used dimethylglyoxime to determine small amounts of palladium in the presence of large amounts of nickel.

Later, Zschiegner[131] used sodium nitrite to separate gold, silver and base metals from palladium. The latter was precipitated by dimethylglyoxime and the complex weighed directly. Holzer[58] however was unable to recommend the direct weighing of the complex since the complete removal of excess reagent resulted in some loss of precipitate. While the use of large excesses of reagent undoubtedly will introduce errors the amount of reagent can be so regulated that direct weighing of the precipitate is possible and procedures toward this end are recorded in modern textbooks;[55] indeed, the metal is seldom used as a weighing form. The safe heating range for the dimethylglyoxime complex was recorded as 45–171° by Champ, Fauconnier and Duval,[18] and as 100–200° by Tashiro.[110] The efficiency of this gravimetric method for determination and separation from other platinum metals was discussed by Ayres and Berg[6]. They found solubility losses insignificant except where small amounts of palladium were to be determined. Separations from platinum, rhodium and iridium were effective except in the presence of large proportions of palladium.

Concerning the question of contamination of the palladium precipitate it has been the author's experience that the character of the prior treatment of the platinum metals will, to a degree, determine the degree of co-precipitation. Undoubtedly dissolution processes in hot sulphuric acid encourage the simultaneous precipitation and perhaps the co-precipitation of the platinum-dimethylglyoxime complex.[9] Boiling hydrochloric solutions of the mixed palladium and platinum salts will encourage co-precipitation of the blue-bronze anisotropic platinum-dimethylglyoxime complex. Serious cases of contamination are usually revealed by a green tint of the yellow palladium complex.[112] A rather peculiar interference with the precipitation of the palladium-dimethylglyoxime complex is encountered in filtrates resulting from removal of associated gold by hydroquinone.[11] In this medium a certain threshold value of palladium concentration is required before palladium can be precipitated. The problem of the dissolution of impure dimethylglyoxime precipitate is not a simple one. The usual process of dissolving the precipitate in *aqua regia* and re-precipitating is not acceptable. Gilchrist[42] has shown that the process results in small but significant losses which can be recovered from the filtrate by fuming with sulphuric acid. However, fuming with sulphuric acid may result in the appearance of palladium oxides resistant even to *aqua regia*. On the other hand ignition processes frequently involve losses by volatilisation of the metal-dimethylglyoxime complex or one of its ignition products. Most assuredly it is desirable to ensure purification of the initial dimethylglyoxime precipitate and where this is not feasible one should arrange the prior treatments to avoid intensive contamination. The author's experience is in agreement with Ayres' findings[6] concerning the solubility losses. With gram amounts of palladium the losses need not be significant even though the presence of palladium in the filtrate can be detected. With small amounts of the metal there is the mechanical difficulty of collecting the finely divided precipitate, which process is of course encouraged by a comparable reduction in volume of liquid. The fact that the palladium can be practically completely converted to the dimethylglyoxime complex is attested by its application, through solvent extraction, to sub-micro determinations.

Although ignition of the palladium complex to metal is not now generally used for gravimetric purposes, there are some who prefer the method, among whom the author is included. The difficulty associated with the danger of volatilisation can be avoided by initial heating with a bunsen burner, which permits a greater manual control than muffle ignition A procedure used with success by the author[11] involves wrapping the complex and filter paper in a second wet paper and igniting, without preliminary slow drying, in the full heat of a Meker burner. It may be that by this process the complex is dissociated before there is an opportunity for volatilisation.

In any case precipitation of palladium by dimethylglyoxime is unreservedly recommended Arising out of its successful application many attempts have been recorded to effect some kind of improvement by the use of other oximes. Those recorded in the literature are benzoylmethylglyoxime, oxalenediamidoxime, salicylaldoxime, α-benzoinoxime, β-furfuraldoxime, α-furildioxime, 1 : 2-*cyclo*hexanedionedioxime, and others of unsuccessful application.

Benzoylmethylglyoxime was proposed by Hanus, Julek and Lukas[51] and later by Holzer.[58] The former recommended precipitation from a boiling hydrochloric acid solution with a 40% excess of reagent, and standing for 12 hours. The precipitate was dried at 105° and weighed. Interference from Pt, Ir, Rh, Os, or Au was eliminated by the addition of hydrochloric acid before adding the reagent. In the case of gold, at least, this statement is not acceptable Holzer[58] preferred this glyoxime or salicylaldoxime for the determination of palladium because, unlike dimethylglyoxime, the purified precipitates could be weighed directly. This favourable comparison is now inadmissible. Holzer also recorded excellent data to indicate the application of salicylaldoxime to the precipitation of palladium and its separation from platinum. However, all three reagents produced insoluble precipitates with gold The first departure from the inner-complex type of precipitate was recorded by Hayes and Chandlee[52,53] who used β-furfuraldoxime as a reagent to precipitate at room temperature the yellow addition compound $Pd(C_4H_3O{\cdot}CH{:}NOH)_2Cl_2$. The excess precipitant, which is water soluble, was readily removed and the precipitate was dried at 110°. Gold interfered, but the remaining platinum metals did not; nor was there interference from a large number of cations including iron, cobalt, and nickel. Determinations could be made in the presence of nitrate or sulphate ions. The usual claims of superiority over the dimethylglyoxime method are made, namely, a greater water solubility of reagent, a more favourable gravimetric factor, and a precipitate of improved physical characteristics.

Similar claims are made for 1·2-*cyclo*hexanedione dioxime,[120] (nioxime) a water soluble precipitant which could be added in as much as 150% excess with no effect upon the accuracy of the determination. Quantitative precipitation was accomplished in the range pH 0·7–5 from a hot solution and the complex $Pd(C_6H_9O_2N_2)_2$ was dried at 110°. The authors' claim for an efficiency of separation from platinum greater than that with dimethylglyoxime cannot be accepted since the method used for the latter reagent involved heating at 60°, a process which encourages contamination from platinum. The data dealing with interfering cations were by no means complete. Of the remaining platinum metals only ruthenium is included. Like dimethylglyoxime, nioxime produces a gold complex which is readily decomposed to gold

α-Furildioxime was used by Reed and Banks[89] for the determination of palladium. Again there is the claim of greater sensitivity, and the purified precipitate could be used as a weighing form or converted to metal. The degree of specificity is comparable to the other oximes. The application of the reagent to nickel was not recommended.

α-Benzoinoxime has been used as a reagent in weakly acid solution of palladium;[87] and oxalenediamidoxime[23] is said to precipitate palladium from solutions of ammonia and ammonium chloride. Duval *et al.*[28] determined the heat stability ranges of the palladium complexes with dimethylglyoxime, methylbenzoylglyoxime, salicylaldoxime, β-furfuraldoxime and *cyclo*hexanedionedioxime. These authors' reference to palladium dimethylglyoxime as a "new" weighing form is inaccurate.

Undoubtedly an attempt by the analyst, inexperienced in the field of platinum metals, to select the most efficient oxime reagent for palladium must be an unrewarding experience The multiplicity of claims for superiority, the lack, in almost every instance, of data concerned with dissolution processes required in practice, the absence of properly determined degrees of interferences, make the task an impossible one. In the present author's opinion, based on a great amount of laboratory practice in this field, there is little to choose between the methods. Dimethylglyoxime remains the preferred reagent for most purposes; it is readily available, inexpensive, sufficiently sensitive and selective, and the precipitate can be handled with ease. Concerning the question of its solubility in water, little difficulty is experienced in purifying the palladium dimethylglyoxime complex. Where water solubility really does become an important consideration the author has found no difficulty with the sodium salt, a reagent which seems to be peculiarly neglected for the precipitation of palladium.

The reactions of the oximes with gold, a frequent associate of palladium, present interesting phenomena concerning which, little data have been recorded. With dimethylglyoxime a mixed precipitate of thin plates may appear in a carefully prepared experiment Under the microscope these can be seen to decompose spontaneously to form mechanically mixed gold. The composition, chemistry and crystallography of these precipitates remain unknown and although literature relating the action of gold with other oximes is not informative there is sufficient to suggest that most of the oximes show an analogous behaviour. Somewhat comparable statements can be made concerning the relationship of platinum and the oximes although in this case there are more data available

Other organic reagents

α-Nitroso-β-naphthol as a quantitative precipitating reagent was first recorded by Schmidt.[97] Slightly acidified solutions of palladium were used and although a formula was given for the precipitate, ignition to metal was recommended. Separations from rhodium and platinum were successful Wunder and Thuringer[127] applied the method for the separation of palladium from copper and iron. Solutions containing no more than 50 mg of palladium were acidified with hydrochloric and acetic acids, and precipitation was carried out from the hot solution. Duval[28] reported the α-nitroso-β-naphthol palladium complex stable up to 245° and found it "well suited for the determination of palladium". An incident of some salutary value involved the claim that α-nitro-β-naphthol precipitated palladium quantitatively.[70] This method had obtained some degree of acceptance before the author concerned discovered and reported[71] that the precipitating constituent was due to an admixture of nitroso-compound present as an impurity. Subsequently and inexplicably, α-nitro-β-naphthol was reported by Duval[28] to produce "yellow needles of the formula $Pd(NO_2C_{10}H_6O)$" which "should be dried below 92°". There is added the statement that in many respects "the α-nitro-β-naphthol method is greatly inferior to the oxime methods". One may assume that the author was unaware of the existence of Mahr's refutation[71] and that the nitro-naphthol used contained the nitroso impurity. The statement of composition, and the distinction between the pyrolysis curves for the two reagents, remain unexplained. The conclusions recorded by Wunder and Thuringer in 1913 that α-nitroso-β-naphthol possesses no advantages over dimethylglyoxime remain true.

During the past three decades additional organic reagents for the gravimetric precipitation of palladium compounds have been recorded. Following an examination of the possible application of quinoline derivatives, the most promising of these, 6-nitroquinoline was recommended by Ogburn and Reismeyer[80] for the direct determination of palladium. Surprisingly the authors offered no data to substantiate this claim; indeed the analytical method proposed involved ignition of the complex to metal. The claim for separation from other platinum metals was also not satisfactorily substantiated. 5-Methyl-8-hydroxyquinoline was used by Sa[95] to precipitate the orange compound $(C_{10}H_8NO)_2Pd.1/2H_2O$ from a hot solution containing excess acetate ion. The complex was purified and dried at 105°. Although no data concerning the relative efficiencies of the methods were available it is unlikely that superiority with respect to specificity and accuracy will be indicated.

The gravimetric application of 1:10-phenanthroline was described by Ryan and Fainer.[94] The complex $C_{12}H_8N_2PdCl_2$ could be precipitated quantitatively from 1 to 20% hydrochloric acid solutions, purified and weighed directly, or ignited to metal. Although no insoluble compounds were formed with Ni, Ir^{3+}, Ir^{4+}, Ru^{3+}, Rh^{3+}, Pt^{4+}, the results for palladium precipitated in the presence of these cations were significantly high. In a later publication[92] a procedure was described for the separation of palladium from platinum and for the determination of milligram amounts of palladium. Duval[28] regarded 1:10-phenanthroline with favour. The thermolysis curve revealed stability at the high temperature of 389°. However, the reagent is expensive, and "the formula of the precipitate changes according to the anion associated with the palladium before precipitation".

The hydrazide of *m*-nitrobenzoic acid will precipitate a yellow palladium complex quantitatively from nitric, hydrochloric and sulphuric acid solutions.[119] Ignition to the metal is required and of a large number of associated metals only gold interferes. The authors included a procedure for the isolation of palladium.

p-Aminoacetophenone in aqueous media was used by Schontal[101] to precipitate yellow $(NH_2{\cdot}C_6{\cdot}H_4{\cdot}CO{\cdot}CH_3)_2PdCl_2$ which could be dried at 80° and weighed directly, or ignited to metal. The data recorded to indicate successful separations from a large number of cations was not indicative of high accuracy but since gold and additional platinum metals were included the method is worthy of further attention. Hovre[59] altered the procedure and applied it to the determination of palladium in jeweller's alloys in which case the palladium compound is ignited to metal.

Datta[24] used *p*-aminosalicylic acid in ethanol solution to precipitate palladium within the pH range 3·7–4·2.

The interesting precipitation of palladium by piaselenol was described by Ziegler and Glemser.[130] The organic weighing form $(C_6H_4N_2Se)_2PdCl_2$ was precipitated in slightly acid solution, purified and dried at 110°. Nickel, cobalt and platinum^{IV} did not interfere.

p-Thiocyanoaniline[84] was used to precipitate $PdCl_2{\cdot}2RNH_2$ from solutions whose pH was greater than 0·25. The complex was stable and could be dried at 130–140°.

Palladium may also be precipitated as *bis*ethylenediaminepalladium tetraiodomercurate[11] $[Pd(en)_2HgI_4]$, which is readily filtered and dried at 115°.[121] There are numerous interferences and the complexities involved in the preparation for precipitation do not encourage the effort to develop a practical procedure.

Wilson and Wilson[129] have proposed 1:2:3-benzotriazole as a precipitant superior to dimethylglyoxime for palladium. The white precipitate of $Pd[C_6H_4NHN_2]_2Cl_2$, deposited from acetate buffered solutions, could be dried safely at 110° to 150°. "Versene" (ethylenediaminetetra-acetic acid) was required to avoid excessive interference Gold and bivalent platinum interfered and the authors regarded the method as primarily useful for precipitating palladium from solutions containing only traces of other platinum metals.

N-Phenyl-*n*-phenylazohydroxylamine as a gravimetric reagent for palladium was recommended with enthusiasm by Sogani and Bhattacharya [104,105] Unfortunately the presentation reveals a significant lack of appreciation of the complexities of the chemistry of the platinum metals and consequently one must view the claims of superiority with some reservation. These authors' reference to the action of organic complexes resulting in the reduction to metallic osmium can hardly be accepted Furthermore, the modified procedure used to separate the palladium complex from associated platinum is subject to the usual difficulties incident to fuming these two metals with sulphuric acid. The interference of copper, which is a frequent associate of the platinum metals is also a serious deficiency. The necessity of adjusting the acidity to pH 2–2·5 in order to increase the specificity is a limiting factor compared to dimethylglyoxime. In any case, the data and procedure as they are presented will not allow a favourable comparison with the dimethylglyoxime or indeed with various other organic precipitants Nevertheless the method is well worthy of attention. The yellow brown compound $[C_{12}H_{10}N_3O]_2\,Pd$ precipitated at pH 1·6–8 has good physical characteristics; it can be used as a weighing form and it has a suitable weight factor The fact that by additional boiling one can eliminate excess of reagent is advantageous The new character of the reagent, and its ease of preparation may indicate improved reagents for cations in general.

Most of the twelve non-oxime organic reagents discussed above are said to possess some superiority over the dimethylglyoxime reagent. It is significant that this precipitant seems to be about the only target. In the present author's opinion it has, in general, withstood all competition from all other organic reagents. One cannot doubt that in a few specific instances of practical analysis certain other reagents will offer some slight advantage and this has been recognised on occasion by the present author.

Inorganic precipitants

The precipitation of palladium as the iodide is applicable principally to relatively pure solutions. The large number of insoluble iodides and the fact that excess of iodide is reported to result in dissolution of the precipitate has discouraged any wide application. On the other hand the precipitate has desirable physical characteristics, and under suitable conditions excellent precision and accuracy are obtained. Scott[102] and Bugbee[16] stated that excess potassium iodide must be avoided and it has been accepted practice to avoid boiling the solution during precipitation. More recently[8] the efficiency of the palladium iodide method has been examined and it was concluded that the aqueous acid medium, up to about 0·8*N*, can be safely boiled during the precipitation process. Furthermore, at least ten times the calculated amount of potassium iodide can be used without loss of palladium. Duval[28] recorded the safe heating range for palladium iodide as 84° to 365°.

The precipitation of palladium by hydrogen sulphide, while complete, is not an acceptable gravimetric procedure. As a weighing form the precipitate is unsuitable and ignition to the oxide or metal is impracticable. Gagliardi and Pietsch[34] recommended thioformamide as a precipitant in hot solutions and claimed that the sulphide was easily filtered and washed. A method of precipitating the weighing form PdS_2H_2O was described by Taimni and Salaria.[108] The procedure involved neutralisation with ammonium hydroxide, addition of excess of ammonium or sodium sulphide, and of large excesses of acetic acid and ammonium acetate; boiling, and washing the precipitate successively with water, ethanol and ether, and drying in a vacuum desiccator. These authors' claim to superiority over the dimethylglyoxime method is not admissible and this sulphide method will probably find very limited applications.

The use of cyanide ion to precipitate white palladium cyanide was described by Rose.[91] According to Duval *et al.*[28] the "white precipitate has no stability whatever" and "it is impossible to weigh the anhydrous cyanide". The method has no advantages and is not recommended.

Precipitations of palladium and other platinum metals as hydrated oxides have been much used. Most of the earlier procedures would of necessity fail to produce a pure precipitate. A successful method for the quantitative precipitation of hydrated palladium^{IV} oxide was perfected by Gilchrist[42] who oxidised by potassium bromate, and neutralised by a special technique to pH 6. The method was recommended as an integral part of a separation of rhodium, iridium and palladium from platinum but the precipitate was not used as a weighing form.

Reducing reagents

The most generally useful reagents for the precipitation of metallic palladium are hydrazine, acetylene, and ethylene. These methods were frequently applied before the discovery of dimethylglyoxime. Thus at the beginning of the twentieth century Jannasch and co-workers[62,63] used hydrazine sulphate or hydrochloride in a hot acidified solution and subsequently ignited the mixed oxides and metal in air and then hydrogen. The efficiency of the hydrazine salt for separating palladium from a variety of cations was also discussed. With mixtures of palladium and copper there was contamination by the latter metal due to the "catalytic action of the precipitated palladium producing hydrogen in the active form of palladium hydride". Similarly, there was interference from platinum, gold, silver, lead, etc. Later work by Paal and Amberger[81] indicated that hydrazine in either acid or alkaline media produced metallic palladium and not a mixture with oxides. These conclusions were supported by Gutbier and Falco.[46] Recently, Burriel and Pérez[17,83] stated that in acid media hydrazine sulphate will not reduce palladium completely although this can be accomplished in the presence of selenium or tellurium.

Acetylene has been recommended as a general replacement for hydrogen sulphide. It was used for the precipitation of palladium and recommended in preference to hydrazine for separations in the presence of copper, platinum, iridium, and rhodium. Either acetylene gas or an aqueous solution of it could be used as the precipitant in an acid medium. The brown precipitate was not a pure substance and ignition to metal was necessary for quantitative determinations [29,30] Separations from osmium were not possible; indeed in the presence of palladium, both metals could be completely precipitated within a short time In acid media gold was precipitated by acetylene, but not in an alkaline medium [69]

To avoid the contaminations incident to the use of acetylene, Ogburn and Brastow[78] preferred ethylene. With this reagent there was no appreciable interference from associated metals, the precipitate was easily filtered, and it could be dried at 105° and weighed. Duval[28] stated that this palladium precipitate was stable up to 384°, with oxidation being initiated at about 410°, forming PdO between 788–830° Ethylene applied to mixtures of the six platinum metals resulted in a positive error in the recovery of the palladium of 0·75%.

A procedure for the precipitation of metallic palladium by formic acid was recorded by Treadwell and Hall.[113] To avoid dissolution of the precipitated palladium the medium was treated with sodium carbonate. The precipitate was ignited at the full heat of the burner but no subsequent reduction was included in the method.

Various other reductants have been used for the determination of palladium. Reagents such as alcohol in alkaline media,[56] carbon monoxide, zinc, etc., present obvious difficulties and few advantages.

It will be evident that there is a superabundance of palladium reagents. The most generally useful reagents are to be found in the organic group; of the latter the present author finds dimethylglyoxime or, if necessary, the sodium salt, sufficiently applicable for gravimetric purposes. These purposes include applications to wide areas of research and assay practice. The novice in this field will wisely refrain from an uncritical appraisal of enthusiastic claims for superiority The chemistry of platinum metals solutions is of the utmost complexity and researchers in this field would do well to present impassively the data as they find them.

RHODIUM

Rhodium is one of the very minor constituents of platinum metal ores. Its analytical isolation has long been a most difficult process. Although the metal resists attack by the usual acid and oxidising mixtures it is dissolved under suitable conditions by sulphuric acid and certain acid sulphate salts. It is this property which was applied until very recently for the quantitative isolation of rhodium by a procedure which was laborious and could only yield inaccurate results. It is unfortunate that this single aqueous dissolving medium should introduce an interference with most of the methods for rhodium determination. This interference is frequently accentuated when the sulphate solutions have been subjected to fuming, a process which is sometimes required for the removal of the associated elements ruthenium and osmium. These facts should be recognised by those researchers who seek to find new reagents for the quantitative determination of the platinum metals.

At the present time analytical methods for the determination of rhodium are few in number. No gravimetric reagent is specific in the practical sense. In general, these reagents find application to the *en masse* isolation of various groups of associated metals and are used for quantitative determination only with solutions of rhodium free of metal cations.

However, limited separations of rhodium may be accomplished by a variety of procedures Certain base metals may be isolated from rhodium by hydrolysis in the presence of nitrite,[56] a method which may become increasingly difficult as the amounts of rhodium approach the microgram level Hydrolysis to the oxide will also separate platinum when the latter exists in the quadrivalent form [41] Gold may be eliminated by a variety of reducing reagents[10] and dimethylglyoxime effectively separates palladium.[56] Ruthenium and osmium are usually separated by distillation. Combinations of iridium and rhodium present the greatest challenge. Selective extraction by treatment with various acids, acid salts and oxidising mixtures has, until recently, been the only quantitative method available This process forms part of long established assay procedures. In some instances its application is futile, in others laborious and inaccurate; in general, particularly when small amounts are concerned or when good accuracy is required, the process of selective extraction by corrosive reagents should be abandoned. Recently, accurate separation of microgram amounts of rhodium and iridium have been effected by selective reduction[56,124] but the reaction products introduce additional difficulty to the subsequent determination of iridium, a problem which, in itself, is sufficiently onerous. Fortunately, there are now available the processes of separation by chromatography[64] and by ion exchange[12,20,106]. These methods offer the greatest hope for those who must determine accurately the proportions of rhodium and iridium in such complex materials as ores and concentrates.

The reagents used for the quantitative precipitation of rhodium are hydrogen sulphide, thiobarbituric acid, 2-mercaptobenzoxazole, sodium hydrogen carbonate, metal reducing reagents, reducing reagents such as hydrazine sulphate, formic acid and titanium^{III} chloride.

Reductions by zinc or magnesium formed a part of many of the earlier procedures for the analytical treatment of assay beads or buttons. Brief procedures for the application of these metal reductants to solutions of rhodium are described by Scott.[102] However, there are no data known to the author which describe the accuracy and precision of these reduction methods. Factors which militate against efficient recovery are the tendency toward re-dissolution of rhodium in the absence of excess reductant while with excess metal reductant contamination becomes inevitable Removal of the latter by the usual process of selective dissolution may be ineffective through the dispersion of rhodium by cell action with the metal reductant, or through the formation of solid solutions when ignition precedes the acid treatment. However, there are available reducing reagents which are suitable for gravimetric determinations within a limited range of rhodium concentrations.

For the precipitation of microgram amounts of rhodium and separation of the latter from iridium, selective reduction by finely dispersed antimony powder produces accurate quantitative recovery[124] Iridium is merely reduced to the three valent state. Solutions of either sulphuric or hydrochloric acids may be used Antimony in the filtrate can be separated from iridium by distillation from fuming sulphuric acid. However, this reduction method has been proved only for quantities of rhodium and iridium beyond the range to which gravimetric methods could be applied

Hydrazine sulphate or hydrate was used by Gutbier and co-workers;[48,49] and Scott[102] recorded a procedure for the reduction by formic acid and subsequent purification by leaching the ignited residue with *aqua regia*. Treatments such as the latter are often ineffective and are not recommended.

A more recently developed procedure[56] designed specifically for the separation of rhodium from iridium involves the selective reduction of the former by titanium^{III} chloride. There is here the difficulty that excess titanium must be removed by cupferron to permit the determination of iridium. The method is not recommended for very small amounts of rhodium and iridium. Comparable difficulties are associated with reduction by chromium^{II} chloride, a procedure proposed by Pshenitsyn[85]

Precipitation by hydrogen sulphide in acid solution remains one of the most useful methods for the determination of rhodium. Unfortunately there is here an interference from sulphuric acid. This effect is said to be eliminated by heat treatment with sufficient hydrochloric acid, resulting in the conversion of the yellow sulphate to the pink chloride complex.[42,102] However, the efficiency of this commonly used method has been disputed[103] and the present author obtained a more satisfactory conversion to the pink solution by fuming to crystals in the presence of sodium or preferably ammonium chloride[2]

Under suitable conditions precipitation by hydrogen sulphide is a highly satisfactory process The precipitate possesses very suitable physical characteristics and is easily coagulated and filtered. However, the rhodium sulphide thus prepared is not easily purified and the washed precipitate is generally ignited to the oxide and subsequently reduced to the metal. Recently a method has been reported for the application of rhodium sulphide as a weighing form. Taimni and Salaria[108] precipitated $RH_2S_3{\cdot}3H_2S$ from a solution made alkaline with ammonium hydroxide then treated with a large excess of sodium sulphide reagent. Subsequently large excesses of acetic acid and ammonium acetate were added and the mixture was boiled. The precipitate was purified by washing with organic solvents and then dried in a vacuum desiccator.

Organic reagents

Only two organic gravimetric reagents for rhodium have been recorded. Thiobarbituric acid[22] was used successfully to precipitate an impure complex which required ignition and reduction to the metal weighing form. The method is neither specific nor usefully selective. Chloride solutions are required and when sulphuric acid is present, conversion to the chloride complex is best accomplished by fuming to dryness in the presence of ammonium chloride. Sodium chloride may be used but there is considerable danger of contamination.[2]

2-Mercaptobenzoxazole or 2-mercaptobenzothiazole in glacial acetic acid were used by Haines and Ryan[50] to precipitate complexes of rhodium from solutions containing ammonium chloride. Dilute solutions of nitric acid were not objectionable. Ignition to the metal weighing form was recommended. The method is, of course, not specific and judging from the published data, offers little or no advantage over the thiobarbituric procedure.

Precipitation to produce hydrated oxides of the platinum metals has a lengthy history. Some of the early methods of hydrolysing were integrated and perfected by Wickers and Gilchrist[56] who have produced quantitative procedures which, for wide application and general usefulness, are outstanding. Although this approach finds perhaps its greatest advantage in the isolation of platinum, the hydrolytic precipitation of rhodium is often preferred to the sulphide method since where re-precipitations are required the oxide is more readily converted to the soluble chloride. The technique of the precipitation is simple, the physical characteristics of the oxide are advantageous and the subsequent conversion to metal is not difficult. However, for the frequently encountered small quantities of rhodium the method encourages serious contamination. The near neutral solution required for the precipitation allows simultaneous precipitation of a wide variety of impurities whose weight, although perhaps small, becomes significant with small amounts of rhodium. The error can, of course, be reduced to a degree by a reduction of the volume of the solution and the quantity of reagents but this precaution does not always eliminate a high percentage error.

Undoubtedly, there is great need for more efficient gravimetric reagents for rhodium. Of those now available for microdeterminations the author prefers thiobarbituric acid. In so far as the determination of milligram or smaller amounts of rhodium is concerned, none of the above reagents is recommended. Fortunately, the very recent techniques of ion exchange and chromatographic procedures are advancing rapidly and the present researches of the author and co-workers indicate that the most difficult separations, such as rhodium from iridium, will be accomplished with efficiency and ease.

IRIDIUM

The analytical difficulties associated with the determination of rhodium apply also to iridium. Added to these there is the fact that, unless very finely divided, iridium is inert to all mineral acids or mixtures of these acids The susceptibility to attack of iridium in very finely divided condition by concentrated mixtures of hydrochloric and nitric has been grossly misapplied, *e g.* procedures which direct the dissolution of iridium in silver bead residues by addition of strong *aqua regia* are quite unacceptable [33] Conversion of the metal or its oxides to soluble iridium salts may be accomplished by a variety of chlorinating procedures; molten fluxes containing sodium peroxide may also be used with the relative disadvantage that crucible material is added to the solution of iridium. The inactivity of iridium is well illustrated by the very useful procedure[38] for the determination of iridium in the presence of platinum by fluxing to form a lead button and subsequently recovering the iridium by selective dissolution of lead and all foreign material by nitric acid

As in the case of rhodium, reagents for gravimetric determinations are few in number and none is, in any practical sense, specific. Those which merit reference or attention are: ammonium chloride, metal reductants, hydrogen sulphide, sodium sulphide, thioformamide, 2-mercaptobenzothiazole, and sodium carbonate.

Precipitation of iridium as ammonium hexachloroiridate is sometimes advantageous as a method of large scale separation For quantitative purposes the precipitate is much too soluble and is not usefully selective. However, there have been recorded instances of acceptable applications; Schoeller[98] used the method to separate iridium from iron.

Some of the very early analytical procedures involved reduction to iridium by zinc. For quantitative work there is little value in the method. The precipitate is always contaminated and the various processes of leaching are ineffective In any case no procedure for this reduction has appeared which can claim even an approach to acceptable accuracy.

The reagent hydrogen sulphide is also not recommended It is generally recognised that complete precipitation is difficult to attain. Various methods of overcoming the resistance to the complete conversion to sulphide have been advocated. Of these the use of pressure and repeated treatments with hydrogen sulphide are frequently recommended The author has yet to succeed in obtaining quantitative sulphide precipitation by any of the recorded procedures, an experience very much at variance with the recently recorded statement that "the most reliable method for the estimation of iridium depends upon its precipitation as sulphide from a hot solution containing 20% hydrochloric acid by volume".[108] Although the same authors[108] developed a modification of the sulphide precipitation which merits further attention, the application of a questionable method for the purpose of comparison does not encourage confidence in the accuracy of the new procedure, this involves precipitation of $Ir_2S_3 10H_2O$, obtained by the addition of a large excess of sodium or ammonium sulphide, followed by similar excesses of acetic acid and ammonium acetate. Purification was carried out by washing successively with aqueous ethanol, ethanol, and ether, and drying *in vacuo*

The difficulties inherent in the quantitative precipitation of iridium by hydrogen sulphide were recognised by Gagliardi and Pietsch[36] who recommended as an alternative the use of thioformamide. It is stated that with this reagent the platinum metals are precipitated in the order Pd–Ru–Pt–Rh–Os–Ir. Thus, it is claimed, one may separate palladium from iridium and a procedure for this purpose is included. The method has little to recommend it.

Although a number of organic reagents will form precipitates with iridium none of these complexes is recommended as a weighing form and only one has been used for quantitative purposes 2-Mercaptobenzothiazole[7] forms a bulky orange precipitate from solutions containing acetic acid and ammonium acetate. A fifteen hour period of digestion is required and concentration of mineral acid must be limited; the optimum concentration is $0.005N$ to $0.01N$. The method is suitable for small amounts of iridium but amounts in excess of about 20 mg produce unmanageable quantities of precipitate. Under these conditions the hydrolytic precipitation described below is more advantageous. However, the reagent can be usefully employed for solutions containing iridium and lead.

For general application no procedure for the gravimetric precipitation of iridium is comparable to the hydrolytic method recorded by Gilchrist.[41] By this procedure the iridium solution is treated with bromate to attain quadrivalency; and by the carefully regulated addition of sodium hydrogen carbonate to an end point with bromocresol purple the iridium is precipitated as the hydrated oxide. This is converted by conventional methods to the metal. For very small amounts of iridium the hydrolytic precipitation is unsuitable to the degree that there are present dissolved constituents which similarly hydrolyse to insoluble precipitates.

Since, with all gravimetric reagents, the weighing form is the metal, one must recognise the fact that hot iridium may lose weight. The explanation for this phenomenon, as also in the case of platinum, is unknown. Hill and Beamish[54] found that ignition at 650° to 675° showed no significant volatilisation but at 800°–950° the loss of weight became very noticeable and could amount to as much as 2–3%.

Most assuredly there is great need for more and better gravimetric reagents for iridium. One must hope that, even though incidentally, the great volume of research in the field of organic chemistry may yield indications of reagents which can be investigated for gravimetric applications. To achieve specificity simultaneously may not be expected but the very promising methods of isolation now being developed will serve adequately as a substitute.

RUTHENIUM

Since no specific reagent is available for the determination of ruthenium it is fortunate that the metal along with osmium may be easily isolated by distillation of its volatile octavalent oxide. While the relative merits of the various distillation processes will be treated in more detail in subsequent papers it may be stated here that the most generally used procedures involve (*a*) treatment of a caustic solution of the metals with chlorine,[111] (*b*) selective removal of osmium by nitric acid followed by oxidation of ruthenium by bromate;[39] (*c*) collective distillation of both metals into hydrogen peroxide by oxidation with perchloric acid and subsequent separation of osmium by selective oxidation with hydrogen peroxide.[123,125] For very small amounts of the metals, a condition invariably found with natural occurrences in ores and concentrates, the present author prefers the oxidation by perchloric acid. The use of nitric acid, which must be removed subsequent to the separation of osmium, sometimes encourages low values for osmium and ruthenium[96,123] and introduces a greater variety of technical difficulties in the determination of the remaining platinum metals.

There exist for ruthenium the usual quota of well known precipitants such as hydrogen sulphide, zinc, magnesium, ethanol etc. In addition to these there are now available procedures for the gravimetric determination by thionalide and by hydrolysis to the hydrated oxide. In all cases the weighing form is the metal, and its preparation involves heating in air and hydrogen.

Reduction by zinc, magnesium or ethanol forms part of many old and some recent analytical procedures. For preliminary separation and for special applications[65] these methods are often exceedingly useful Recipes for their application to distillates containing only ruthenium are described in a number of text books[102] and analytical literature contains a great variety of procedures in which have been integrated one or more of these reducing reagents.[86] However, for accurate analytical work reduction to ruthenium by any metal is not recommended. The complete reduction requires an excess of reductant, which must subsequently be removed by an acid or oxidising leaching process, a technique which is always suspect. In any case more efficient precipitants are available. For the latter reason hydrogen sulphide is also not recommended. This opinion is based upon general considerations since the method has not been used for ruthenium in the present author's laboratory.

Recently, a sulphide precipitation has been recorded[108] which offers promise of useful applications. The procedure involves addition of a large excess of sodium sulphide to a slightly ammoniacal solution of ruthenium chloride, followed by acetic acid and ammonium acetate. The precipitate of $Ru_2S_3.2H_2O$, purified by successive washings with water, ethanol and ether, and dried *in vacuo*, was weighed directly. The results recorded indicate high accuracy and precision.

The evolution of hydrolytic processes applied to the platinum metals has been characterised by many contributions A good degree of perfection has been reached through the researches at the Washington Bureau of Standards. Out of these there has become available one of the most satisfactory methods for the precipitation of ruthenium as the hydrated oxide of tervalent ruthenium [39] The technique is comparable to that required for the similar precipitations recorded above. However, the tendency toward contamination of precipitates formed in near neutral solutions is apparent here also and becomes significant for very small amounts of ruthenium since comparable reduction in weights and volumes of reagents is seldom feasible, particularly when distillations have preceded the precipitation

The single organic quantitative precipitant for ruthenium recorded in the literature is thioglycollic-β-aminonaphthalide or "thionalide".[90] Precipitation of the complex is complete in 0·2–0·5N hydrochloric acid. Small amounts of sodium chloride in solution do not interfere In nitric acid solution, low ruthenium values are obtained Since the precipitate cannot be used as a weighing form, ignition in air and then in hydrogen is required.

During the development of the method the quantitative recovery of ruthenium was confirmed directly and by exhaustive examination of the filtrates by both distillation and by radioactive tracer technique.[111] It was concluded "that the thionalide precipitation was, under the recommended conditions,[90] complete to less than 1 part in 10,000 on 6 mg of ruthenium". Since that time many hundreds of determinations of ruthenium by thionalide have been made in the present author's laboratory with excellent accuracy and precision. However, recent literature contains several references indicating that the determination of ruthenium by thionalide may be attended by low results. These references all have their origin in the statement[32] that "with semimicro quantities the results tend to be low—the maximum error amounting to about 10%." It would seem that this estimate is not based upon experience with the method but rather upon an indiscriminate use of values provided in the original publication[90] to indicate the adverse effects of certain dissolved constituents. Obviously, the inclusion of such exploratory data should eliminate any significance which may have been given to the above criticism. While the method is recommended it is well to realise that thionalide is by no means a specific reagent and in the presence of many associated metals ruthenium must first be isolated.

OSMIUM

In most natural occurrences of the platinum metals osmium forms a small part of the relatively small proportion of what is usually termed "the insolubles". In this residue osmium is assumed to exist as some type of "iridosmine". This nomenclature persists despite the fact that very little is known about the chemical or mineralogical properties of iridosmines and still less is known about the properties of the so-called iridosmines in the "insoluble" encountered during the analysis of platinum ores and concentrates. Some of the problems associated with these analyses have been discussed recently by Westland and Beamish [122,125] It is an astonishing fact that analytical literature contains no record of the successful application of any procedure for the direct determination of osmium in ores. One may assume with confidence that even those industries concerned with the recovery of osmium in ores are unaware of their percentage recovery of this elusive element and still less of the quantities lost during the various stages of platinum metals recovery. Obviously gravimetric reagents for osmium can find no direct application to the determination of the small amounts to be found in ores. However, from time to time one is required to ascertain the composition of minerals such as "iridosmines" which do contain high proportions of osmium. Most fortunately, one may isolate osmium easily from associated metals by distillation of the octavalent oxide and for such distillates gravimetric methods may be useful. A variety of the classical precipitants have been used and some remain as an integral part of established assay procedures. Various standard reducing reagents such as aluminium,[67] hydrazine[82] and formaldehyde[82] have been applied. None is recommended. Sulphide precipitation has been frequently attempted but always without success. Where gravimetric reagents are required one may now choose from the following:—sodium hydrogen carbonate, strychnine sulphate, thionalide and 2-phenylbenzothiazole Methods of precipitation of osmium as the hydrated dioxide have evolved by many stages to become a very useful gravimetric procedure. Gilchrist[40] precipitated the oxide from a boiling solution adjusted to pH 1·5–6·3 by the careful addition of sodium hydrogen carbonate. Since ignition in air must be avoided, some type of filtering crucible is required For this purpose, asbestos filters, Monroe crucibles, or porcelain filtering crucibles are satisfactory The author uses the last medium, preferably the Berlin A2 grade. To avoid losses by deflagration during ignition the dioxide is impregnated with ammonium chloride. It is interesting to note that, whereas osmium metal will volatilise as the octavalent oxide at room temperature, when the reduced residue of osmium is allowed to cool in an atmosphere of carbon dioxide the osmium metal is strangely stable. Allan and Beamish[1] modified slightly the above procedure with a view to applying it to milligram samples To avoid losses of osmium to the filtrate and washings, which sometimes result from a lack of experience in the neutralising technique, the hydrated oxide is washed with ethanol. Because precipitations are usually made with distillates, and because these distillates are usually submitted to some preliminary heating there is more or less encouragement of contamination from reagents and glass ware. Under these conditions it is to be expected that positive errors will be characteristic of the hydrolytic method. Allan and Beamish[1] found that, for small samples, these errors are practically always significant and where good accuracy is required they may be sufficiently serious to disallow the method. Obviously prolonged treatment of distillates cause increasing positive errors. It may occur to the analyst that a simple and direct determination of the error would result from volatilisation of the heated osmium metal in air. Unfortunately one may here encounter a phenomenon for which there has been no explanation. The ignited residue of osmium, silica etc., is sometimes converted to a residue from which osmium is not removed even at red heat. Inexplicably, this retention of osmium will vary with the character of the absorbing distillate; *e.g.* it is more serious with hydrobromic acid than with the hydrochloric–sulphur dioxide absorbents. It is partly for these reasons that the author cannot recommend the hydrolytic method where milligram samples and distillations are involved and where high accuracy is required.

While many organic reagents have been found to precipitate osmium complexes none of the latter could be used as weighing forms. Since ignition in air is inadmissible there has been little encouragement to seek quantitative organic precipitants Strychnine sulphate was used by Ogburn and Miller[79] to produce quantitative precipitation of a canary-yellow complex which was used as a weighing form; but since the latter was not a pure substance the authors used an experimentally determined correction factor, a subterfuge which is seldom satisfactory and was not so in this case.[40] Further work on the strychnine precipitant was reported by Hoffman *et al*,[57] who were able to use this reagent for quantitative purposes through the discovery that certain osmium organic complexes could indeed be ignited. An ignition in hydrogen was made possible by the catalytic influence of the metal to produce volatile organic compounds, presumably methane etc The red brown complex of strychnine and bromo-osmate was quantitatively produced in neutral media and ignited in hydrogen to the metal weighing form. However, the method applied to ammonium chloro-osmate and to distillates in sulphur dioxide–hydrochloric acid yielded incomplete precipitation. The negative error was of the order of 0·1 to 0·2 mg

By a similar procedure 2-phenylbenzothiazole can be used to precipitate from the bromo-osmate solution, but, as with strychnine, there is incomplete precipitation with the chloro-salt or the sulphur dioxide–hydrochloric distillates. The method of ignition is that used for the strychnine complex but with the former reagent there is a tendency to liquefy during ignition in hydrogen. Possible losses, due to this liquid passing through the porcelain filter, can be eliminated by the use of a small porcelain cap upon which the crucible is placed. In a later application of this reagent to hydrobromic acid distillates obtained from sulphuric acid–hydrogen peroxide oxidations and involving amounts of osmium as low as two milligram, Westland and Beamish[125] found additions of hydroxylamine hydrochloride were required to initiate precipitation, which occurred slowly; a period of about twenty-four hours was required to ensure quantitative recovery Furthermore, washing with dilute hydrochloric acid was preferable to the use of hydrobromic acid. These variations in behaviour were probably due to the presence of sulphuric acid in the distillate Presumably, for the same cause, the use of thionalide[57] was inadmissible because of the difficulty of obtaining coagulation This reagent also was first recorded by Hoffman[57] who found that, unlike strychnine sulphate and 2-phenylbenzothiazole, it could be used to determine osmium in sulphur dioxide–hydrochloric acid solutions. The thionalide-osmium precipitate whose ratio of constituents is 3 : 1, is also not readily purified and hence ignition in hydrogen is required. There is an advantage to the above three procedures not associated with most gravimetric determinations It was found that accurate blanks could be determined by volatilising the reduced osmium The residues of iron, silicon, copper and magnesium, when examined spectrographically, revealed no osmium content. Presumably, these co-precipitated impurities failed upon ignition to form the peculiarly resistant osmium residue discussed above. Magnesium in the residue had its origin from the thionalide which requires the metal for its production. The precipitants, strychnine and 2-phenylbenzothiazole offer greater ease of operation and require less time than thionalide. However, the thionalide complex usually coagulates well and less care need be taken with its ignition. The precipitation by strychnine sulphate has the disadvantage of being made in neutral or slightly acid media, in which case certain other metals may be precipitated simultaneously as hydrated oxides. The procedure using 2-phenylbenzothiazole is made in a strongly acid medium and hence overcomes this difficulty.

It is necessary to deal with a seemingly obvious method for the determination of osmium in acid distillates. This method involves the evaporation of the volatile absorbent and the subsequent drying and ignition in hydrogen of the collected osmium. The difficulty with this simple procedure concerns the accumulation of the impurities which are not readily removed by selective leaching. While the method may be used for approximate determinations, it has no advantages and is, of course, not recommended for accurate analysis.

A somewhat unusual approach to osmium determination is recorded by Musil and Pietsch[73] who distilled osmium in a stream of oxygen into a previously weighed bulb containing potassium hydroxide. The method may have some value in specific instances but it is not recommended for general use.

Zusammenfassung—Es wird ein Übersicht mit Literaturreferate bis Juni 1957 von quantitativen gravimetrischen Methoden der Analyse fur sechs Platin-metalle angegeben Ein Versuch wird kritisch und auf vergleichender Basis gemacht, alle annehmbaren Methoden zu beurteilen.

Die komplizierten Probleme der en-masse-Isolation aus naturlichen Quellen werden nicht berucksichtigt, aber die Interferenzen, die aus begrenzten Trennungen entstehen, werden nicht behandelt

Résumé—L'exposé passe en revue les méthodes d'analyse quantitative et gravimétrique pour les six métaux du groupe du platine jusqu'au mois de juin 1957. On a tenté d'évaluer de façon critique et comparative toutes les méthodes acceptables Bien que l'on n'ait pas pu examiner les problèmes compliqués de l'isolement en masses des sources naturelles, les interférances résultant de séparations limitées ont été prises en considération

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Talanta, 1958, Vol 1, pp 30–38, Pergamon Press Ltd , London

REACTIONS OF THIOACETAMIDE IN ALKALINE BUFFER SYSTEMS

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(*Received* 15 *February* 1958)

Summary—Measurements have shown that the rate of formation of sulphide from thioacetamide is greater in the presence of ammonia and carbonate buffer systems than that predicted from previous measurements in sodium hydroxide solutions

In solutions buffered with ammonia and ammonium chloride at pH 10, the rate of sulphide formation is first-order with respect to the thioacetamide and second-order with respect to the ammonia concentration, the third-order rate constant was found to be 0 055 litre^2 mole^{-1} min^{-1} at 90° The energy of activation was calculated to be 12 kcal per mole from 60° to 90°

In carbonate–hydrogen buffers the rate of formation of sulphide has a first-order dependence on both thioacetamide and carbonate ion concentrations, but has an inverse half-order dependence on hydrogen carbonate ion. The rate constant was calculated to be 0 015 litre$^{1/2}$ mole$^{-1/2}$ min^{-1} at 90°

A PREVIOUS investigation[3] has shown that in sodium hydroxide solutions the hydroxide-catalysed hydrolysis of thioacetamide proceeds by two reactions to yield in one case thioacetate ion and ammonia and in the other acetamide and sulphide ion. Each reaction is first-order with respect to both the thioacetamide and the hydroxyl ion concentrations and the second-order rate constants are about 6 and 2 litre mole^{-1} min^{-1} at 90°, respectively. The acetamide and thioacetate subsequently hydrolyze at much slower rates; the second-order rate constant for the acetamide hydrolysis[4] is 0.24 litre mole^{-1} min^{-1} and that for the thioacetate hydrolysis[3] is 0.019 litre mole^{-1} min^{-1} at 90°.

Since ammonia is formed by hydrolysis of thioacetamide, it was of interest to determine what effect, if any, ammonia has on the rate of hydrolysis of thioacetamide or the reaction products. In addition, such information would be of value in the use of thioacetamide as a sulphide precipitant in ammonia buffer systems. Preliminary experiments showed that when a large excess of ammonium hydroxide was added initially to reaction solutions containing thioacetamide and sodium hydroxide the rate of formation of sulphide was greater than in the absence of the ammonia. However, after sufficient time had elapsed to insure essentially complete hydrolysis of the thioacetamide, the rate of formation of sulphide became characteristic for the hydroxide-catalysed hydrolysis of thioacetate observed in sodium hydroxide solutions previously.[3] From these experiments it was concluded that ammonia was increasing the rate of formation of sulphide from thioacetamide, but that within the limits of experimental accuracy it had no effect on the formation of sulphide from thioacetate.

To determine the specific effect of ammonia, studies of the rate of formation of sulphide from thioacetamide in solutions buffered at about pH 10 with ammonium hydroxide and ammonium chloride have been made.

When carbonate–hydrogen carbonate buffers were used in an attempt to measure the formation of sulphide from thioacetamide in solutions of approximately pH 10, it was found that the rate of formation of sulphide was about twenty times faster than that predicted on the basis of the thioacetamide and hydroxyl ion concentrations and the previously determined rate constant.[3] As a result, experiments were performed to determine the effect of the carbonate–bicarbonate buffer.

The details of these studies and their results are discussed below.

EXPERIMENTAL

Reagents

Thioacetamide solutions were prepared by weight from Arapahoe reagent (Lot 1402) The white solid dissolved to give clear, colourless solutions. These solutions were never kept longer than three weeks

Ammonium hydroxide solutions were prepared by diluting concentrated reagent grade (15*VF*, volume formal) ammonium hydroxide with distilled water and were standardized against a hydrochloric acid solution

Ammonium chloride solutions were prepared by weighing

Sodium carbonate and sodium hydrogen carbonate solutions were prepared and standardized against hydrochloric acid

A sodium perchlorate solution was used for the adjustment of the ionic strength

A buffer solution (pH 4–5) was prepared by mixing two volumes of 6*VF* acetic acid with one volume of 6*VF* sodium hydroxide.

Collecting solutions for hydrogen sulphide were prepared by dissolving cadmium chloride in 6*VF* ammonium hydroxide to give solutions 0 4*VF* in cadmium chloride

A standard potassium iodate solution was prepared by weight

A 0 1*VF* sodium thiosulphate solution was prepared and standardized against the potassium iodate solution

Apparatus

The reaction tube consisted of a 38 × 200-mm test-tube fitted with a two-hole rubber stopper. One hole was enlarged to allow a 10-ml pipette to be inserted into the tube for sampling. A thermometer was inserted through the second hole in the stopper. The tube was surrounded by a water bath which maintained the temperature at 90° ± 1°.

The apparatus for removing hydrogen sulphide from each sample consisted of a 22 × 175-mm test-tube containing the buffered sample. A sintered-glass gas bubbling tube, through which nitrogen was passed, reached to the bottom of the test-tube. The hydrogen sulphide was swept through a drawn capillary tube into a 15 × 125-mm test-tube containing the collecting solution

Procedure

A reaction solution was prepared from distilled water and the required stock solutions and was pre-heated to slightly above 90° The desired volume of thioacetamide solution at room temperature was pipetted into the reaction solution Afterwards the temperature was maintained at 90° ± 1° Samples were removed at timed intervals and transferred into 22 × 175-mm test-tubes They were immediately placed in an ice bath to quench the reaction The pH of each sample was adjusted to 4–5 by means of the acetic acid-acetate buffer, the hydrogen sulphide swept by nitrogen into the collecting solution, the resulting cadmium sulphide precipitate centrifuged, and the clear centrifugate drawn off. The sulphide in the precipitate was determined iodometrically as described by Swift and Butler

The apparatus and procedure are described more fully in a paper by Butler, Peters, and Swift[3] which presents a study of the hydrolysis reactions of thioacetamide in sodium hydroxide solutions.

RESULTS AND DISCUSSION

Ammonia–ammonium ion buffer systems

A reaction temperature of 90° was used to allow the rate of formation of sulphide to be followed easily. In all experiments the initial ratio of ammonium hydroxide to ammonium chloride was five. The terms ammonia and ammonium hydroxide and their formulae are used indiscriminately to indicate the total concentrations of these compounds. The ionic strength of reaction solutions for all experiments was adjusted to 0.30 with sodium perchlorate solution. In these studies the rate of formation of sulphide ranged from about 10–200 times faster than that calculated from previous data[3] and the prevailing thioacetamide and hydroxyl ion concentrations. Consequently the contribution of the hydroxyl ion catalysed hydrolysis was assumed to be negligible. Also, the preliminary assumption was made that the rate of disappearance of thioacetamide was equal to the rate of formation of sulphide, and the concentration of unreacted thioacetamide was calculated indirectly by analyzing samples of the reaction solutions for sulphide at timed intervals during the reaction. Justification for this assumption is seen by the fact that the curves obtained by plotting the logarithm of the calculated thioacetamide concentration against time showed good linearity.

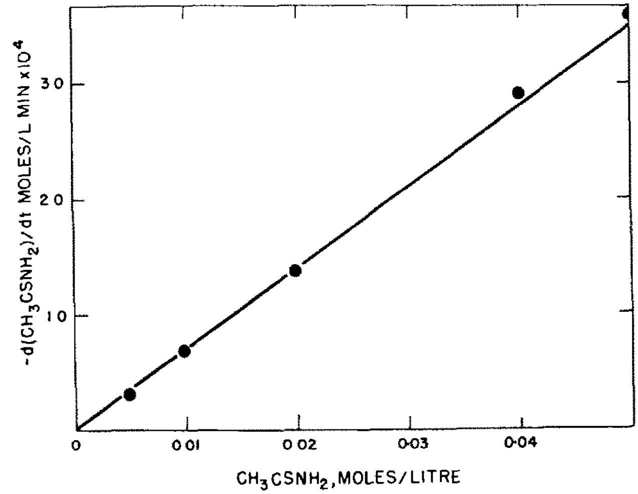


FIG 1 Rate of disappearance of thioacetamide at 90° as a function of thioacetamide concentration

In performing these investigations there was danger of volatilisation of ammonia from the reaction solutions, especially since the temperatures of the reaction solutions and the concentrations of ammonia were relatively high. Experiments to determine the magnitude of this effect showed that the total loss of ammonia by volatilisation from solutions 0.35 *VF* in ammonia was about 3% during the first 60-min period of reaction. As a result, with reaction solutions more concentrated in ammonia the total time of the measurements was shortened to minimise loss of ammonia. This effect was neglected in calculating the rate constants.

Some experiments where the reaction times were extended to two or three hours showed a decrease in the concentration of sulphide. This effect could be attributable to atmospheric oxidation of sulphide, but when dry nitrogen gas was bubbled through the stock solutions before preparing the reaction solutions, in order to attempt to remove oxygen no difference was observed in the result. Consequently, in all experiments the reaction time was restricted to a maximum of 60 min in order to minimise this effect to within the accuracy of the experimental measurements.

Rate constants and order of the reaction. Experiments were conducted at 90° in which the initial concentration of ammonia was 0.354*VF* and the ammonium chloride was 0.071*VF*. In these experiments the initial concentration of thioacetamide was varied from 0.00500 to 0.0500*VF* (Table I). Fig. 1 shows that the rate of disappearance of thioacetamide is first-order with respect to the thioacetamide concentration. The first-order kinetic expression for disappearance of thioacetamide may be written as

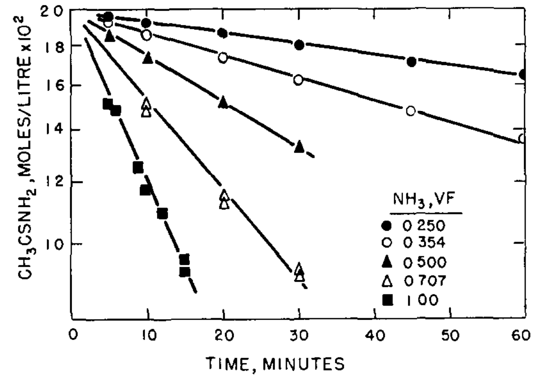


FIG 2 Plot of thioacetamide concentration against time, showing second-order dependence of the rate of reaction on the ammonia concentration

$$-\frac{d[CH_3CSNH_2]}{dt} = k[CH_3CSNH_2]$$

where the rate constant, k, is 0.0069 ± 0.00037 min^{-1} at 90° in solutions which are initially 0.354*VF* in ammonia.

The effect of ammonia on the rate of formation of sulphide was determined by experiments with reaction solutions ranging in ammonia concentrations from 0.250 to 1.00*VF*, and with the thioacetamide concentration initially 0.0200*VF*. As shown in Fig. 2, the rate of disappearance of thioacetamide was found to be second-order with respect to the ammonia concentration. The third-order kinetic equation is expressed by

$$-\frac{d[CH_3CSNH_2]}{dt} = k'[CH_3CSNH_2][NH_3]^2$$

TABLE I RATE OF FORMATION OF SULPHIDE AND FIRST-ORDER RATE CONSTANT FOR REACTION OF THIOACETAMIDE IN AMMONIA SOLUTIONS AT 90°

Series	CH_3CSNH_2, *VF*[a]	$-d[CH_3CSNH_2]/dt$ ($\times 10^4$) mole l^{-1} min^{-1}	First-order rate constant, k (min^{-1})
1	0.00500	0.31	0.0062
2	0.0100	0.69	0.0069
3	0.0200	1.38	0.0069
4	0.0400	2.91	0.0073
5	0.0500	3.59	0.0072
		Average	0.0069 ± 0.00037

[a] In all experiments the initial concentration of ammonia was 0.354*VF*, ammonium chloride was 0.071*VF*, and the ionic strength was 0.30. Initial concentrations are given for 25°

In Table II are shown the third-order rate constants calculated for each series of experiments. The third-order rate constant for the formation of sulphide in ammoniacal thioacetamide solutions at 90° is 0.055 ± 0.0010 litre^2 mole^{-2} min^{-1}.

TABLE II THIRD-ORDER RATE CONSTANT FOR REACTION OF THIOACETAMIDE IN AMMONIACAL SOLUTIONS AT 90°

Series	NH_3, VF[a]	Third-order rate constant k' (l ^{2} mole^{-2} min^{-1})
1	0 250	0 055
2	0.354	0 054
3	0 500	0 054
4	0 707	0 056
5	1.00	0 054
	Average	0.055 ± 0 0010

[a] In all experiments the initial concentration of thioacetamide was 0.0200 *VF*, the ammonium chloride concentration was one-fifth that of ammonia, the ionic strength was 0.30 Initial concentrations are given for 25°.

Variation with temperature of third-order rate constant. Experiments were performed to determine the variation in the rate of formation of sulphide in the temperature range from 60° to 90°. The reaction solutions were initially 0.0500 *VF* in thioacetamide, 0.500 *VF* in ammonia, and 0.100 *VF* in ammonium chloride. The ionic strength was 0.30. Table III shows the values obtained for the third-order rate constant for the temperatures studied. From the slope of the curve in Fig. 3, which is a plot of $-\log k'$ against $1/T$, the energy of activation was calculated to be 12 kcal. mole^{-1}.

Effect of ammonium ion on rate of formation of sulphide. Since ammonium ion is a poor nucleophilic agent, it was expected that it would have no effect on the rate of formation of sulphide. To investigate this problem two similar experiments were performed. Each reaction solution was initially 0 0200 *VF* in thioacetamide and 0.250 *VF* in ammonia, and had an ionic strength of 0.30. The first experiment had an ammonium chloride concentration of 0.0500 *VF*, the second had an ammonium chloride concentration of 0 100 *VF*. In each experiment the average rate of formation of sulphide during the first sixty minutes of the reaction was 6.7×10^{-5} mole litre^{-1} min^{-1}

TABLE III. VARIATION WITH TEMPERATURE OF THIRD-ORDER RATE CONSTANT FOR FORMATION OF SULPHIDE FROM THIOACETAMIDE IN AMMONIACAL SOLUTIONS[a]

Temperature (°C)	Third-order rate constant, k' (l ^{2} mole^{-2} min^{-1})
60	0 012
70	0 021
80	0 030
90	0 055

[a] Thioacetamide, 0 0500 *VF*; ammonia, 0 500 *VF*, ammonium chloride, 0 100 *VF*, ionic strength, 0 30 Initial concentrations are given for 25°.

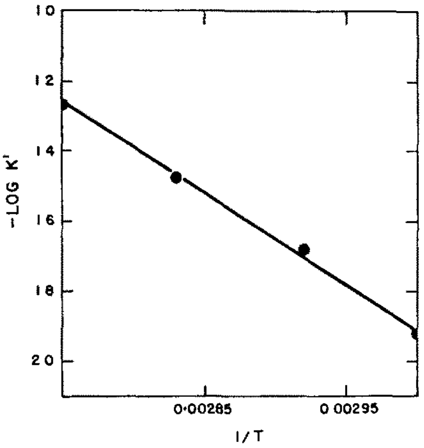
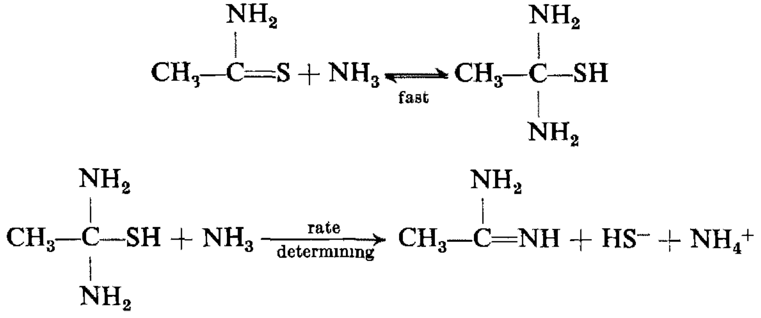


FIG 3 Rate of the ammonia–thioacetamide reaction as a function of temperature

at 90°. Within the limits of experimental accuracy, it was concluded that ammonium ion did not affect the rate of formation of sulphide.

Mechanism of the reaction The following mechanism involving the reaction of one molecule of thioacetamide and two molecules of ammonia to produce an amidine has been formulated which is in agreement with the kinetic equation shown above:



$$CH_3{-}\overset{\overset{NH_2}{|}}{C}{=}S + NH_3 \underset{\text{fast}}{\rightleftharpoons} CH_3{-}\underset{\underset{NH_2}{|}}{\overset{\overset{NH_2}{|}}{C}}{-}SH$$

$$CH_3{-}\underset{\underset{NH_2}{|}}{\overset{\overset{NH_2}{|}}{C}}{-}SH + NH_3 \xrightarrow[\text{determining}]{\text{rate}} CH_3{-}\overset{\overset{NH_2}{|}}{C}{=}NH + HS^- + NH_4^+$$

This mechanism accounts for the second-order dependence on the ammonia concentration and is in agreement with the experimental result that ammonium ion does not affect the rate of the reaction.

Carbonate–hydrogen carbonate buffer systems

Experiments were conducted in which various initial concentrations of thioacetamide, sodium carbonate, and sodium hydrogen carbonate were used. The ionic strength of the reaction solutions, with the exceptions indicated in Table IV, was adjusted with the sodium perchlorate solution to 0.75. In these experiments the hydroxyl ion concentration was buffered at different values between approximately 5×10^{-5} and $2 \times 10^{-4}M$ at room temperature. By analyzing the reaction solutions for sulphide at timed intervals during the experiments, the rate of disappearance of thioacetamide was obtained by difference. In the experiments of all series, with the exception of Series 6, the reaction was continued for a period of time so short that the change in thioacetamide concentration did not exceed 10%. At the pH of the

TABLE IV. RATE CONSTANTS AND RATE OF FORMATION OF SULPHIDE AT 90°C IN SOLUTIONS BUFFERED WITH CARBONATE–HYDROGEN CARBONATE

Series[a]	CH_3CSNH_2, *VF*	Na_2CO_3, *VF*	$NaHCO_3$, *VF*	$-d[CH_3CSNH_2]/dt$, moles ($\times 10^5$) l^{-1} min^{-1}	Rate constant k_3, ($l^{1/2}$ $mole^{-1/2}$ min^{-1})
1	0.0200	0.0600	0.200	3.7	0.014
2	0.0200	0.0600	0.100	5.0	0.013
3	0.0200	0.120	0.200	7.9	0.015
4	0.0200	0.120	0.100	11.0	0.016
5	0.0400	0.120	0.100	22.0	0.015
				Average	0.015 ± 0.0014
6[b]	0.0400	0.240	0.200	28.0	
7[c]	0.0200	0.120	0.100	3.1	

[a] In all experiments, with exceptions indicated, the ionic strength was 0.75. Initial concentrations are given for 25°.

[b] Ionic strength was 1.0. Change in thioacetamide concentration was 14%.

[c] Ionic strength was 1.5.

reaction solutions, the additional change in thioacetamide concentration resulting from hydroxyl ion catalyzed hydrolysis of thioacetamide to ammonia and thioacetate was calculated from previous data[3] to be only about 3% of the total initial concentration of thioacetamide. Because this latter hydrolysis would have little effect on the rate of formation of sulphide, it was neglected in calculating the rate constant. When values for the logarithm of thioacetamide concentration were plotted against time, the curves obtained were essentially straight lines, indicating that the latter assumption was justified within the experimental accuracy of the measurements involved. The linear nature of the curves also implied that the reaction of thioacetamide to form sulphide was the only significant reaction occurring in these solutions. The calculated values for the rate of formation of sulphide from thioacetamide are shown in Table IV. From the data obtained from these experiments, the rate constant and order of the reaction were determined.

Order of reaction and velocity constant. Comparison of the data in Series 4 and 5 in Table IV shows that the rate of sulphide formation was doubled by a two-fold increase in the thioacetamide concentration. This result implied that the reaction is first order with respect to thioacetamide concentration.

$$-\frac{d[CH_3CSNH_2]}{dt} = k_1[CH_3CSNH_2]$$

The data of Series 1 and 3 and Series 2 and 4 indicate the effect on the rate of sulphide formation caused by doubling the sodium carbonate concentration. The rate of formation of sulphide was found to be essentially proportional to the carbonate concentration which meant that the reaction is also first-order with respect to the carbonate ion concentration.

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = k_2[\mathrm{CH_3CSNH_2}][\mathrm{CO_3}^{=}]$$

The more than two-fold increase in the rate of sulphide formation is in agreement with that predicted from the increase in hydroxyl ion concentration caused by doubling the carbonate concentration while that of the hydrogen carbonate was constant.

The data of Table IV, Series 1 and 2 and Series 3 and 4, show that doubling the concentration of the hydrogen carbonate decreased the rate of sulphide production by the factor 1.4. This result implies that the hydrogen carbonate ion exerts a half-order inhibition on the rate of sulphide formation. Therefore, the overall kinetic equation for disappearance of thioacetamide in solutions buffered with carbonate and hydrogen carbonate is given by the rate expression

$$-\frac{d[\mathrm{CH_3CSNH_2}]}{dt} = k_3\frac{[\mathrm{CH_3CSNH_2}][\mathrm{CO_3}^{=}]}{[\mathrm{HCO_3}^{-}]^{1/2}}$$

where the rate constant, k_3, with standard deviation was calculated to be 0.015 ± 0.0014 litre$^{1/2}$ mole$^{-1/2}$ min^{-1} at 90° in solutions with an ionic strength of 0.75.

As yet no plausible mechanism which will explain the above rate expression has been formulated.

Effect of ionic strength. To check the effect of ionic strength on this reaction, Series 4 was repeated except that the ionic strength was increased from 0.75 to 1.5 by increasing the concentration of sodium perchlorate. Comparison of the rates of sulphide formation calculated for Series 4 and 7 shows that the rate decreased by the factor 3.6.

ANALYTICAL CONSIDERATIONS

Thioacetamide has achieved considerable analytical interest not only as a substitute for hydrogen sulphide but as a means for effecting the controlled precipitation of various metal sulphides from homogeneous solutions. This latter procedure offers the possibility of improving the physical characteristics of the precipitates and of decreasing co-precipitation when separations are involved.

Both carbonate and ammonia buffer systems have been used for certain sulphide separations. In order to attain optimum conditions for the use of thioacetamide in such separations, information regarding the rate of formation of sulphide from thioacetamide in such solutions is required. The above studies have shown that in these buffer systems the concentrations of the buffer constituents, and not the hydroxide concentration, are the controlling factors in the rate of sulphide formation. However before this information can be used with certainty it will be necessary to determine for each element if precipitation of the metal sulphide can take place by a "direct reaction" such as that which has been observed in acid solutions for lead,[5] cadmium,[1] zinc and nickel.[2] This "direct reaction" is first-order with respect to both the cation and to the thioacetamide, and inversely half-order with respect to the hydrogen ion concentration. Preliminary studies of the precipitation of nickel sulphide by thioacetamide from ammonical solutions have shown that both the thioacetamide–ammonia reaction and a "direct reaction" are involved to a significant extent.

The above experiments have shown the possibility that any proton-accepting reagent might catalyse the formation of sulphide from thioacetamide. Furthermore, these experiments have emphasised again that thioacetamide should not be used indiscriminately for the precipitation of sulphides without a knowledge of the behaviour of this reagent with the particular element being precipitated under the specific reaction conditions.

Acknowledgement—The authors are indebted to the National Science Foundation for financial support during this investigation

Zusammenfassung—Durch Messung wird es bewiesen dass die Geschwindigkeit der Sulphid-Bildung von Thioacetamid schneller in der Anwesenheit der Ammoniak- und Carbonat-Puffer-Systeme vor sich geht als die von vorhergehenden Messungen in Natronlauge zu erwarten waren.

In Losungen mit Ammoniak und Ammonium-chlorid an pH 10 gepuffert, ist die Geschwindigkeit der Sulphid-Bildung erster Ordnung bezuglich des Thioacetamids und zweiter Ordnung bezuglich des Ammoniaks, die Dritte-Ordnung-Geschwindigkeits-Konstante war 0,055 L^{2}Mol^{-2} Minute^{-1} an 90° Die Aktivierungs-Energie wird auf 12 Kcal/Mol von 60° bis 90° berechnet

In Carbonat-Wasserstoffcarbonat-Puffern ist die Geschwindigkeit der Sulphid-Bildung Primar-Ordnen in Abhangigkeit von Thioacetamid und Carbonat-Ion-Konzentrationen, aber von Wasserstoff-carbonat ein umgekehrtes Halb-Ordnen Die Geschwindigkeits-Konstante wird als 0,015 L$^{1/2}$Mol^{-1} Minute^{-1} an 90° berechnet

Résumé—On a établi expérimentalement que la vitesse de formation du sulfure à partir de la thioacétamide est plus grande en milieux tampon ammoniaque et carbonate que celle prévue au cours des mesures effectués antérieurement en milieu sodique

En milieu tampon ammoniaque—chlorure d'ammonium à pH 10, la vitesse de formation du sulfure est de premier ordre par rapport à la thioacétamide et de second ordre par rapport à la concentration de l'ammoniaque: la constante de troisième ordre était de 0,055 litre^2 mole^{-2} minute^{-1} à 90°. L'énergie d'activation a été évaluée à 60° á 90°.

En milieu carbonate-carbonate d'hydrogène la vitesse de formation du sulfure a une dépendance de premier ordre par rapport aux les concentrations et de la thioacétamide et de l'ion carbonate, mais une dépendance de demi-ordre inversément proportionelle à l'ion carbonate d'hydrogène

La constante de vitesse a été évaluée á 0,015 litre$^{1/2}$ mole$^{1/2}$ minute^{-1} à 90°

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Contribution No 2308 from the Gates and Crellin Laboratories of Chemistry, Pasadena, Calif

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PAPER CHROMATOGRAPHIC ANALYSIS OF SELENIUM, TELLURIUM, POLONIUM, AND BISMUTH

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(*Received* 3 *March* 1958)

Summary—The chromatographic analysis of ^{210}Po, ^{210}Bi, ^{127,129}Te, and ^{75}Se in hydrochloric acid and hydrofluoric acid developing media is described. This method of isolation of ^{210}Po from bismuth targets gives in a single operation clean samples at 100% yield The solutions of ^{210}Po were obtained in very small volume and were suitable for high resolution α-pulse analysis.

A REVIEW of the literature has revealed only one application[1] of the paper chromatographic method for the movement of polonium tracer. This has also been noted by Bagnall[2] in his recent and extensive review of the chemistry of polonium. Tellurium, the lighter homologue of polonium, serves as a carrier in the separation of polonium from relatively large amounts of neutron-irradiated bismuth The neutron-irradiated metallic tellurium prepared for this study was found to contain appreciable quantities of selenium. This was easily identified with the gamma scintillation spectrometer on the chromatogram shown in Fig. 3. The behaviour of fission product tellurium with this developing medium was known from previous work.[3] Since the selenium did not interfere with the experiments, a special purification of the tellurium tracer was not made. For this reason, the selenium is not always clear on the autoradiographs, but the identification with the gamma spectrometer was easily made.

EXPERIMENTAL

^{210}Bi and ^{210}Po were obtained by a one-week thermal neutron irradiation of bismuth metal in the maximum neutron flux of CP-5 (10^{12} neutrons/cm^2 sec) The bismuth was allowed to decay until sufficient quantity of the ^{210}Po daughter activity appeared Tellurium and selenium tracers were also obtained by thermal neutron irradiation for one month of the natural isotopic compositions of the free elements, followed by more than one month's cooling time. The selenium was present as an impurity in the tellurium metal

The paper was Whatman 3MM strips about 2.0 cm wide. The strips were developed approximately 25 cm by ascending chromatography beyond the original spots The developing time was approximately 2–3 hr Polythene cylinders were used to contain the hydrofluoric acid solvents

Autoradiographs were made to locate the various alpha and beta radioactive species as a demonstration of the procedures To differentiate between alpha and beta active nuclides, a 1.0 mil aluminium foil was placed between the film and paper strips on the one side, and a second film strip was placed directly in contact with the paper on the other side and exposed 10–15 hr In Fig 2, an example of such a pair of film strips is shown. In actual practice, however, a thin-window Geiger counter was generally used to scan the paper strips The autoradiographs of Figs 1, 2, and 3 were prepared using Kodak Type AA film This is finer grain and gives greater contrast than No-Screen X-ray film The Type AA film is six times slower than the No-Screen X-ray film

Tellurium metal was dissolved in concentrated nitric acid with hydrogen peroxide added to form telluric acid Solutions were also prepared by dissolution in *aqua regia* The irradiated bismuth solutions were prepared by dissolution in concentrated nitric acid (*aqua regia*) Some solutions were evaporated to dryness and the residue dissolved in concentrated hydrochloric acid Chromatograms with the nitric acid or mixed nitric–hydrochloric acid solutions gave the same results After the samples were applied to the paper strip they were air-dried approximately one hour, with one exception In Fig 2, with the *tert*-butanol, *iso*propyl ether and hydrochloric acid solution, the chromatogram of polonium and bismuth was developed after only a 10-min drying period Longer drying periods resulted in less movement of the polonium and increased tailing

The bismuth and tellurium content applied to the paper strips in the figures was approximately 0.3 mg for each element with tracer polonium and negligible amounts of selenium

RESULTS

No solvent mixture was found that would separate polonium and tellurium in hydrochloric acid medium. Some of the better results were with the solvent mixtures demonstrated in Figs 1 and 2. Lower hydrochloric acid concentrations decreased the movement of both polonium and bismuth almost proportionately and tended to increase tailing of both elements A number of combinations of various ketones or ethers and alcohols with hydrochloric acid gave results similar to those shown in Figs. 1 and 2. Both the alcohol and hydrochloric acid variables controlled the movement of bismuth and polonium. The ethers or ketones usually gave a sharper definition of the spots in the paper.

Separation of all four elements together was effected with methylethylketone–hydrofluoric acid. This is shown in Fig. 3. It was noted that polonium and tellurium interacted appreciably to give a smaller separation than expected from their individual chromatograms

The elements were also isolated with concentrated (49 %) hydrofluoric acid. The bismuth again did not move and the movement of the polonium was somewhat less than with the methylethylketone–hydrofluoric acid solvent shown in Fig 3 The movement of tellurium with concentrated hydrofluoric acid has been reported[3] previously.

Zusammenfassung—Die papierchromatographische Analyse von ^{210}Po, ^{210}Bi, ^{127,129}Te und ^{75}Se in Salzsaure und Fluorwasserstoffsaure als Losungsmittel wird beschrieben Dieses Verfahren fur Isolation von ^{210}Po aus Wismuth-Scheiben gibt in einer einzigen Operation reine Proben von 100% Ausbeute Die Losungen von ^{210}Po in einem sehr kleinen Volum werden erhalten und sie waren fur Hochauflosung-α-Impulsanalyse geeignet

Résumé—Description de l'analyse chromatographique du ^{210}Po, du ^{210}Bi, du ^{127,129}Te, du ^{75}Se, utilisant comme développants l'acide chlorhydrique et l'acide fluorhydrique Cette méthode de séparation du ^{217}Po du bismuth bombardé par des neutrons donne en une seule opération des échantillons purs avec un rendement de 100 pour cent On a obtenu les solutions du ^{217}Po dans un très faible volume et celles-ci ont permis l'analyse aux α-rayons de haute résolution

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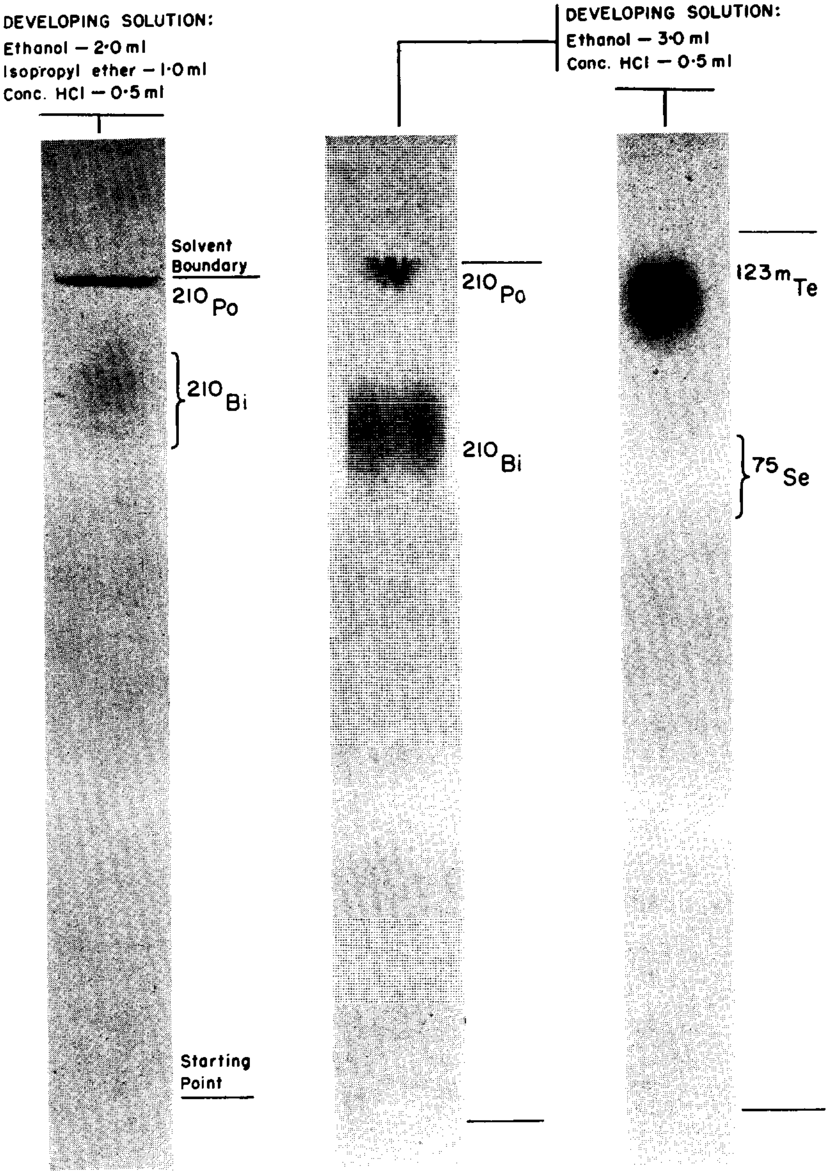

FIG. 1.—Chromatographic separation of polonium and bismuth, and selenium and tellurium.

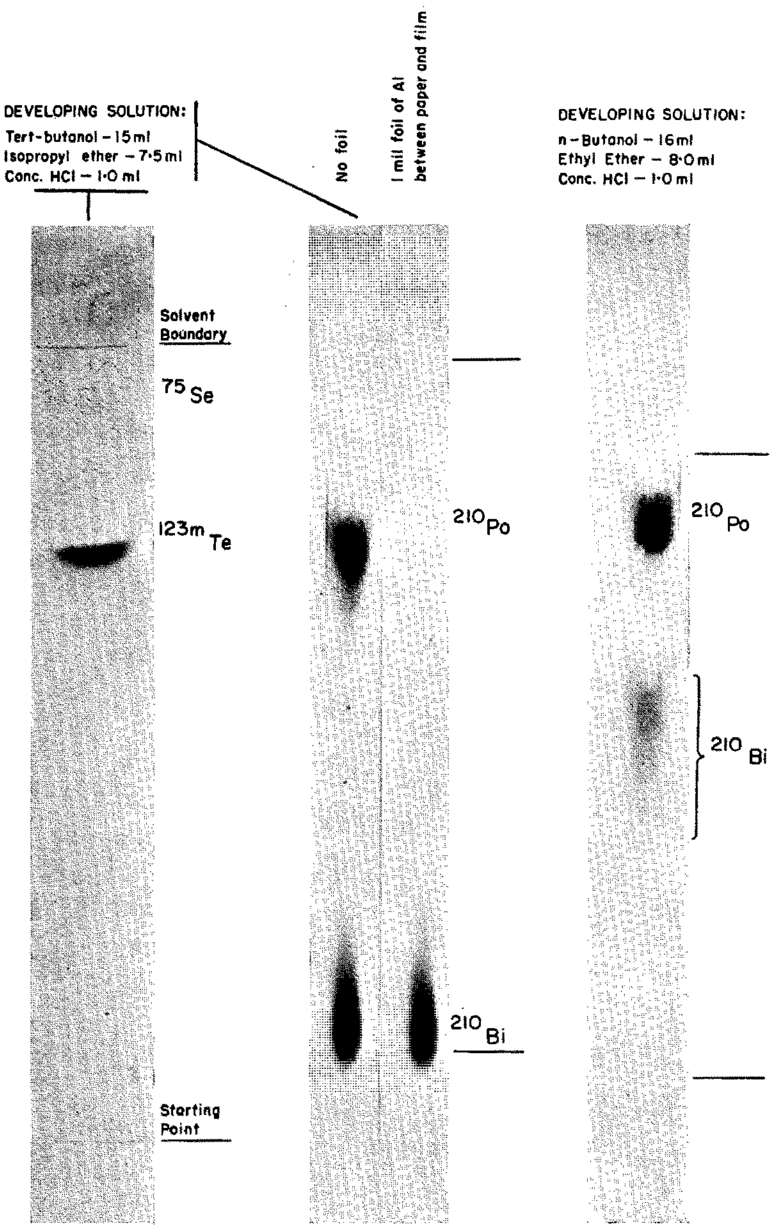

FIG. 2.—Chromatographic separation of selenium, tellurium, polonium and bismuth.

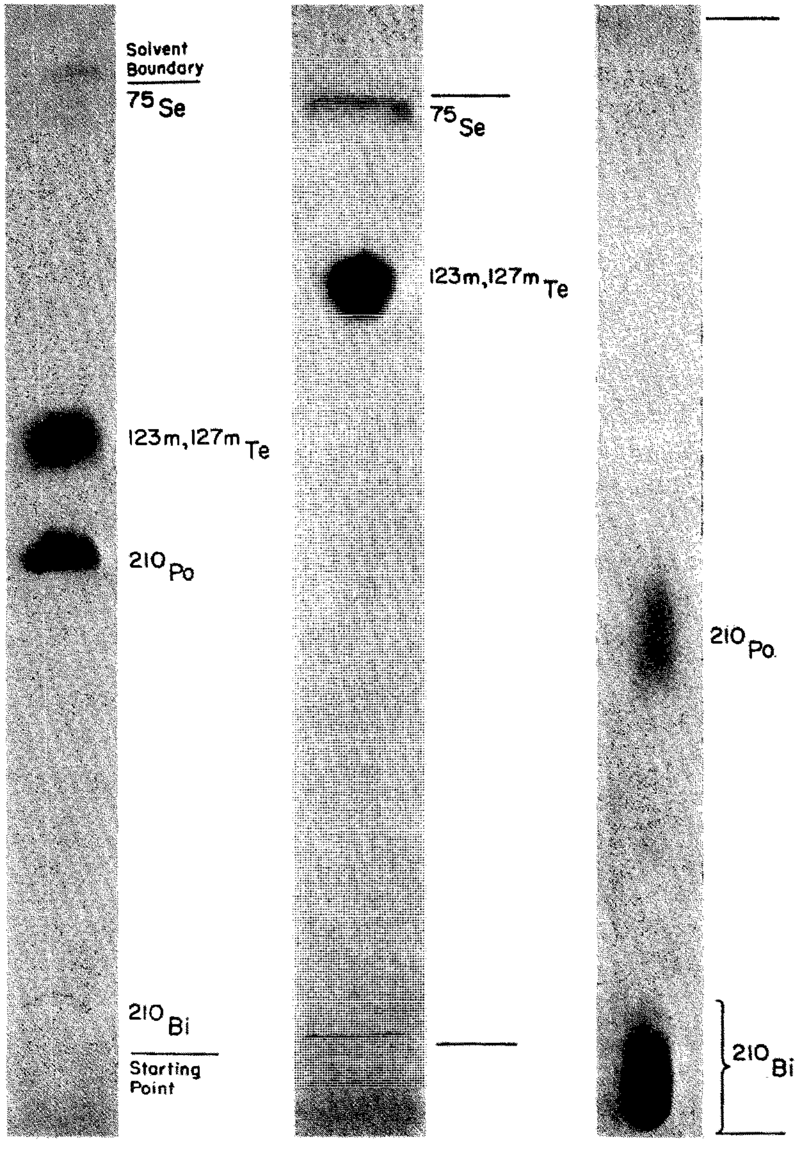

Fig. 3.—Chromatographic separation of tellurium and selenium, and polonium and bismuth. (Developing solution 60 g of 49% hydrofluoric acid per 100 ml methyl ethyl ketone.)

Talanta, 1958, Vol 1, pp 41–45, Pergamon Press Ltd, London

SODIUM HYDROGEN DIGLYCOLATE AS A REFERENCE BUFFER

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(*Received* 20 *February* 1958)

Summary—A 0 2M solution of sodium hydrogen diglycolate, easily prepared from the commercially available salt, has a pH of 3 40 ± 0 02 The pH of this solution is constant over a wide temperature range A 0 2M sodium hydrogen diglycolate solution has a high buffer capacity The pH is not changed greatly by addition of salt up to a concentration of 0 05M Dilution of the 0 2M solution by a factor of two does not affect the pH more than ±0 02 pH units The solution may be stored for considerable time with little variation in pH Sodium hydrogen diglycolate is non-hygroscopic and available in primary standard grade Of the common metal ions only Hg_2^{2+} is precipitated by the buffer

These properties make sodium hydrogen diglycolate useful as a reference buffer for standardisation of electrode systems, and as a buffer in various analytical and biochemical procedures

INTRODUCTION

THE accurate measurement of the pH of aqueous solutions has been facilitated by the development of reproducible electrodes, and by the use of reliable buffers for the standardisation of the electrode systems. A recent article[1] reviews the National Bureau of Standards pH references These references owe their excellent reproducibility and reliability to their accurate pH assignment, their high buffer capacity, and their purity.

Acid salts of organic acids are frequently used as reference buffers Two such buffers are potassium hydrogen phthalate[7] and potassium hydrogen tartrate[9] The accuracy of practical pH measurements is extended as the number of reference buffers is increased to cover a larger pH range. Recently, a new standard in alkalimetry, sodium hydrogen diglycolate, has been proposed[8] Just as potassium hydrogen phthalate is ideally suited[2] for the standardisation of pH assemblies at pH 4·00, sodium hydrogen diglycolate exhibits the desired properties of a reference buffer at pH 3·40. Sodium hydrogen diglycolate,[5] $NaOOC—CH_2—O—CH_2—COOH$, is non-hygroscopic, available in high purity* and is an excellent buffer.

EXPERIMENTAL

Initial pH studies were made with a Beckman model G pH meter. The reference electrode was a saturated calomel electrode (No 270), and the indicating electrode was a glass electrode (No 290), supplied by the manufacturer Potassium hydrogen phthalate, and potassium hydrogen tartrate, prepared as described by Bates[2] were used as reference buffers Their respective values are 4 00, and 3 57 pH for 20° The pH of sodium hydrogen diglycolate was measured in solutions of concentrations 0 33M (saturated) to 0 001M Table I shows the pH to be constant over a wide concentration range, with the value 3 40 ± 0 01 at 20° for a 0 2M solution To prepare a buffer having a pH of 3 40 ± 0 02, approximately 3 g of sodium hydrogen diglycolate are dissolved in 100 ml of water Since the pH of sodium hydrogen diglycolate is about 0 6 pH units smaller than that of water saturated with carbon dioxide at one atmosphere, the small amount of dissolved carbon dioxide

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* From G F. Smith Chemical Co, P O Box 1611, Columbus, Ohio.

TABLE I. DILUTION EFFECT ON pH

Molarity of NaHD	pH
0·33 (sat.)	3·38
0·25	3·40
0·20	3·40
0·15	3·41
0·10	3·42
0·08	3·44
0·05	3·49
0·03	3·52
0·01	3·58
0·005	3·64
0·001	3·78

from the atmosphere has no significant effect on the pH. Indeed, a 0·2*M* solution of sodium hydrogen diglycolate has a buffer capacity sufficiently great that several milliequivalents of hydrochloric acid may be added to a litre of the buffer without changing the pH more than ±0·02 pH units

Buffer capacity

The exact capacity of the buffer was determined for a 0·2*M* sodium hydrogen diglycolate solution by adding known amounts of strong sodium hydroxide solution and of strong hydrochloric acid solution. The concentrations of the sodium hydroxide and the hydrochloric acid were large enough to ensure that dilution effects were negligible. Table II shows the change of pH in a 0·2*M* buffer solution resulting from these additions.

The Van Slyke buffer value β is defined[7] as

$$\equiv \frac{db}{d\,\mathrm{pH}}$$

β is a differential ratio and db is an increment of strong base in gram equivalents. β may be calculated from the equation

$$\beta = 2{\cdot}303\left[\frac{KCm\mathrm{H}}{(K + m\mathrm{H})^2} + m_{\mathrm{H}} + m_{\mathrm{OH}}\right]$$

The buffer capacity, β, for sodium hydrogen diglycolate was found to be 0·087. This value compares favourably with the buffer capacity of potassium hydrogen phthalate and potassium hydrogen tartrate $\beta_{\max}$ for saturated solutions of these buffers is about 0·12 However, a smaller weight of sodium hydrogen diglycolate is required than of either potassium hydrogen tartrate or potassium hydrogen phthalate to achieve an equivalent buffer action because of the lower molecular weight of sodium hydrogen diglycolate.

Determination of the pH *of* 0·2*M sodium hydrogen diglycolate*

The pH of a 0·2*M* solution of sodium hydrogen diglycolate was measured using a Beckman model H-2 pH meter. A glass indicator electrode (4990–80), with a saturated potassium chloride calomel reference (4970) was employed This was checked using a Leeds and Northrup pH meter with a glass indicator electrode (1199–44) and a saturated potassium chloride calomel reference (1199–31) The value obtained was 3·40 ± 0·03 To obtain a value independent of the glass electrode assemblies a hydrogen electrode was used. The potentiometer was calibrated with a standard Weston cell The pH of a 0·2*M* solution of sodium hydrogen diglycolate measured 3·41 ± 0·02 pH units at 25° Standard potassium hydrogen phthalate solution measured 4·00 pH at 25°, and standard potassium hydrogen tartrate solution measured 3·59 at 25° using the same electrode system These values are within ±0·02 pH units of the Bureau of Standard values[6]

TABLE II. BUFFER CAPACITY

meq NaOH*	pH	meq HCl*	pH
0·00	3·40	0·00	3·40
0·35	3·40	0·33	3·40
0·71	3·42	0·66	3·35
1·06	3·44	1·00	3·32
1·42	3·47	1·33	3·29
1·75	3·49	1·66	3·24
2·12	3·52	1·99	3·22
2·47	3·54	2·32	3·19
2·82	3·57	2·65	3·14
3·17	3·60	2·98	3·11
3·51	3·63	3·31	3·09
4·22	3·70	3·65	3·05
4·93	3·76	4·31	3·00
5·69	3·79	4·97	2·97
6·32	3·82	5·64	2·92
7·02	3·89	6·63	2·82
7·72	3·95	7·95	2·72
8·71	4·01	9·29	2·58
10·01	4·08	9·95	2·43
10·90	4·29	11·31	2·38
12·32	4·51	12·63	2·18
13·01	4·75	13·92	1·98
13·72	5·18	15·25	1·74

* added to 50 ml of 0·145*M* NaHD.

A third check of the pH of sodium hydrogen diglycolate solutions was obtained by calculation using[10] the ionisation constant $K_1 = 1·1 \times 10^{-3}$, and[11] the ionisation constant $K_2 = 3·7 \times 10^{-5}$. These values were obtained from conductivity measurements [10] Using these, the pH of a saturated solution of sodium hydrogen diglycolate is calculated to be 3·37 pH units at 25°. This value is in excellent agreement with the experimental value reported in Table I

Salt effect

To determine the salt effect on the pH of an 0·2*M* solution of sodium hydrogen diglycolate, known amounts of solid potassium chloride or sodium chloride were added The pH was measured with a model G Beckman reference system previously described Salt concentrations up to 1·0*M* were used Table III shows that salt concentrations up to 0·05*M* may be tolerated with a change of pH no greater than ±0·02.

Effect of temperature on pH

The change in pH as a function of temperature was studied In the range of 10° to 40° a model G (Beckman) pH meter was used. A model H-2 (Beckman) was employed for the extreme temperature ranges, those below 10° and above 40° The electrode systems were calibrated at each temperature using the values for potassium hydrogen phthalate reported by Bates [4] Table IV shows that the pH of 0·2*M* sodium hydrogen diglycolate is 3·40 ± 0·02 for the temperature range of 10–35°

Reproducibility

To check the reproducibility of sodium hydrogen diglycolate as a buffer three separate lots were prepared. The pH of 0·2*M* solutions made from these lots was 3·40 ± 0·01 in each case.

TABLE III. SALT EFFECT ON pH OF NaHD SOLUTIONS

Molarity of salt	NaCl pH	KCl pH
0.000	3.40	3.40
0.005	3.40	3.40
0.010	3.40	3.40
0.05	3.39	3.39
0.10	3.37	3.38
0.3	3.29	3.35*
0.6	3.21*	3.33
1.0	3.17	3.30

* pptn. of buffer occurs

TABLE IV. TEMPERATURE EFFECT ON pH

KHP	NaHD	Temp. °C
4.01	3.40 ± 0.03	0
4.00	3.40 ± 0.01	10
4.00	3.40 ± 0.01	15
4.00	3.40 ± 0.01	20
4.01	3.40 ± 0.01	25
4.01	3.40 ± 0.01	30
4.02	3.41 ± 0.01	35
4.03	3.43 ± 0.01	40
4.06	3.45 ± 0.03	50
4.10	3.46 ± 0.03	60
4.12	3.47 ± 0.03	70
4.16	3.49 ± 0.03	80

Stability

To study the stability of the buffer, a 0.2*M* solution was allowed to stand eleven months in a stoppered glass bottle. A very slight sediment appeared in the solution and the pH measured 3.45 ± 0.02. Although 0.2*M* solutions of sodium hydrogen diglycolate show little change on standing for long periods, it is recommended that fresh buffer solutions be prepared as needed to avoid any possibility of decomposition.

Zusammenfassung—Eine 0,2*M* Losung von Natrium Wasserstoff-diglycolat hat pH 3,40 ± 0,02 und wird von dem allgemein erhaltlichen Salz hergestellt. pH dieser Losung ist uber einem bruten Temperatur-Gebiet konstant und hat eine hohe Puffer-Kapazitat. Der Zusatz von Salz bis Konzentration von 0,05*M* bringt keine grosse Anderung mit sich.

Zweifacher Verdunning der 0,2*M* Losung beeinflusst pH nicht mehr als ±0,02 Einheit. Man kann fur langere Zeit die Losung mit nur kleiner Änderung in pH aufbewahren. Natrium Wasserstoff-diglycolat ist hygroskopisch und ist in primare Normal-Grad anwendbar. Nur Hg_2^{2+} wird durch den Puffer niedergeschlagen.

Durch diese Eigenschaften ist diese Verbindung anwendbar als Referenz-Puffer fur das Normalisieren von Elektroden-Systemen, und als Puffer in analytischen und biochemischen Verfahren.

Résumé—Une solution acide 0,2*M* de diglycolate de sodium, facilement préparée à partir du sel commercial a un pH de 3,40 ± 0,02. Le pH de cette solution est constant entre des limites de température assez larges. Une solution 0,2*M* de diglycolate de sodium a de hautes capacités comme tampon

L'addition d'un sel jusqu'à une concentration de 0,05*M* influe peu le pH Lorsqu'on dilue la solution par un facteur de deux le pH ne varie que de ±0,02 unité La solution se conserve pendant un temps considérable sans beaucoup de variation du pH. Le diglycolate de sodium n'est pas hygroscopique, il est vendu à l'état de pureté conforme à un étalon. Parmi les ions métalliques courants seul le Hg_2^{2+} est précipité par le tampon

Ces propriétés permettent l'utilisation du diglycolate de sodium comme tampon de référence pour l'étalonnage des systèmes aux électrodes, et comme tampon dans divers procédés des chimie analytique et biologique

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PHOTOMETRIC TITRATION OF PHENOLS

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(*Received* 4 *March* 1958)

Summary—A photometric titration method for the determination of phenols has been developed which is applicable to concentrations of phenols of 10^{-3} molar or greater with an average deviation of about 1%. Phenols with aqueous pK_A values ranging from 5 to approximately 11 were titrated without difficulty. Also, differentiating titrations of phenol mixtures were successfully performed.

ALTHOUGH a large number of methods for the determination of phenols may be found in the literature, most of these have serious limitations, the most common of which is the failure of the method to give positive results with a wide variety of phenols. In particular, colorimetric and bromination methods depend upon certain positions in the ring being unsubstituted. Even with the required ring positions free, many substituted phenols either fail to react or react in an unknown or undependable way. Some methods are not specific for phenols as a class but give identical results with other compounds such as alcohols, aromatic amines, and carboxylic acids. This disadvantage is encountered with bromination, acetylation, benzoylation, and reaction with lithium aluminium hydride Many reactions such as acetylation, benzoylation and bromination are time consuming and lack a high degree of precision and accuracy.

The potentiometric titration of phenols in basic solvents with strong bases using a variety of electrode pairs has proved to be the most accurate method for a variety of phenols. Mass, Elliott and Hall[6] successfully titrated phenols in ethylenediamine using sodium aminoethoxide as titrant and a hydrogen–calomel or antimony–antimony electrode system. Fritz and Lisicki[3] were able to titrate phenol in butylamine with 1% accuracy using a glass–antimony electrode combination and sodium methoxide in benzene–methanol as the titrant. Phenols were titrated in dimethylformamide using a glass–calomel electrode system by Deal and Wyld;[2] and Harlow, Noble and Wyld[5] used a polarised platinum wire as an indicating electrode for the titration of phenols in ethylenediamine The most severe limitation of these potentiometric methods is the inability to determine phenols in the presence of other weak acids.

The application of photometric titration to the determination of phenols appears to offer a precise and accurate method which would be free of most of the limitations encountered with other methods Goddu and Hume[4] were able to titrate a few substituted phenols in the visible region of the spectrum by a simple photometric technique. In the procedure reported here, a wide variety of phenols in butylamine were titrated with sodium hydroxide solution in methanol. Monochromatic radiation was passed through the titration vessel and the change in absorbance of the reaction product, the appropriate phenate ion, was used to detect the equivalence point. In addition, the method has been used to titrate mixtures of phenols.

APPARATUS AND REAGENTS

A 0 05*M* solution of sodium hydroxide was prepared by dissolving reagent grade sodium hydroxide in absolute ethanol The solution was filtered and stored under nitrogen in polyethylene bottles. The standardisation of this solution was accomplished by titrating weighed samples of reagent-grade benzoic acid dissolved in ethanol using Thymol blue as indicator.

Eastmans' highest purity butylamine was redistilled before use

Standard phenol solutions were prepared by dissolving distilled reagent grade phenol in butylamine and were standardised by bromination using a standard bromate–bromide solution.

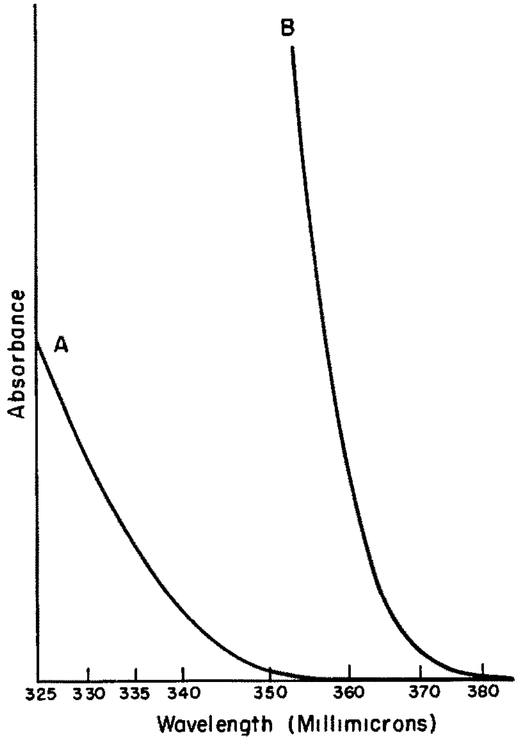

FIG. 1 —Absorption spectra of *p*-hydroxydiphenyl and its phenate anion.
A *p*-hydroxydiphenyl B. *p*-hydroxydiphenyl anion

p-Chlorophenol, 2:4 6-trichlorophenol, and α-phenyl-*p*-cresol were each recrystallised three times from petroleum ether, dried in a vacuum desiccator, and weighed as pure compounds All other phenols were used without further purification

The photometric titration apparatus consisted of a Beckman Model DU monochromator and ultraviolet light source, a cubical glass cell of 125-ml capacity, and an American Instrument Company photoelectric microphotometer unit A calibrated 10-ml microburette was employed, and both mechanical and magnetic stirring were used

PROCEDURES

The ultraviolet and visible absorption spectrum of each phenol and its phenate anion were determined with a Beckman DK–1 Spectrophotometer In every case examined, neutralisation of a phenol resulted in a shift in absorbance to longer wavelengths (Fig 1) A wavelength at which only the phenate anion absorbed was chosen for titration The instrument was set initially at zero absorbance at the wavelength selected by adjustment of the slit width

Titration of a 0 1-milliequivalent sample of a phenol with 0 05*N* alcoholic sodium hydroxide was carried out using 100 ml of butylamine as solvent The titrant was added in 0 2-ml increments and the absorbance values were plotted against titrant volume Straight lines were drawn through

TABLE I —TITRATION RESULTS FOR 0 001M SOLUTIONS OF PHENOL

Wavelength	Meq taken	Meq. found	Deviation	Error
331	0 101	0 102	0 002	0 001
		0 0995	0 0005	0 0015
		0 0985	0 0015	0 0025
		0 0985	0 0015	0 0025
		0.101	0 001	0 000
		0 101	0 001	0 000
		0 0995	0 0005	0 0015
		0 101	0 001	0 000
		0 0985	0 0015	0 0025
		0 101	0 001	0 000
		Av 0 100	0 0012	0 0012

Average deviation	1 2%
Average error	1 2%

the linear portions of the plots, and the titrant volume measured between the two intersections gave the volume of base required to titrate each sample of phenol

During the titration the solution in the cell was stirred continuously and nitrogen was passed through the cell compartment

RESULTS AND DISCUSSION

The results of the titration of eleven different phenols each titrated individually at a wavelength at which the only absorbing species in solution was the phenate ion are shown in Tables I and II. In the case of very weakly acidic phenols an initial horizontal region of zero absorbance was obtained on the titration curve (Fig. 2). This initial volume of titrant was used to titrate the carbon dioxide dissolved in the

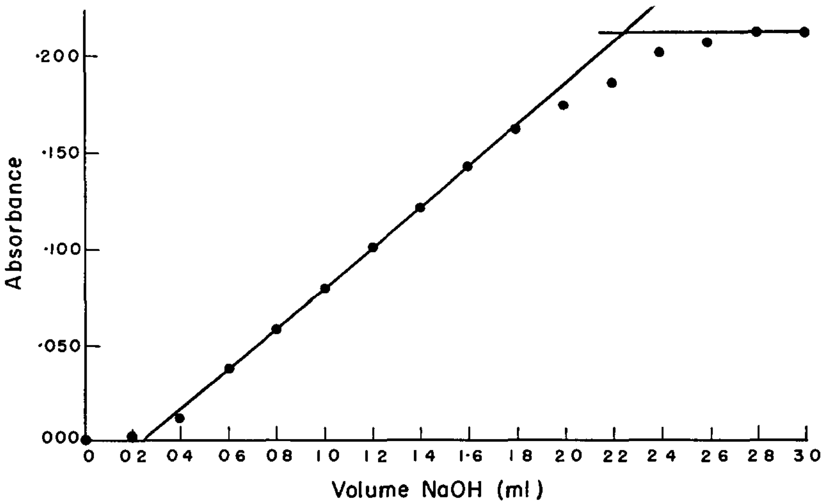

FIG. 2 —Photometric titration curve for p-hydroxydiphenyl

TABLE II.—RESULTS OF PHOTOMETRIC TITRATION OF PHENOLS

Phenol titrated	Wavelength (mμ)	Meq taken	Meq. found	% Recovery
8-Hydroxyquinoline	479	0 100	0 100	100
			0 0994	99 4
			0 0989	98 9
			0 0989	98 9
			0 0984	98 4
p-Hydroxydiphenyl	372	0 100	0 101	101
			0 102	102
			0 103	103
4-Methylumbelliferone (4-methyl-7-hydroxycoumarin)	444	0 101	0 101	100
			0 101	100
			0 102	101
Methylsalicylate	380	0 0984	0.102	104
			0.102	104
			0 102	104
Phenylsalicylate	382	0 100	0 100	100
			0 101	101
			0 101	101
p-Nitrophenol	482	0 100	0 0980	98 0
			0 0995	99 5
			0 0970	97 0
2:4:6-Trichlorophenol	358	0.100	0 0985	98.5
			0 100	100
			0.101	101
2:4-Dibromophenol	360	0 100	0 101	101
			0.102	102
			0.102	102
4-Chloro-3-methylphenol	341	0 101	0.101	100
			0 101	100
			0 0996	98 6
2.4-Dimethylphenol	341	0 100	0 0962	96 2
			0.0962	96 2
			0.0977	97 7

butylamine. However, the carbon dioxide content of the butylamine solvent can be varied over a wide range without any change in the titration results for any phenol.

Attempts to titrate solutions of phenols which were less concentrated than 0.001M were unsuccessful and invariably gave high results. Evidently most phenols are too weakly acidic to be titrated at concentrations less than 0 001M due to the fact that, even though titrant may be added beyond the equivalence point until an absorbance plateau is reached, the slope of the initial portion of the curve will be too low. Therefore, extrapolation to intersect the plateau line resulted in high values.

There seemed to be no upper limit in the pK_A value for a phenol which would prevent its being titrated successfully by this method. The weakest acids tried (aqueous pK_A values of 11 or greater) were titrated without difficulty. It should be pointed out,

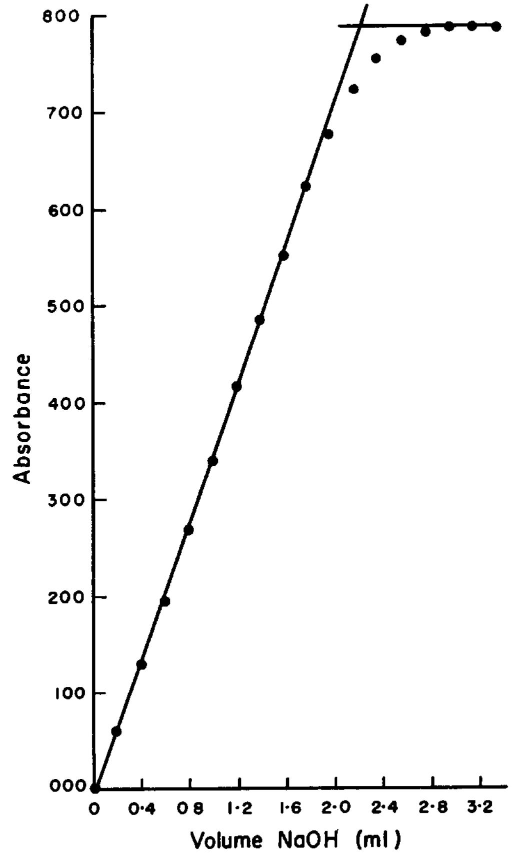

FIG. 3.—Photometric titration curve for 2 4-dibromophenol in the presence of phenol.

however, that it is not possible to titrate a strong phenol by this procedure without some modification. For example, it has been shown that, in pyridine, *p*-nitrophenol is essentially un-ionised, the dinitrophenols are partially ionised, and 2:4:6-trinitrophenol is completely ionised.[1] It would not be possible, therefore, to titrate 2:4:6-trinitrophenol by measurement of phenate absorbance. Titration of such a strong acid could be accomplished by the addition of phenol to the solution; the appearance of the phenate (of phenol) absorbance could be used as the indicator of the equivalence point for the titration of the strong acid.

After the titration procedure had been shown to be successful with individual phenols, differentiating titrations of mixtures of phenols were attempted. In any mixture of phenols, that one which is the strongest acid will be titrated first. Therefore, the procedure used was to titrate the mixtures at the wavelength at which the phenol which was the strongest acid had been titrated individually. If there was a sufficient difference in acidity between this phenol and the others to permit establishment of an initial linear section of the titration curve, the correct equivalence point for the strongest phenol could be determined in the usual manner. Such a titration curve is shown in Fig. 3 for the titration of 2:4-dibromophenol in an equimolar mixture of 2:4-dibromophenol and phenol.

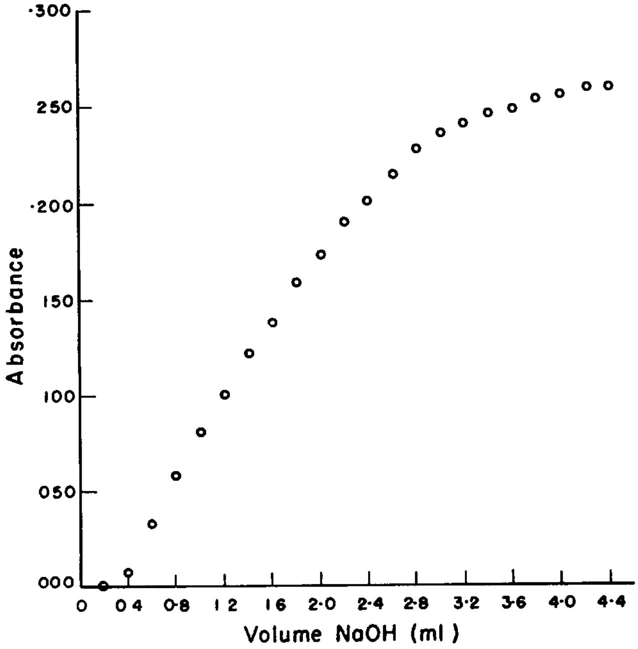

FIG. 4.—Photometric titration curve of a mixture of *p*-hydroxydiphenyl and 2:4-dimethylphenol

If the acidities of the phenols in a mixture are too nearly the same, the titration curve has no linear region at the beginning; only a continuous curve is noticed until the plateau is reached. An example of this type of curve is shown in Fig. 4 for the titration of an equimolar mixture of 2:4-dimethylphenol and *p*-hydroxydiphenyl.

Table III lists the mixtures in which one phenol could be differentially titrated. The first phenol listed in each mixture was the one which could be determined. Table IV lists the phenol mixtures which could not be differentiated. Apparently it is not possible to predict which phenols may be differentially titrated on the basis of aqueous pK_A values alone. For example, *p*-chlorophenol (pK_A 9.0) and phenol (pK_A 9.89) were differentially titrated, but 8-hydroxyquinoline (pK_A 5) and 2,4,6-trichlorophenol (pK_A 7.0) could not be. Also, although methylsalicylate has an aqueous pK_A of 10 or 11, in butylamine it appears to be an acid of sufficient strength to permit its differential titration in a mixture with phenol. On the other hand, it is too strong an acid to permit its differential titration when mixed with *p*-nitrophenol (pK_A 6.85–7.0). Table V lists the phenols titrated in order of increasing acid strength in butylamine

TABLE III —RESULTS OF DIFFERENTIAL TITRATION OF PHENOL MIXTURES

Mixture*	Wavelength	Meq. taken†	Meq. found†	% Recovery†
Phenylsalicylate (phenol)	382	0 100	0 102 0 0983 0 0983	102 98 6 98 6
Methylsalicylate (phenol)	380	0 0984	0 0962 0.0983	97.8 99 9
Methylsalicylate (α-phenyl-*p*-cresol)	380	0 0984	0.0962 0.0973	97 8 98 9
Phenylsalicylate (*p*-hydroxydiphenyl)	382	0 100	0 101 0.102	101 102
8-Hydroxyquinoline (methylsalicylate)	479	0 100	0 0999 0.100	99 9 100
p-Nitrophenol (*p*-hydroxydiphenyl)	482	0.100	0.0990 0 0995	99 0 99.5
2:4:6-Trichlorophenol (α-phenyl-*p*-cresol)	358	0 100	0 101 0 102	101 102
p-Chlorophenol (phenol)	336	0 101	0 102 0 103	101 102
2 4-Dibromophenol (*p*-chlorophenol)	360	0 100	0 0991 0 101	99.1 101
p-Nitrophenol (4-chloro-3-methylphenol)	482	0.100	0.0999 0 0988	99 9 98 8
2 4 6-Trichlorophenol (4-chloro-3-methylphenol)	358	0.100	0 100 0 101	100 101
p-Nitrophenol (*p*-chlorophenol)	482	0 100	0 100 0 101	100 101
2 4-Dibromophenol (phenol)	360	0 100	0 0994 0 0988	99 4 98.8
2 4-Dibromophenol (phenol) (2:4-dimethylphenol) (α-phenyl-*p*-cresol)	360	0 100	0 100 0 101	100 101
2 4-Dibromophenol (0 01M phenol)	360		0 0988 0 100	98 8 100

* For each mixture, the first phenol listed was the one determined by differential titration The phenol in parentheses was not determined.

† Values are for the first phenol listed in each mixture.

TABLE IV—PHENOL MIXTURES WHICH COULD NOT BE DIFFERENTIALLY TITRATED

p-Hydroxydiphenyl α-Phenyl-*p*-cresol	8-Hydroxyquinoline 2 4:6-Trichlorophenol
p-Hydroxydiphenyl Phenol	8-Hydroxyquinoline 2:4-Dibromophenol
4-Methylumbelliferone Methylsalicylate	4-Chloro-3-methylphenol 2.4-Dimethylphenol
p-Nitrophenol 8-Hydroxyquinoline	4-Chloro-3-methylphenol *p*-Chlorophenol
p-Nitrophenol 2.4.6-Trichlorophenol	*p*-Hydroxydiphenyl 2:4-Dimethylphenol
α-Phenyl-*p*-cresol Phenol	Phenylsalicylate Methylsalicylate

TABLE V RELATIVE ACIDITIES OF PHENOLS IN BUTYLAMINE

Compound	Aqueous pK_A
α-Phenyl-*p*-cresol	11.0–11.5*
p-Hydroxydiphenyl	
2:4-Dimethylphenol	10 58
Phenol	9 89
4-Chloro-3-methylphenol	10 5–11 0*
p-Chlorophenol	9 02, 9 05
4-Methylumbelliferone	
Phenylsalicylate	
Methylsalicylate	11 0, 10 19
2:4-Dibromophenol	9.3*
2·4 6-Trichlorophenol	7.0
p-Nitrophenol	7 00; 6 85
8-Hydroxyquinoline	5.0

* Value determined by measurement of pH half-way to equivalence point when titrated in ethanol–water mixture with aqueous sodium hydroxide.

Salicylic acid, *p*-hydroxybenzoic acid and thiophenol were found to give insoluble salts when titrated in butylamine with alcoholic sodium hydroxide. Although these acids could not be titrated photometrically because of this insoluble salt formation, other titrants, such as quaternary ammonium hydroxides, would probably produce more soluble salts with these phenols. Only two acids, uric acid and tyrosine, were found to be insoluble in butylamine.

Zusammenfassung—Es wird ein photometrisches Titrationsverfahren fur die Bestimmung von Phenolen entwickelt, das für eine Konzentration von $10^{-3}M$ oder mehr mit einer Durchschnitts-Abweichung von ungefahr 1 % verwendbar ist.

Man kann ohne Schwerigkeit Phenole mit pK_A-Werte im Wasser von 5 bis ungefahr 11 titrieren und auch Differential-Titrationen von Phenol-mischungen erfolgreich durchführen.

Résumé—Les auteurs ont mis au point une méthode de dosage des phénols par titrage photométrique. Cette méthdoe est applicable aux concentrations molaires en phénol de 10^{-3} ou plus, avec un écart moyen d'environ 1% On a pu titrer sans difficulté des phénols dont pK_A aqueuse sont compris entre 5 et approximativement 11. On a pu également effectuer avec succès des titrages de différenciation des mélanges des phénols

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A NEW EXTRACTION METHOD FOR THE DETERMINATION OF COPPER

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(*Received* 27 *February* 1958)

Summary—It has been shown that copper^I pyridinohalide complexes, and in particular the bromide and iodide complexes, may be utilized for the rapid separation of copper from a number of other cations by extraction with chloroform. The copper in the extract may suitably be determined complexometrically Zinc can be masked by iminodiacetic acid, this procedure fails, however, in the case of cadmium and mercury which pass into the chloroform layer even in the presence of iminodiacetic acid

EXTRACTION methods are becoming increasingly important in analytical chemistry. The extraction methods used in metallurgical analysis have recently been reviewed by West.[1] The extraction of copper has been carried out by a number of methods;[2] small amounts are most commonly extracted as the diethyldithiocarbamate complex and then determined colorimetrically; larger amounts are extracted as copper^{II} dipyridinothiocyanate. For the separation of traces of copper from nickel and cobalt, Alimarin and Koreneva have proposed extraction of the salicylaldimine complex.[3] We have now investigated the extraction of copper^I pyridinohalide complexes, followed by complexometric determination of copper.

The copper^I halides are well known to be soluble in pyridine. Various complex salts such as $Cu(Py)_2X$,[4–6] $Cu(Py)_3X$,[4,7] or $CuX\,HX.(Py)_{1-2}$[8] have been described. However, no attempts to utilise such complexes analytically appear to have been recorded.

We have now found that copper may be extracted in the form of its complexes from solutions containing copper^I, pyridine, and chloride, bromide or iodide ions by organic solvents such as chloroform. This solvent also dissolves the pyridinohalides, in particular the pyridinoiodides of zinc (cf.[9]), cadmium, and mercury. By using iminodiacetic acid in the extraction procedure it has proved possible to achieve the separation of copper and zinc.

The complexometric titration of copper was carried out in weakly acid solution with Glycinethymol Blue as indicator,[10] or in alkaline solution with 3:4-dihydroxy-4′-nitroazobenzene.[11] Other cations were titrated using Xylenol Orange[12,13] or Methylthymol Blue.[14]

EXPERIMENTAL AND RESULTS

Reagents

Solutions of suitable salts of various cations (0 05*M*) were prepared from analytical-reagent grade chemicals and standardized by the customary procedures.

A standard 0 05*M* solution of disodium ethylenediaminetetra-acetate was prepared from "Chelaton 3" (Chemapol, Prague) in the usual manner

The indicators Glycinethymol Blue, Xylenol Orange and Methylthymol Blue (all from Chemapol, Prague) were used as 1 100 mixtures with sodium chloride, the 3:4-dihydroxy-4′-nitroazobenzene as 0 1% solution in ethanol.

All other reagents used, such as pyridine, chloroform, iminodiacetic acid, and hexamethylenetetramine, were of analytical-reagent grades

Apparatus

Separating funnels of 100 ml capacity similar to those described by Hunter and Miller[9] were used.

Reduction of copper and extraction of the copper^{I} pyridinohalide complexes

The most satisfactory reagent for reduction of copper^{II} ions in solutions buffered with pyridine proved to be hydroxylamine hydrochloride. In a series of experiments the efficiency of the chloroform extraction was examined, using a constant excess of hydroxylamine hydrochloride and various amounts of pyridine.

TABLE I PERCENTAGE OF COPPER EXTRACTED INTO CHLOROFORM IN THE PRESENCE OF VARIOUS AMOUNTS OF PYRIDINE AND OF CHLORIDE, BROMIDE, OR IODIDE

1 ml of 1*M*	Pyridine, ml					
	0·2	0·5	1	2	3	5
Cl^-[a]	66·1	76·2	91·5	92·5	89·9	86·5
Br^-	96·0	97·9	98·9	99·3	99·0	98·6
I^-	99·3	99·5	99·7	99·7	99·5	98·6

[a] Added as hydroxylamine hydrochloride only.

10 Ml of 0·05*M* $CuSO_4$ were treated with 1 ml of 1*M* hydroxylamine hydrochloride and the appropriate amount of pyridine, and the solution extracted once with 10 ml of chloroform. The copper content of each phase was determined separately by the procedure described below. Two further sets of experiments were carried out in the same way but with the addition of 1 ml of 1*M* KBr or 1*M* KI, respectively, to each solution. The results are summarised in Table I

An increase in the halide concentration was found to lead to improved extraction, thus with 2 ml of (pyridine-chloride) complex the further addition of 2 ml of 1*M* NaCl increased the percentage of copper extracted from 92·5 to 95·5.

When 1 ml of 1*M* NaCl was added instead of the hydroxylamine hydrochloride, 3·8% of the copper passed into the chloroform phase; in an analogous experiment with KBr, 30·4%; and when KI was used the halide sufficed to bring about reduction and 94·0% of the copper was found in the extract.

In the presence of iminodiacetic acid the reduction of copper^{II} by hydroxylamine hydrochloride proceeds less readily, particularly in the presence of chloride ions only. Even when iodide solutions are used larger amounts of hydroxylamine hydrochloride (5 ml of 1*M* solution) and more thorough shaking are required. Reduction with ascorbic acid readily takes place in the presence of iodide or bromide, less readily in solutions containing chloride.

Behaviour of certain other cations under the conditions used for the extraction of copper

Further series of experiments were carried out using 10 ml of 0·05*M* solutions of Ni^{2+}, Co^{2+}, Fe^{3+}, Ca^{2+}, Ag^{+}, Au^{3+}, VO_3^{-}, Mn^{2+}, UO_2^{2+}, Pd^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Bi^{3+}, MoO_4^{2-} salts with 1 ml of 1*M* hydroxylamine hydrochloride, and 2 ml of pyridine, with or without the addition of KBr or KI; each solution was extracted once with 10 ml of chloroform. Some of the cations (Fe, Al, U, Mo, Ag) give rise to precipitates which remain suspended in the aqueous phase so that the chloroform can be run off without difficulty. Au and Pd are reduced to the metals; here, too, separation of the chloroform layer is straightforward Bi and Pb form precipitates suspended in both phases so that filtration is necessary All other cations remain in solution. In some cases the chloroform layer was analysed for the cation concerned; the results are shown in Table II.

Complexometric determination of copper in the chloroform extract

(1) *Titration with 3:4-dihydroxy-4′-nitroazobenzene in alkaline solution.*[11] The chloroform extract is layered with 100 ml of distilled water in a titration flask; 5 ml of concentrated aqueous ammonia and 5 ml of 0·5*N* NaOH are added followed by a few drops of the indicator solution, and the solution

is titrated with 0·05*M* Complexone to a pure blue tint. Toward the end-point thorough shaking is necessary since the last traces of copper are extracted from the chloroform layer with some difficulty.

(2) *Titration with Glycinethymol Blue in weakly acid solution* [10] The extract is evaporated in a titration flask on the water-bath to remove the chloroform and some of the pyridine. Concentrated nitric acid is added dropwise until the colour changes and the solution is boiled to decompose the halide complexes (in the case of iodine, free iodide escapes). The solution is diluted to 200–300 ml with distilled water, some Glycinethymol Blue is added followed by sufficient hexamethylenetetramine to give an intense blue coloration, and the solution is titrated with 0·05*M* Complexone to a yellow or emerald-green tint (depending on the amount of copper present).

TABLE II. PERCENTAGE EXTRACTION OF VARIOUS METALS INTO CHLOROFORM IN THE PRESENCE OF PYRIDINE AND CHLORIDE, BROMIDE, OR IODIDE

Cation	1 ml of 1*M*		
	Cl^-	Br^-	I^-
Zn^{2+}	41·8	48·2	58·0
		97·5[a]	
Cd^{2+}	69·5[b]	30·5[b]	99·0
Hg^{2+}	96·5	99·7	99·7
Co^{2+}	—	<0·3	0·6
Ni^{2+}	0·3	0·6	1·6
Pb^{2+}	—	<1[c]	<1[c]

[a] 10 ml of 1*M* KBr.

[b] A precipitate not readily soluble in chloroform is formed; the results cannot be regarded as expressing equilibrium conditions.

[c] Precipitates are formed; filtration of the extract was necessary

Note: The second procedure is to be preferred for accurate work The amount of indicator which must be used is governed by the amount of copper present since the colour of the indicator at the end-point must cover that of the blue copper–ethylenediaminetetra-acetate complex The acidity of the solution increases in the course of the titration; if the blue colour of the indicator gradually fades, more hexamethylenetetramine must be added.

Examples of the separation of copper from other cations

(1) *Separation of copper from cobalt, nickel, iron, aluminium, uranium, manganese, molybdenum, and vanadium* A mixture of 10 ml of 0·05*M* Cu^{2+}, 10 ml of 0·05*M* Ni^{2+}, and 10 ml of 0·05*M* Co^{2+} was treated with 1 ml of 1*M* hydroxylamine hydrochloride, 2 ml of pyridine, and 2 ml of 1*M* KBr. The solution was extracted with three 10-ml lots of chloroform, 1 ml of pyridine being added before the second and third extraction Each extract was in turn washed in a second separating funnel with a mixture of 5 ml of water, 1 ml of pyridine, 1 ml of 1*M* hydroxylamine hydrochloride, and 1 ml of 1*M* KBr; before the washing of the second and third chloroform extracts, 1 ml of pyridine was again added to the aqueous mixture The chloroform extracts were combined in a titration flask and the copper determined by the procedure described above, using Glycinethymol Blue as indicator

By the same procedure, copper was determined in the presence of Fe^{3+}, Al^{3+}, UO_2^{2+}, Mn^{2+}, Mo^{VI}, and V^{V} The results are recorded in Table III

The low results obtained in the presence of aluminium and molybdenum are evidently due to some of the copper being carried down in the precipitates

(2) *Separation of copper and zinc* A mixture of 10 ml of 0·05*M* Cu^{2+} and 10 ml of 0·05*M* Zn^{2+} was treated with about 0·5 g of iminodiacetic acid, 2 ml of pyridine, 0·2 g of ascorbic acid, and 5 ml of 1*M* KI The mixture was extracted with three successive 10-ml lots of chloroform as described above, and each extract was again washed in a second separating funnel with a mixture of 5 ml of

water, 1 ml of $1M$ KI, and 1 ml of pyridine containing small amounts of iminodiacetic acid and ascorbic acid. The copper was titrated using Glycinethymol Blue as described above The zinc in the aqueous phase could be titrated using Xylenol Orange[12,13] or Methylthymol Blue[14] regardless of the presence of iminodiacetic acid; the end-points were somewhat less sharp than in pure solution but nevertheless readily detected

A similar procedure (with bromide in place of iodide) was used for separation of copper from aluminium or lead, no precipitates were formed under these conditions. The results obtained are included in Table III

TABLE III. DETERMINATION OF COPPER IN THE PRESENCE OF OTHER CATIONS (GIVEN 10 ml OF $0·05M$ Cu^{2+} AND 10 ml OF $0·05M$ SOLUTIONS OF THE APPROPRIATE CATION)

Metal added	Found ml of $0·05M$ Cu^{2+}
$Ni^{2+} + Co^{2+}$	9·99
Fe^{3+}	9·98
Al^{3+}	9·93; 9·98[a]
Mo[b]	9·88
V[c]	9·99
Mn^{2+}	10·00
UO_2^{2+}	9·98
Zn^{2+}	9·98[a]
Pb^{2+}	10·05[a]

[a] In the presence of iminodiacetic acid

[b] As ammonium molybdate.

[c] As ammonium vanadate

Note The iminodiacetic acid may also be added to the aqueous phase in the second separating funnel only In this way both zinc and copper may be isolated and separately determined in complex mixtures, the copper being found in the chloroform extract and the zinc in the aqueous phase in the second separating funnel.

Zusammenfassung—Es wurde gezeigt, dass die Chloroform-extraktion der Kupfer(I)-pyridino-halogenid-Komplexe, besonders des Bromids und des Jodids, fur die rasche Trennung des Kupfers von einer Reihe anderer Kationen benutzt werden kann Das Kupfer wird im Chloroformextrakt komplexometrisch bestimmt. Zink kann mit Iminodiessigsaure maskiert werden Eine solche Tarnung ist jedoch fur Cadmium und Quecksilber unbrauchbar, weil diese Elemente auch in der Anwesenheit der Iminodiessigsaure in die Chloroformschicht ubergehen

Résumé—On a montré que les complexes pyridinohalogéniques du cuivre-I, et en particulier les complexes du bromure et de l'iodure, permettent la séparation rapide du cuivre d'avec un certain nombre d'autres cations par extraction par le chloroforme. Le dosage complexométrique du cuivre extrait est alors possible Le zinc peut être masqué par l'acide iminodiacétique. ce procédé ne réussit pourtant pas dans les cas du cadmium et du mercure, qui passent dans la couche chloroformique même en présence de l'acide iminodiacétique

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ZUR THEORIE DER VISUELLEN INDICATION UND SELECTIVITÄT KOMPLEXOMETRISCHER TITRATIONEN

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(*Received* 14 *January* 1958)

Zusammenfassung—Aufgrund vereinfachender Annahmen, die jedoch in der Praxis weitgehend zutreffen, werden Formeln abgeleitet, die nach Einsetzen der nötigen Parameter rasch ein Aussage über Lage und Güte von Endpunkten bei komplexometrischen Titrationen liefern Das Problem der Selectivität wird behandelt Als ungefähre Anhaltswerte ergaben sich folgende Daten Um unter durchschnittlichen Bedingungen (0,1% Fehler und Metallionenkonzentration etwa 0,01*M*) eine komplexometrische Titration durchzuführen, muss die Stabilitätskonstante des zu titrierenden Metalles mindestens 10^8 sein Der Indicatorkomplex muss eine Konstante von wenigstens 10^4 besitzen Störmetalle bei Titrationen ohne Indicator müssen bei Anwesenheit äquimolarer Mengen wenigstens eine 10^6-mal kleinere Stabilitätskonstante aufweisen In Gegenwart eines komplexbildenden Indicators muss sich die Stabilität des Indicatorkomplexes wenigstens um den Faktor 10^{-4} von der des Titrationskomplexes unterscheiden. Ein Störmetall muss mindestens 10^{-10} bis 10^{-8} mal schwächer binden als das Hauptmetall

EINLEITUNG

DIE Behandlung titrimetrischer Probleme ist am übersichtlichsten und einleuchtendsten, wenn man die Titrationskurven berechnet und diskutiert. Diesbezügliche Berechnungen und graphische Darstellungen sind von verschiedenen Autoren mitgeteilt worden und auch Schwarzenbach hat eindrucksvolle Beispiele in seiner Monographie[1] gegeben, soweit es komplexometrische Titrationen betrifft Allein die Durchrechnung einer vollen Kurve ist zeitraubend. Wir haben es uns daher zum Ziele gesetzt Formeln abzuleiten, aus denen man durch blosses Einsetzen der nötigen Zahlenwerte sofort zu Resultaten kommt, die ein Abschätzen der zu erwartenden Situation (Lage des Endpunktes, dessen Güte, Fehler der Titration usw.) gestattet. Für die komplexometrische Titration eines einzelnen Metalles unter Verwendung eines komplexbildenden Indicators wurde solch eine Ableitung schon früher mitgeteilt[2]. In einer anderen Arbeit wurden Ansätze gemacht[3], das Problem der Titration von Zweimetallsystemen ohne Indicator zu behandeln. In der vorliegenden Publikation ist die Weiterführung und Verfeinerung dieses Beginnens niedergelegt und die Formulierung für Ein- und Zweimetallsysteme mit und ohne Indicator wird geschlossen dargestellt. Dies bedeutet zugleich die Behandlung des Selectivitätsproblemes komplexometrischer Titrationen.

VEREINFACHUNGEN UND SYMBOLE

Solche Ableitungen sind natürlich nicht ohne vereinfachende Annanmen möglich, wenn vermeiden werden soll, dass die Formeln einen Umfang annehmen, der ihre Diskussion und praktische Handhabung illusorisch macht. Allein es wurde strikte darauf geachtet, bei den Vereinfachungen den Boden der Wirklichkeit nicht zu verlieren. Durchrechnung zahlreicher Probleme, für die alle Daten aus der Literatur bekannt waren, haben ausgezeichnete Übereinstimmung zwischen Theorie und

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Praxis gezeigt und darüber hinaus waren Berechnungen dieser Art oftmals ein zuverlässiger Leitfaden bei der Ausarbeitung neuer Methoden.

Voraus sei bemerkt, dass es sich in vorliegender Arbeit bei allen Stabilitätskonstanten, wenn nicht ausdrücklich anders bemerkt, um die scheinbaren Konstanten handelt. D.h. man hat die absoluten Konstanten gemass den jeweils herrschenden Titrationsbedingungen umzurechnen und zwar durch Berucksichtigung des α_H-Wertes für den Einfluss des pH der Lösung und des β_A-Wertes für die Wirkung eines allenfalls anwesenden weiteren Komplex bildners Zur näheren Einsicht sei diesbezüglich auf Schwarzenbach's Buch[1] verwiesen.

Die abgeleiteten Formeln gelten nur für Komplexe Metall: Komplexbildner = 1 : 1. Der Komplexbildner (Titrator) ist stets durch das Symbol Y gekennzeichnet und bedeutet keineswegs ausschliesslich EDTA Nachfolgende weitere Symbole werden durchlaufend verwendet:

K_M, K_N	scheinbare Stabilitätskonstante eines 1 : 1 Chelates zwischen Titrationsmittel und Metall M bzw N.
K_I	scheinbare Stabilitatskonstante des 1 . 1 Komplexes zwischen Indicator und Metall.
K_{abs}	absolute Stabilitätskonstante.
z	Titrationsfehler in Prozenten.
C_Y, C_M, C_I	Totalkonzentration des Titrationsmittels, Metalles bzw. Indicators in Molen/Liter.
$a = \frac{[M]}{C_M}$	Bruchteil an freiem, d h. nicht an das Titrationsmittel gebundenen Metalles bezogen auf die Totalkonzentration.
$\varphi = \frac{[MI]}{C_I}$	Bruchteil des an das Metall gebundenen Indicators, bezogen auf seine Totalkonzentration.
[ ]	bedeutet durchwegs Konzentration in Molen/Liter. Die Komplexe MY, NY oder MI sind um, Unklarheiten zu vermeiden, als solche geschrieben, ohne die sonst üblichen Klammern.

TITRATION EINES EINZELNEN METALLES OHNE INDICATOR

Grundformeln

Der einfachste Fall ist die Titration eines Metalles, ohne dass ein komplexbildender Indicator verwendet wird. Der Endpunkt werde physikalisch, d.h. potentiometrisch, spectrophotometrisch, amperometrisch oder sonst wie angezeigt. Es ist ohne weiters einzusehen dass bei zu geringer Stabilitat des Titrationskomplexes durch einen zu hohen Grad an Dissoziation der Endpunkt "verwischt" sein wird, oder, graphisch ausgedrückt, der Sprung im Endpunkt nicht scharf ausgeprägt sein kann. Mathematisch erhalten wir folgende Formulierung.

Wir legen fest, dass der Endpunkt erreicht sei, wenn nur mehr z Prozente des Metalles nicht an den Titrationkomplex gebunden sind und operieren mit den folgenden drei Gleichungen, die in jedem Punkte der Titration erfüllt sein mussen

$$K_M = \frac{[MY]}{[M] . [Y]} \tag{1}$$

$$C_M = [MY] + [M] \tag{2}$$

$$C_Y = [MY] + [Y] \tag{3}$$

Solange der gestattete Fehler z sehr klein ist, kann in erster Näherung im oder nahe am Endpunkt $C_M = C_Y$ gesetzt werden. Daraus folgt nach (2) und (3) dass $[M] = [Y]$. Ferner ist definitionsgemäss $[M] = z \, . \, 10^{-2} \, . \, C_M$. Setzt man das in (1) ein, so folgt

$$K_M = \frac{1 - z \, . \, 10^{-2}}{C_M \, . \, z^2 \, . \, 10^{-4}} \tag{4}$$

Solange der Fehler klein ist gilt, $1 \gg z \, . \, 10^{-2}$ und die Formel vereinfacht sich zu

$$K_M = \frac{10^4}{C_M \, . \, z^2} \tag{5}$$

Daraus lässt sich für vorgegebenes K_M der Fehler berechnen zu

$$z = \frac{10^2}{\sqrt{K_M \, . \, C_M}} \tag{6}$$

In dieser vereinfachten, bereits anderwärts gegebenen Ableitung ist jedoch ausser acht gelassen, dass bei Erreichen des praktischen Endpunktes $C_M \neq C_Y$ ist und weiters ist nicht festgelegt, wann der Endpunkt als erreicht gelten soll. Eine verfeinerte Ableitung ergibt sich aus folgenden Überlegungen. Nach wie vor gelten natürlich die Gleichungen (1)–(3). Wir legen nun fest, dass der Endpunkt erreicht sein soll, wenn nur mehr der Bruchteil a an Metall nicht an den Komplexbildner gebunden ist. (Üblichen Bedingungen entsprechend ist a etwa 10^{-3} bis 10^{-4}.) Somit ergibt sich $[M] = a \, . \, C_M$. Dies in Kombination mit (1) bis (3) ergibt nach C_Y aufgelöst

$$C_Y = \frac{(1 - a) \, . \, (K_M \, . \, a \, . \, C_M + 1)}{K_M \, . \, a} \tag{7}$$

Der prozentuale Fehler ist definitionsgemäss

$$z \equiv \frac{C_Y - C_M}{C_M} \, . \, 100 \tag{8}$$

Einsetzen von (7) in (8) ergibt nun

$$z = \frac{1 - a \, . \, (K_M \, . \, a \, . \, C_M + 1)}{K_M \, . \, a \, . \, C_M} \, . \, 100 \tag{9}$$

Multipliziert man die Klammer aus und berücksichtigt, dass $a \ll 1$ so erhält man

$$z = \frac{1 - K_M \, . \, a^2 \, . \, C_M}{K_M \, . \, a \, . \, C_M} \, . \, 100 \tag{10}$$

Für sehr grosses K_M gilt $1 \ll K_M \, . \, a^2 \; C_M$ und wir erhalten $z \, . \, 10^{-2} = -a$ Wie zu erwarten kann bei hohen Stabilitäten, die Genauigkeit nahezu beliebig weit getrieben werden und hängt nur davon ab, wie wir den Endpunkt als erreicht festsetzen. Die Eigendissoziation des Komplexes spielt ja keine Rolle.

Wird K_M dagegen klein, so gilt $1 \gg K_M \, . \, a^2 \, . \, C_M$ und es resultiert

$$z = \frac{10^2}{K_M \;\; a \, . \, C_M} \tag{11}$$

das Analogon zu (6) wenn $a = z \,.\, 10^{-2}$ gesetzt wird. Der Vorteil der verfeinerten Ableitung wird hierdurch sofort offenkundig, denn wir können nun Fehler und Endpunktsdefinition trennen.

Es sei hier bemerkt, dass man aus Formel (7) die Titrationskurven berechnen kann, indem man a als "Titrationsgrad" variiert. Es gilt ja $\mathrm{pM} = -\log(a \,.\, C_{\mathrm{M}})$. Üblicherweise wird als pM der negative Logarithmus der Konzentration der "freien" Metallionen aufgetragen, d.h. der weder an das Titrationsmittel noch an sonst einen Komplexbildner gebundenen. Im Falle also ein weiterer Komplexbildner (z.B. aus dem Puffer) anwesend ist, sind die mit der vorliegenden Formel errechneten pM-Werte kleiner. Dies ist aber völlig unwesentlich, da ja nicht *pM-Werte* sondern *pM-Differenzen* ausschlaggebend sind. Im ubrigen kann man die mit den a-Werten erhaltenen Kurven ohne weiters durch Addition der $\log \beta_{\mathrm{A}}$-Werte des betreffenden weiteren Komplexbildners auf die üblichen Kurven umrechnen.

Grenze der Titrierbarkeit

Die bisherigen Ableitungen erlauben nun die Beantwortung der Frage, welchen Mindestbetrag K_{M} besitzen muss, um bei vorgegebenem, gestatteten Fehler die Titration noch möglich erscheinen zu lassen. Operieren wir der Einfachkeit halber mit Formel (5), so ergibt sich für einen Fehler von 0,1 % und $C_{\mathrm{M}} = 10^{-2}$ dass die (scheinbare!!!) Stabilitätskonstante mindestens 10^8 sein muss. Dieser Wert variiert natürlich mit dem erlaubten Fehler, der Endpunktsdefinition und der Metallionenkonzentration beträchtlich. Wir wollen uns 10^8 aber als einen durchschnittlichen Anhaltspunkt stets gegenwärtig halten.

Es sei betont, dass bei physikalischen Indicationen und auch sonst nicht die Lage des Endpunktes allein fürd ie Güte der Titration massgebend ist, sondern auch die Art, wie der Endpunkt erreicht wird. Wie man dies formelmässig erfassen kann, wird später gezeigt werden. Hier sei nur darauf verwiesen, dass bei den oftmals verwendeten graphischen Verfahren zum Auffinden des Endpunktes, ungünstige Verhältnisse doch zu brauchbaren Ergebnissen führen können, wenn eine Extrapolation von zwei Kurvenästen möglich ist.

TITRATION EINES METALLES NEBEN EINEM ZWEITEN OHNE KOMPLEXBILDENDEN INDICATOR

Grundformeln

Es ist klar, dass die Möglichkeit ein Metall neben einem (oder mehreren) anderen zu titrieren, vom Verhältnis der Stabilitätskonstanten des Komplexes des zu titrierenden Metalles zu der des Störkomplexes abhängt. Offenbar wird die Titration umso günstiger verlaufen, je mehr die beiden Konstanten differieren. Diese rein qualitative Aussage ist jedoch ungenügend und es muss untersucht werden um wieviel die Konstanten differieren müssen, wenn ein vorgegebener Fehler nicht überschritten werden soll, oder mit welchem Fehler bei einem gegebenen Konstantenverhältnis zu rechnen ist.

Voraussetzung sei, dass zwei Metalle, M und N, anwesend sind, wobei nur M titriert werden soll, sodass also gelten muss $K_{\mathrm{M}} > K_{\mathrm{N}}$.

Eine grobe, vereinfachte Ableitung lässt sich sofort geben, wenn man wie im vorigen Abschnitte erst einmal annimmt, dass beide Konstanten genügend hoch sind, sodass die Dissoziation der beiden Komplexe im Endpunkte vernachlässigt werden kann. Folgendes Gleichgewicht liegt dann vor:

$$\mathrm{MY} + \mathrm{N} \rightleftharpoons \mathrm{NY} + \mathrm{M} \tag{12}$$

Im Falle einer guten Titration soll das Gleichgewicht möglichst weit nach links verschoben sein. Unter Verwendung der früher gegebenen Definition für die Konstanten erhält man den Ansatz

$$\frac{[\mathrm{NY}] \,.\, [\mathrm{M}]}{[\mathrm{MY}] \,.\, [\mathrm{N}]} = \frac{K_\mathrm{N}}{K_\mathrm{M}} \tag{13}$$

Im theoretischen Endpunkte mus gelten $C_\mathrm{M} = C_\mathrm{Y}$. Da die Eigendissoziation der Komplexe vernachlässigt werden soll, stammt praktisch alles freie Metall M aus der Verdrängungsreaktion, sodass gilt $[\mathrm{M}] = [\mathrm{NY}]$. Der erlaubte Fehler sei $z\%$ und somit $[\mathrm{M}] = z \,.\, 10^{-2} \,.\, C_\mathrm{M} = [\mathrm{NY}]$. Da der Fehler klein gehalten werden soll, gilt ferner in erster Näherung $[\mathrm{MY}] = C_\mathrm{M}$ sowie $[\mathrm{N}] = C_\mathrm{N}$. Setzt man das alles in (13) ein so kommt

$$z = 100 \,.\, \sqrt{\frac{C_\mathrm{N} \,.\, K_\mathrm{N}}{C_\mathrm{M} \,.\, K_\mathrm{M}}} \tag{14}$$

Das Konstantenverhältnis ergibt sich zu

$$\frac{K_\mathrm{N}}{K_\mathrm{M}} = z^2 \,.\, 10^{-4} \,.\, \frac{C_\mathrm{N}}{C_\mathrm{M}} \tag{15}$$

Für einen Fall, bei dem jedoch die Konstanten so nieder sind, dass die Eigendissoziation der Komplexe nicht vernachlässigt werden darf, und wenn man weiters einführen will, wann der Endpunkt als erreicht gilt, ist eine verfeinerte Ableitung nötig. Folgende Gleichungen müssen in jedem Stadium der Titration erfüllt sein

$$K_\mathrm{M} = \frac{[\mathrm{MY}]}{[\mathrm{M}] \,.\, [\mathrm{Y}]} \tag{16}$$

$$K_\mathrm{N} = \frac{[\mathrm{NY}]}{[\mathrm{N}] \,.\, [\mathrm{Y}]} \tag{17}$$

$$C_\mathrm{Y} = [\mathrm{MY}] + [\mathrm{NY}] + [\mathrm{Y}] \tag{18}$$

$$C_\mathrm{M} = [\mathrm{MY}] + [\mathrm{M}] \tag{19}$$

$$C_\mathrm{N} = [\mathrm{NY}] + [\mathrm{N}] \tag{20}$$

Der Endpunkt sei wieder als erreicht angenommen, wenn $[\mathrm{M}] = a \,.\, C_\mathrm{M}$. Daraus ergibt sich $[\mathrm{MY}] = C_\mathrm{M} \,.\, (1 - a)$. Diese beiden Ausdrücke mit (16) kombiniert ergeben

$$[\mathrm{Y}] = \frac{1 - a}{K_\mathrm{M} \,.\, a} \tag{21}$$

Nun berechnet man [NY] aus (18) und [N] aus (20). Dies sowie (21) wird in (17) eingesetzt und nach C_Y aufgelöst, wonach man erhält

$$C_Y = \frac{\left(\frac{K_M}{K_N} \cdot \frac{1-a}{a} + 1\right) \cdot \left[C_M \cdot (1-a) + \frac{1-a}{K_M \cdot a}\right] + C_N \cdot \frac{K_N}{K_M} \cdot \frac{1-a}{a}}{\frac{K_N}{K_M} \cdot \frac{1-a}{a} + 1} \qquad (22)$$

(22) kann wieder zur berechnung der Titrationskurve harangezogen werden und auch hier gelten die bezüglich (7) am Ende des vorigen Abschnittes gemachten Aussagen.

Der nach (8) definierte, erlaubte Fehler errechnet sich zu

$$z = \frac{\left(\frac{K_N}{K_M} \cdot \frac{1-a}{a} + 1\right) \cdot \left(\frac{1-a}{K_M \cdot a} - a \cdot C_M\right) + C_N \cdot \frac{K_N}{K_M} \, \frac{1-a}{a}}{C_M \cdot \left(\frac{K_N}{K_M} \cdot \frac{1-a}{a} + 1\right)} \cdot 100 \qquad (23)$$

Setzt man in (23) $C_N = K_N = 0$, so ergibt sich (9), was zur Kontrolle dienen kann.

Nun gilt bei einer vernünftigen Titration natürlich $1 \gg a$ womit sich (23) vereinfacht zu

$$z = \frac{\left(\frac{K_N}{K_M} + a\right) \cdot \left(\frac{1}{K_M \cdot a} - a \cdot C_M\right) + C_N \cdot \frac{K_N}{K_M}}{C_M \cdot \left(\frac{K_N}{K_M} + a\right)} \cdot 100 \qquad (24)$$

Ist nun $K_M \gg K_N$ so wird $a \gg K_N/K_M$ und man erhält

$$z = \frac{a \cdot \left(\frac{1}{K_M \cdot a} - a \cdot C_M\right) + C_N \cdot \frac{K_N}{K_M}}{C_M \cdot a} \cdot 100 \qquad (25)$$

Der erste Ausdruck im Zähler ist bei speziellen Bedingungen Null, auf alle Fälle aber bei einigermassen gunstigen Titrationsbedingungen gegen den zweiten zu vernachlässigen. Dann folgt

$$z = \frac{C_N \cdot K_N}{C_M \cdot K_M \cdot a} \cdot 100 \qquad (26)$$

Das ist das analoge Verhaltnis zu (14) wie bei (11) zu (6).

Liegen die Konstanten verhaltnismässig nahe beieinander (Grenzwert siehe unten), so muss mit der genauen Formel (24) gearbeitet werden, wie folgendes Beispiel zeigt. Es sei $K_M = 10^{10}$, $K_N = 10^7$, $a = 10^{-3}$ und $C_M = C_N = 10^{-2}$. Dann ergibt sich nach (26) $z = 100\%$ während (24) den korrekten Wert von 50% liefert.

Das oben bezüglich graphisch erhaltenen Endpunktes Gesagte gilt auch hier. Bemerkenswert ist ferner, dass die Formel (24) bei genauer Inspektion zeigt, dass der Fehler u.U. kompensiert werden kann, was sich ebenfalls an praktischen Beispielen zeigen lässt.

Grenzwert des Konstantenverhältnisses.

Als allgemeinen Anhaltswert errechnen wir auch hier wieder einen Grenzwert fur durchschnittliche Titrationsbedingungen. Der Endpunkt gelte als erreicht wenn $a = 10^{-3}$. Der gestattete Fehler sei 0,1% und die Konzentrationen von M und N seien äquimolar zu 10^{-2} festgelegt. Aus (26) erhält man dann für $K_N/K_M = 10^{-6}$.

Einen in derselben Grössenordnung liegenden Wert erhält man aus (24), wenn berücksichtigt wird, dass K_M nicht unter 10^8 sinken darf, da ja die Titration sonst ohnehin illusorisch wird. Auch hier ändert sich naturlich der Wert des Konstantenverhältnisses stark mit den Bedingungen, doch sei als ungefährer Anhaltswert 10^{-6} festgehalten.

Man erkennt nun unschwer, dass z.B. bei EDTA-Titrationen eine nur beschrankte Selectivitat bestehen kann. Nur die stark bindenden Metalle wie etwa Fe-III, Th, In, Ga, Bi, Hg usw. konnen selectiv titriert werde. Die anderen Metalle nur neben den Erdalkalien und im günstigsten Falle neben Mangan. Wo unter Ausschluss eines komplexbildenden Indicators gearbeitet wird, ist auch bei Verwendung anderer Titrationsmittel das Verhältnis von etwa sechs Zehnerpotenzen immer gewahrt. Man vergleiche hierzu die photometrische Titration von Kupfer mit Trien[3,4]. In der Arbeit sind sämtliche Konstanten angefuhrt. Aus Platzmangel kann in Details hier nicht eingegangen werden. Tatsächlich führten die theoretischen Berechnungen zur praktischen Erprobung dieses Titrationsmittels Die potentiometrische Titration von Calcium neben Magnesium mit Äthylenglycol-*bis*-(β-aminoäthyläther)-N,N,N',N' tetraessigsäure ($K_{\text{abs Ca}} = 10^{10,7}$, $K_{\text{abs Mg}} = 10^{5,4}$) ist ein anderes Beispiel[5].

TITRATION EINES METALLES NEBEN EINEM KOMPLEXBILDENDEN INDICATOR

Vereinfachungen

Die Behandlung dieses Problems ist in allen Einzelheiten bereits anderwärts mitgeteilt worden.[2] Der Vollständigkeit halber und als Grundlage fur das Verständnis der folgenden Abschnitte sei jedoch auch hier ein kurze Darstellung gegeben. Um eine mathematische Behandlung zu ermöglichen sind einige Vereinfachungen bezüglich des Indicators zu machen. Auch diese Annahmen sollen so getroffen werden, dass sie in der Praxis vollig oder mit ausreichender Genauigkeit erfullt sind.

(*a*) es handle sich um einen Zweifarbenindicator.

(*b*) Die Farben vor und nach dem Endpunkte seien in Bezug auf das menschliche Auge von gleicher oder annähernd gleicher Intensität und hinreichend komplementär.

(*c*) Das zu titrierende Metall bilde mit dem Indicator ausschliesslich einen 1 : 1 Komplex oder doch in so überwiegendem Ausmasse, dass höhere Komplexe vernachlässigt werden können.

(*d*) Das menschliche Auge sei imstande gerade jenen Farbwechsel wahrzunehmen, der durch 10% Änderung in der Form des Indicators (frei oder ans Metall gebunden) verursacht wird. Demnach ist der Endpunkt erreicht, wenn 90% des Indicators frei sind.

Grundformeln

Es ist klar, dass die Stabilitatskonstante des Indicatorkomplexes kleiner sein muss als die des Titrationskomplexes. Es ist auch ohne weiteres einzusehen, dass Schwierigkeiten auftreten müssen, wenn der Unterschied in den Konstanten nicht genügend gross ist. Der Endpunkt wird zu spat erscheinen und schleppend sein * Die Hauptfrage, die also erst zu beantworten ist, lautet, wie gross muss die Differenz in den Konstanten sein, um ein einwandfreies Resultat zu erhalten. Begnügt man sich fürs erste wieder mit einer Näherung, so sind die Ableitungen recht einfach. Im Endpunkt liegt folgendes Gleichgewicht vor

$$MI + Y \rightleftharpoons MY + I \tag{27}$$

Daraus ergibt sich unter Berücksichtigung der entsprechenden Stabilitätskonstanten

$$\frac{[MY]\ [I]}{[MI]\,.\,[Y]} = \frac{K_M}{K_I} \tag{28}$$

Sind die beiden Konstanten hinreichend gross, sodass die Dissoziation der Komplexe vernachlässigt werden kann, so gilt nahe dem und im Endpunkt $[MY] = C_M$. Gemäss Punkt (*d*) im vorigen Abschnitt ist im Endpunkt $[I] = 0{,}9\,.\,C_I$, woraus folgt, dass $[MI] = 0{,}1\ C_I$. Aus der Gleichung $C_Y = [MY] + [Y]$ errechnet sich $[Y] = C_Y - C_M$. Setzt man das alles an die entsprechenden Stellen von (28) so ergibt sich

$$\frac{9\,.\,C_M}{C_Y - C_M} = \frac{K_M}{K_I} \tag{29}$$

Durch Kombination dieses Ausdruckes mit der Definition des Titrationsfehlers nach (8) erhalt man

$$z = \frac{K_I}{K_M}\,.\,10^3 \tag{30}$$

wenn man näherungsweise 10 anstatt 9 setzt. Man erkennt also, dass für einen erlaubten Fehler von z.B. 0,1% die Konstanten sich um vier Zehnerpotenzen unterscheiden müssen

Diese vereinfachte Ableitung berücksichtigt auch hier wieder nicht die Dissoziation der beiden Komplexe und lasst auch keine Aussage uber die Güte des Endpunktes,

---

* Ausdrucke, wie "unscharf, schleppend, ziehend, schlecht, schwach" usw. im Zusammenhange mit Endpunkten sind u U vieldeutig. Einmal kann sich die Aussage auf den Farbwechsel beziehen und es ist gemeint dass die beiden Grenzfarben fur das menschliche Auge nicht genugend unterschiedlich, d h komplementar sind Zum anderen aber kann gemeint sein, dass der Farbwechsel nicht mit einem genugend kleinen Bruchteil an Titrationsmittel erreicht wird So z B. ist bei einer Saure-Basen-Titration Methylrot kontrastreicher als Methylorange Ein bei der Titration einer starken Saure mit einer starken Base einwandfrei arbeitender Indicator hingegen wird bei der Titration einer schwachen Saure "schleppen" Die Ausarbeitung einer neuen Klassifikation von Indicatoren nach diesen Gesichtspunkten ist in Zusammenarbeit mit Dr. C. N. Reilley derzeit im Gange und wird spater anderwarts veroffentlicht werden.

ob scharf oder schleppend, zu. Die verfeinerte Ableitung verläuft wie folgt. Wahrend der gesamten Titration gelten folgende Gleichungen

$$K_M = \frac{[MY]}{[M] . [Y]} \tag{31}$$

$$K_I = \frac{[MI]}{[M] . [I]} \tag{32}$$

$$C_I = [MI] + [I] \tag{33}$$

$$C_M = [MY] + [MI] + [M] \tag{34}$$

$$C_Y = [MY] + [Y] \tag{35}$$

Kombiniert man (33), (34) und (35) mit (31) und (32) so erhält man

$$K_M = \frac{[MY]}{(C_M - [MY] - [MI]) . (C_Y - [MY])} \tag{36}$$

$$K_I = \frac{[MI]}{(C_M - [MY] - [MI]) . (C_I - [MI])} \tag{37}$$

Berechnet man aus (37) den Wert für [MY] und setzt in (36) ein, so ergibt sich nach Auflösen

$$C_Y = \left(C_M - [MI] - \frac{I}{K_I} . \frac{[MI]}{C_I - [MI]}\right) . \left(\frac{C_I - [MI]}{[MI]} . \frac{K_I}{K_M} + 1\right) \tag{38}$$

Daraus lasst sich die Umschlagskurve im interessierenden Teil, nämlich nahe dem Endpunkte errechnen. Zur Vereinfachung definieren wir

$$\varphi \equiv \frac{[MI]}{C_I} \tag{39}$$

wonach sich ergibt

$$C_Y = \left(C_M - \varphi . C_I - \frac{1}{K_I} . \frac{\varphi}{1 - \varphi}\right) . \left(\frac{1 - \varphi}{\varphi} . \frac{K_I}{K_M} + 1\right) \tag{40}$$

In Abb. 1 sind einige Kurven fur verschiedene Werte der Parameter berechnet, wobei φ auf der Abszisse und, um die Kurven für verschiedene Konzentrationen beisammen zu haben, C_Y/C_M auf der Ordinate aufgetragen sind. Man erkennt nun leicht, dass die Fromel (40) nicht nur die Lage des Endpunktes zu berechnen gestattet sondern auch über die Güte des Endpunktes Auskunft gibt, je nachdem ob die Kurve flach oder steil die Senkrechte für $\varphi = 0,1$ schneidet. Setzt man diesen Wert für φ in Formel (40) ein [Endpunkt gemass Punkt (*d*) im vorigen Abschnitt] und kombiniert mit (8) so errechnet sich der prozentuale Fehler zu

$$z = \frac{100}{C_M} . \left[9 . \frac{K_I}{K_M} . C_M - 0,1\, C_I . \left(1 + 9\frac{K_I}{K_M}\right) - \frac{1}{K_M} - \frac{1}{9 . K_I}\right] \tag{41}$$

$1/K_M$ ist so klein, dass es gegen das nächst grössere Glied vernachlässigt werden kann. Ferner ist $9 . K_I/K_M \ll 1$ womit sich die Formel vereinfacht zu

$$z = \frac{100}{C_M} . \left(9 . \frac{K_I}{K_M} . C_M - 0,1 . C_I - \frac{1}{9 . K_I}\right) \tag{42}$$

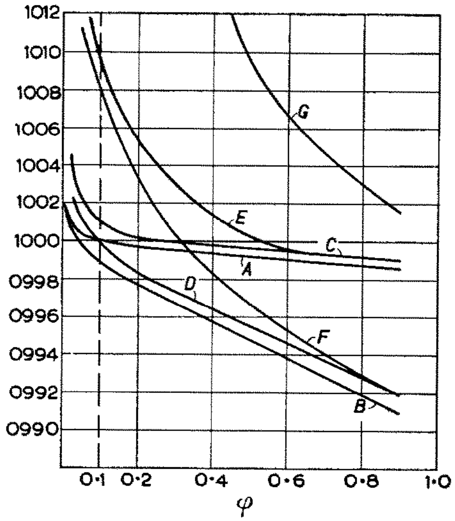

ABB. 1. Umschlagskurven fur verschiedene Werte der Parameter in Formel (40). In allen Fallen ist $C_I = 10^{-5}$ und $K_I = 10^{11}$.

Kurve	K_M	K_I/K_M	C_M
A	10^{16}	10^{-5}	10^{-2}
B	10^{16}	10^{-5}	10^{-3}
C	10^{15}	10^{-4}	10^{-2}
D	10^{15}	10^{-4}	10^{-3}
E	10^{14}	10^{-3}	10^{-2}
F	10^{14}	10^{-3}	10^{-3}
G	10^{13}	10^{-2} (!!)	10^{-2}

Ist die Indicatorkonstante genugend gross und die Indicatorkonzentration hinreichend klein, so können die beiden negativen Glieder in (42) vernachläsiigt werden und es folgt vereinfachung zu (30). Ist jedoch die Indikatorkonstante sehr gross und $K_M \gg K_I$, so erhält man $z = -10 \, . \, C_I/C_M$, was aussagt, dass der Endpunkt äusserst scharf ist und praktisch erreicht wird, indem mit einem geringen Bruchteil an Masslösung gerade noch das am Indicator haftende Metall entfernt wird.

Grenzwert fur K_I

Ist die Indicatorkonstante klein, dann wird durch Dissoziation fruhzeitig Indicator in der freien Form erscheinen und der Endpunkt wird verfrüht sein und uberdies schleppen. Nehmen wir zur Vereinfachung an, dass durch K_M und durch das Verhältnis K_I/K_M keine Komplikationen eingefuhrt werden, dass also $K_M \gg K_I$, dann kann in (42) das erste Glied in der Klammer vernachlässigt werden und man erhält für K_I den Ausdruck

$$K_I = -\frac{1}{9 \, . \, C_M \, . \left(z \, . \, 10^{-2} + 0{,}1 \, . \, \frac{C_I}{C_M}\right)} \qquad (43)$$

Setzt man mittlere Titrationsbedingungen ein, etwa $C_M = 10^{-2}$, $C_I = 10^{-5}$ und $z = -0{,}1$ (da ja ein negativer Fehler resultieren muss), so erhält man, wenn wieder 10 anstatt 9 gesetzt wird, den Wert $K_I \simeq 10^4$ als Grenze. Auch dieser Wert variiert mit den Bedingungen und soll ebenfalls nur als grössenordnungsmassiger Anhaltspunkt festgehalten werden.

Wie eine genauere Inspektion von (42) zeigt, können auch hier wieder Fehler kompensiert werden, was z.B. bei der Titration von Magnesium mit EDTA und Erio T als Indicator teilweise der Fall ist.

Grenzwert für das Konstantenverhältnis K_I/K_M

Aus (42) errechnet sich das Konstantenverhältnis zu

$$\frac{K_I}{K_M} = \frac{z\ 10^{-2}}{9} + \frac{0{,}1}{9} \cdot \frac{C_I}{C_M} + \frac{1}{81 \,.\, K_I \,.\, C_M} \tag{44}$$

Man erkennt sofort, dass, wenn nicht extreme Genauigkeit (z sehr klein) gefordert wird, K_I nicht äusserst ungünstig liegt und die Lösung nicht zu stark verdünnt ist, die beiden letzten Glieder wegfallen und (44) in die vereinfachte Form (30) übergeht. Auch wenn die eben gemachten Annahmen nicht zutreffen, bleibt die Grössenordnung für den Grenzwert des Konstantenverhältnisses, nämlich 10^{-4} erhalten.

Güte des Endpunktes

Eingangs wurde in Punkt (*d*) festgelegt, dass das menschliche Auge nur auf eine Änderung von Mindestens 10% in der Form des Indicators anspreche. Die Gute des Endpunktes lässt sich nun bestimmen durch die Anzahl der Tropfen an Masslosung die solch eine Änderung bei Erreichen des Endpunktes bewirkt. Demnach wäre also die Änderung gerade eben noch zu erkennen, wenn φ von 0,2 nach 0,1 wechselt. Wir erhalten also durch Einsetzen der entsprechenden Werte für φ in (40) und Subtraktion der beiden Gleichungen den Wert fur ΔC_Y

$$\Delta C_Y = 5 \,.\, \frac{K_I}{K_M} \,.\, C_M + 0{,}1 \,.\, C_I + \frac{5}{36} \cdot \frac{1}{K_I} \tag{45}$$

wobei ein einem auftretenden Ausdruck $-K_I/K_M$ gegen eins vernachlässigt wurde.

Die Molarität der verwendeten Masslösung sei m, das Volum der Titrationslösung im oder nahe am Endpunkte sei V_e ml, die Anzahl der Tropfen n und die Grösse eines Tropfens w ml. Dann ist die Zahl der Millimole an Metall, die zum Durchschreiten des Endpunktsintervalles noch zu titrieren sind $\Delta C_Y \,.\, V_e$. Dies entspricht $w \,.\, n \,.\, m$ Millimolen Titrationsmittel. Gleichsetzen der beiden Ausdrücke erlaubt die Berechnung von ΔC_Y und dies ergibt mit (45) kombiniert

$$\frac{w \,.\, n \,.\, m}{V_e} = 5 \frac{K_I}{K_M} \,.\, C_M + 0{,}1\ \ C_I + \frac{5}{36} \cdot \frac{1}{K_I} \tag{46}$$

Aus diesem Ausdruck lässt sich die Güte des Endpunktes berechnen, indem man herausfindet, wieviele Tropfen oder Tropfenbruchteile zum Durchschreiten des Intervalles $\varphi = 0{,}2 \rightarrow \varphi = 0{,}1$ notig sind. Ist die Indicatorkonstante sehr gross und das Konstantenverhältnis sehr klein, so haben wir den Idealfall vorliegen, wo tatsachlich nur das letzte Restchen am Indicator haftenden Metalles entfernt werden muss, um das Endpunktsintervall scharf zu druchschreiten.

Ein praktisches Beispiel sei durchgerechnet. Folgende Daten sind gegeben für die Titration von Magnesium und Zink mit EDTA und Erio T als Indicator in Ammoniakpuffer von pH 10: $w = 0{,}05$ ml, $V_e = 25$ ml, $C_I = 10^{-5}$, $C_M = m = 10^{-3}$, $K_{MgY} = 10^{8,39}$, $K_{MgI} = 10^{5,44}$, $K_{ZnY} = 10^{16,20}$ und $K_{ZnI} = 10^{11,4}$. Die Konstanten sind fur den Einfluss des pH korrigiert. Berücksichtigen des Ammiak-Einflusses ist nicht nötig, da sich die β_A-Werte kürzen. Für die Magnesiumtitration ergibt sich 3 und fur die Zinkbestimmung 0,5 Tropfen. Dies ist durchaus in guter Übereinstimmung mit der praktischen Erfahrung, wenn man berücksichtigt, dass die Komplementaritat der Farben vernachlässigt wurde und die Annahme des Endpunktintervalles naturgemass einer gewissen Willkür nicht entbehrt.

TITRATION EINES METALLES NEBEN EINEM ZWEITEN UNTER VERWENDUNG EINES KOMPLEXBILDENDEN INDICATORS

Grundformeln

Dieser Fall, von allen der komplizierteste, ist eine Kombination der in den Abschnitten 4 und 5 behandelten Situationen. Um wieder von vereinfachten Verhältnissen auszugehen, sei auch hier vorerst die Eigendissoziation der Komplexe vernachlässigt. Anwesend seien das Metall M, das titriert werden soll, das Stormetall N und der Indicator I. Nur M bildet mit I einen Komplex. Würde auch N einen Indicatorkomplex bilden so ware es eine Simultantitration die leicht gemäss Abschnitt 4 zu behandeln ist

Im Endpunkte konkurrieren die Komplexe gemäss dem Gleichgewichte

$$MY + N + I \rightleftharpoons NY + MI \tag{47}$$

Je weiter das Gleichgewicht nach links verschoben ist, desto günstiger liegen die Verhältnisse fur die Titration. Unter Einführung der entsprechenden Stabilitats-konstanten erhält man aus (47) sofort

$$\frac{[NY] \,.\, [MI]}{[MY] \,.\, [N] \,.\, [I]} = \frac{K_N \; K_I}{K_M} \tag{48}$$

In ahnlicher Art, wie es schon früher geschehen ist, setzen wir nun folgendes fest. Der Endpunkt sei erreicht, wenn $[MI] = 0{,}1 \,.\, C_I$ und demnach $[I] = 0{,}9 \,.\, C_I$. $[MY] = C_M$. Der Fehler z sagt aus, wieviel vom Metall N mittitriert wird, also $[NY] = z \,.\, 10^{-2} \,.\, C_M$. Wenn der Fehler nicht zu gross ist, gilt näherungsweise $[N] = C_N$. Setzt man das in (48) ein, so folgt, wenn wieder $9 \simeq 10$ genähert wird

$$z = \frac{K_N \,.\, K_I}{K_M} \,.\, C_N \,.\, 10^3 \tag{49}$$

Wie zu erwarten, wird der Fehler umso grosser, je mehr Fremdmetall anwesend ist und je stabiler dessen Komplex ist. Der Fehler steigt auch an, wenn die Indicatorkonstante zu nahe an K_M kommt, weil ja das eine Verschiebung des Gleichgewichtes (47) nach rechts bedeutet.

Man sieht unschwer ein, dass es nunmehr nicht leicht ist, einfache Konstantenverhältnisse anzugeben, weil ja den beiden Konstanten im Zähler nur eine im Nenner gegenübersteht und die wechselseitige Beeinflussung komplizierter ist. Deswegen ist hier die verfeinerte Ableitung von grösserer Bedeutung. Die Formel ist aber auch, wie gleich gezeigt werden wird, wesentlich komplizierter und nicht so durchsichtig, wenn man sie diskutieren will.

In jedem Punkte der Titration müssen nachstehende Beziehungen erfüllt wein

$$K_M = \frac{[MY]}{[M]\,.\,[Y]} \tag{50}$$

$$K_N = \frac{[NY]}{[N]\,.\,[Y]} \tag{51}$$

$$K_I = \frac{[MI]}{[M]\,.\,[I]} \tag{52}$$

$$C_N = [NY] + [N] \tag{53}$$

$$C_M = [MY] + [MI] + [M] \tag{54}$$

$$C_Y = [MY] + [NY] + [Y] \tag{55}$$

$$C_I = [MI] + [I] \tag{56}$$

Wie die Rechnung durchgeführt wird, sei in knappen Zugen angegegeben. Man berechnet N aus (53), setzt den Wert in (51) ein und lost nach NY auf. Diesen Wert, sowie den aus (50) für Y erhaltenen setzt man in (55) ein und erhält nach C_Y aufgelöst

$$C_Y = [MY] + \frac{C_N \dfrac{K_N}{K_M} \dfrac{[MY]}{[M]}}{\dfrac{K_N}{K_M} \dfrac{[MY]}{[M]} + 1} + \frac{[MY]}{K_M [M]} \tag{57}$$

Durch Kombination von (52), (54) und (56) erhält man unter Einführung der Definition für φ die Ausdrücke $[M] = \frac{1}{1-\varphi} \frac{1}{K_I}$ und $[MY] = C_M - \varphi\,.\,C_I - \frac{\varphi}{1-\varphi}\,.\,\frac{1}{K_I}$. Setzt man diese schliesslich in (57) ein und arrangiert zweckentsprechend, so erhält man am Ende

$$C_Y = \frac{\left(C_M - \varphi C_I - \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_I}\right)\left\{\dfrac{K_N}{K_M}\left[\left(C_M - \varphi C_I - \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_I}\right) \times \left(1 + \dfrac{1-\varphi}{\varphi} \dfrac{K_I}{K_M}\right) + C_N\right] + \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_I}\left(1 + \dfrac{1-\varphi}{\varphi} \dfrac{K_I}{K_M}\right)\right\}}{\dfrac{K_N}{K_M}\left(C_M - \varphi C_I - \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_I}\right) + \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_I}} \tag{58}$$

Setzt man zur Kontrolle $C_N = K_N = 0$, so resultiert Formel (40) für den Fall, dass nur ein Metall anwesend ist.

Aus (58) errechnet sich der Wert für C_Y im Endpunkte, er sei als $C_{Y,0,1}$ bezeichnet, indem man $\varphi = 0{,}1$ einsetzt, wobei erlaubterweise $\frac{1-\varphi}{\varphi}\,.\,\frac{K_I}{K_M}$ gegen 1 vernachlässigt wurde, zu

$$C_{Y,0,1} = \frac{\left(C_M - 0{,}1C_I - \dfrac{1}{9K_I}\right)\left[\dfrac{K_N}{K_M}\left(C_M - 0{,}1C_I - \dfrac{1}{9K_I} + C_N\right) + \dfrac{1}{9K_I}\right]}{\dfrac{K_N}{K_M}\left(C_M - 0{,}1C_I - \dfrac{1}{9K_I}\right) + \dfrac{1}{9K_I}} \tag{59}$$

Gemäss der Definition des Titrationsfehlers nach (8) bekommen wir in Kombination mit dem letzten Ausdrucke

$$z = \frac{\frac{K_N}{K_M} \cdot C_M \; C_N - \left(\frac{K_N}{K_M} \cdot C_M + \frac{1}{9K_I}\right) \cdot \left(0{,}1 C_I + \frac{1}{9K_I}\right)}{C_M \left(\frac{K_N}{K_M} \cdot C_M + \frac{1}{9K_I}\right)} \cdot 100 \qquad (60)$$

Man ersieht daraus, dass ein zu früher Endpunkt, verursacht durch ein zu kleines K_I ganz oder teilweise kompensiert werden kann, wenn K_N/K_M genügend klein ist. Im allgemeinen ist jedoch der zweite Ausdruck im Zähler gegen den ersten zu vernachlässigen und wir erhalten die Näherungsformel

$$z = \frac{\frac{K_N}{K_M} \cdot C_N}{\frac{K_N}{K_M} \cdot C_M + \frac{1}{9K_I}} \cdot 100 \qquad (61)$$

Diese geht in den Ausdruck (49) (vereinfachte Ableitung) über, wenn die Verhältnisse so liegen, dass im Nenner das erste Glied vernachlässigt werden kann *) Man sieht aber, dass die exakte Ableitung (60) und auch (61) etwas andere Funktionen sind im vergleich zur groben Formel (49) als es in den früheren Abschnitten der Fall war!

Grenzwerte

Wie schon oben erwähnt, ist es nun nicht mehr möglich einfache Grenzwerte anzugeben. Immerhin kann man unter Annahme durchschnittlicher Bedingungen ($C_M = C_N = 10^{-2}$, $C_I = 10^{-5}$ und $z = 0{,}1\,\%$) zu einem groben Anhaltswert kommen, wenn man folgende Überlegungen anstellt. Da ja bereits ohne Indicator das Verhältnis K_N/K_M höchstens 10^{-6} werden darf, kommt im allgemeinen eine Titration neben einem Störmetall nur für Metalle in Frage, deren absolute Konstanten höher liegen als 10^{12}. Liegt nun K_I nicht an der Grenze von 10^4 sondern, wie üblich, um einige Zehnerpotenzen höher, so ergibt sich als ungefährer Grenzwert für K_N/K_M etwa 10^{-10} bis 10^{-8}. Hohe Indicatorkonstanten können diesen Zahlen jedoch beträchtlich verändern.

Güte des Endpunktes

Auch hier hängt die Güte des Endpunktes vom Verhältnis K_I/K_M ab, wird aber obendrein noch durch den Wert von K_N beeinflusst. Rein mathematisch ist die Ableitung einer Formel analog zu (45) durchaus möglich. Der resultierende Ausdruck aber ist lang und undurchsichtig. Vereinfachungen sind zwar möglich, hängen aber stark von den jeweiligen Verhältnissen ab. Es ist daher wenig zweckmassig solch eine Formel zu entwickeln. Einfacher gelangt man zum Ziele, wenn man in (58) die entprechenden Werte der Parameter einsetzt und einmal für $\varphi = 0{,}1$ und ein zweitesmal 0,2 substituiert. Dann wird schnell ersichtlich welche Glieder vernachlässigt werden können. Substraktion der beiden nun erhaltenene Werte für $C_{Y,0,1}$ und $C_{Y,0,2}$ voneinander ergibt ΔC_Y, welches analog zu (46) mit der nötigen Menge Masslösung in Beziehung gesetzt wird. So erhält man die gewünschte Auskunft für

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* Dies ist nur dann nicht zutreffend, wenn entweder C_M oder C_N sehr klein werden Im ersteren Falle ist sodann die volle Formel anzuwenden Im zweiten Falle jedoch erübrigt sich die ganze Rechnung, da ja dann seitens des zweiten Metalles kaum eine Störung zu erwarten ist

jeden speziellen Fall in einfacherer Weise als wenn eine undurchsichtige Formel gehandhabt werden muss. Durchrechnung einiger Falle, fur die alle Daten aus der Literatur bekannt sind, zeigte, dass auch das erhältnis K_N/K_M fur die Güte des Endpunktes massgeblich ist. Generelle Daten mitzuteilen ist aus bereits erwahnten Gründen unmöglich

SELECTIVITAT KOMPLEXOMETRISCHER TITRATIONEN

Die Ableitungen zeigen bereits zur genuge, wie es um die Selectivität komplexometrischer Titrationen bestellt ist. Überblickt man die Tabelle der Stabilitätskonstanten der EDTA Komplexe der Metalle, so ergibt sich sofort, dass nur eine relativ geringe Selectivitat besteht, wie schon oben näher ausgeführt wurde. Um die Selectivität zu steigern hat man nun verschiedene Mittel zur verfugung. Einmal kann in beschranktem Ausmasse durch Änderung der scheinbaren Stabilitätskonstanten uber den pH-Einfluss eine Verbesserung erzielt werden. Diese Möglichkeiten sind genugend bekannt und erschopft, als dass hier in Details eingegangen werden muss. Bemerkenswert ist lediglich, dass die verwickelten Verhältnisse in den Beziehungen zwischen K_N, K_M und K_I dem Parameter K_I/K_M eine entscheidende Rolle einräumen. Demnach muss also die Suche nach neuen Indicatoren, wenn man die Steigerung der Selectivität im Auge hat, so vorwärts getrieben werden, dass man nicht nur selectivere oder spezifische Indicatoren zu finden sich bemüht, sondern vor allem auch, dass diese Indicatoren in betreff auf das zu titrierende Metall eine möglichst geringe Stabilitätskonstante aufweisen mussen. Natürlich aber nicht eine so niedere, dass dadurch ungute Verhältnisse auftreten Ist nämlich die Indicatorkonstante zu hoch, so wird auch bei einem völlig spezifischen Indicator in Anwesenheit eines Fremdmetalles stets ein Simultantitration resultieren.

Die Verwendung von Maskierungsmitteln ist eine weitere Möglichkeit. Der Einfluss von Maskierungsmitteln, soweit es sich um komplexbildende Substanzen handelt ist rechnerisch leicht zu erfassen, wenn man mit den β_A-Werten operiert, die ja sofort zu den scheinbaren Stabilitatskonstanten führen, die in den Formeln ausschliesslich Verwendung finden. Es werden aber durch die komplexbildenden Maskierungsmittel nicht nur die Stabilitaten der Komplexe der Stormetalle sondern nur zu oft auch die der zu titrierenden Metalle beeinflusst, was dann natürlich oftmals zu Unannehmlichkeiten führt.

Weiters ist zu beachten, dass die in der Literatur mitgeteilten Werte für die Konstanten sich auf Messungen bei einer bestimmten ionalen Stärke (meist 0,1) beziehen, in der Praxis die Lösungen jedoch diesen Wert nicht erreichen oder überschreiten. Leider ist über die Änderung der Stabilitätskonstanten mit wechselnder ionaler Stärke wenig bekannt.

Die analytische Behandlung von Multikomponentsystemen wird natürlich stark erleichtert, wenn man die Zahl der komplexformenden Titrationsmittel erhöht, und zwar in der Richtung, dass selectivere Titranten eingeführt werden. Auch diese Richtung ist zur Zeit in steigender Entwicklung, so dass eine noch weitere Verbreitung komplexometrischer Titrationen mit all ihren Vorteilen zu erwarten ist.

SCHLUSSBEMERKUNG

Abschliessend sei bemerkt, dass der Anwendung der mitgeteilten Formeln auf praktische Probleme eine gewisse Beschränkung auferlegt ist. Diese besteht nicht etwa darin, dass die Vereinfachungen nicht zutreffen oder zu grosse Fehler verursachen Der Grund liegt vielmehr darin, dass für die meisten Konstanten, die nötigen Daten nicht vorliegen. Dies aber kann naturlich nicht den Ableitungen angelastet werden. Die in zahlreichen Laboratoriem laufenden Untersuchungen, die notigen Konstanten zu bestimmen, geben jedoch gute Hoffnung, dass in absehbarer Zeit das notige Zahlenmaterial zur Verfügung stehen wird, wonach die Formeln für die Entwicklung neuer Verfahren noch bessere Dienste leisten werden als es bisher schon der Fall war.

Eines sei jedoch ausdrücklich betont Alle Ableitungen basieren auf *Gleichgewichtskonstanten* und daher sind die Ableitungen nur anwendbar, wenn Gleichgewicht erreicht ist, d.h. fur die Praxis der Titration, wenn sich das Gleichgewicht praktisch momentan oder zumindest doch genugend schnell einstellt Wenn langsame Gleichgewichtseinstellung erfolgt, so liegen vollig anders geartete Verhältnisse vor. Es konnen dann "robuste" Komplexe auftreten, deren Konstante viel höher zu liegen scheint, als es tatsachlich der Fall ist Solche Verzogerungen in der Gleichgewichtseinstellung bedeuten jedoch nicht immer einen Nachteil. Es sind vielmehr Fälle bekannt, da sie eine erhebliche Steigerung der Selectivität ermöglichen. Die theoretische Behandlung dieser Verhältnisse ist jedoch sehr kompliziert und würde den Rahmen der vorliegenden Arbeit sprengen.

Summary—Assuming some simplifications not very divergent from practical conditions, formulae are derived which allow rapid calculation of the position and the quality of the end-point in complexometric titrations. The problem of selectivity is dealt with. The approximate limiting values for the average titration conditions (error 0 1 % and metal ion concentration 0 01*M*) are as follows to titrate a metal complexometrically, the stability constant of its titration complex must be at least 10^8, the stability constant of the indicator complex should be not less than 10^4, in the case of a titration without an indicator, the complex of a foreign metal must differ in stability by a factor of at least 10^{-6}; the stability constant for a complex-forming indicator must be at least 10^4 times smaller that that of the titration complex, in the case of a titration with an indicator, the complex of a foreign metal must be about 10^8–10^{10} times smaller in stability in order to avoid interference causing an error exceeding the value mentioned above

Résumé—Admettant certaines simplifications qui s'écartent peu des conditions pratiques on a dérivé des formules qui permettent de calculer rapidement la position et la qualité de la fin du titrage dans les titrages complexométriques. Le problème de la sélectivité est étudié Les limites approchées pour les conditions normales de titrage (erreur 0,1 % et concentration de l'ion metal 0,01*M*) sont comme suit dans le titrage complexométrique d'un métal la constante de stabilité du complexe de titrage doit être au moins 10^8; la constante du complexe avec l'indicateur ne doit pas être inférieure à 10^4, dans le cas de titrage sans indicateur le complexe d'un métal étranger doit différer en stabilité d'un facteur d'au moins 10^{-6}, la constante d'un indicateur complexant doit être au moins 10^4 fois plus petite que celle du complexe de titrage, dans le cas d'un titrage avec indicateur le complexe avec un métal étranger doit avoir une constante de 10^8 à 10^{10} fois plus petite pour éviter une interférance pouvant causer une erreur excédant la valeur limite mentionnée ci-dessus

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DETERMINATION OF TRACES OF IRON IN METALLIC COPPER

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(*Received* 5 *March* 1958)

Summary—*Tris*-(4 7-diphenyl-1 10-phenanthroline)-iron^{II} reacts with cyanide in a neutral solution to form a violet coloured complex, dicyano-*bis*-(4:7-diphenyl-1:10-phenanthroline)-iron^{II} Use of this complex for the determination of iron in copper metal has been described The method is applicable for the determination of 1 to 10 p p m. of iron in copper metal.

THE colorimetric determination of small quantities of iron in the presence of large quantities of copper by the 1:10-phenanthroline method is complicated by the fact that sufficient 1:10-phenanthroline must be added to complex both the copper and the iron It is the purpose of this paper to describe a method which circumvents the difficulty and makes economically feasible the determination of traces of iron in pure copper.

The determination is based upon the violet colour of dicyano-*bis*-(1:10-phenanthroline)-iron^{II} or of dicyano-*bis*-(4:7-diphenyl-1:10-phenanthroline)-iron^{II}, formed when a solution containing iron and the phenanthroline is treated with cyanide and extracted with an organic solvent. Copper in either valence state is converted to the colourless complex ion, $Cu(CN)_3^{2-}$, which is more stable than the cuprous-phenanthroline ion. The nature of the complexes requires that the ferrous-1:10-phenanthroline complex be formed first and that the mixture then be treated with cyanide. In the reverse procedure, *i e.* the treatment of a solution of iron with cyanide and then the phenanthroline, the desired iron-phenanthroline compound is not formed.

Because of the large difference in concentration between the copper and iron present it would be expected from mass action that the phenanthroline would be taken up by the copper rather than by the iron. Some method is required therefore to prevent the reaction between the phenanthroline and the copper at least until the ferrous complex has had an opportunity to form. In the method here proposed, the copper is removed from the reaction by precipitation as the thiocyanate before the addition of the phenanthroline. The cuprous thiocyanate is then redissolved by the addition of cyanide; any iron co-precipitated with it is thus returned to the solution

Of the organic solvents chloroform and nitrobenzene are most satisfactory for extracting the iron-phenanthroline cyanide. There is some advantage in using bathophenanthroline (4:7-diphenyl-1:10-phenanthroline) rather than 1:10-phenanthroline inasmuch as the iron is completely removed by one extraction into chloroform using bathophenanthroline whereas four or five extractions are required using 1:10-phenanthroline. Nitrobenzene is slightly better than chloroform as the solvent for 1:10-phenanthroline but the advantage is not sufficient to offset its disagreeable properties.

EXPERIMENTAL WORK AND RECOMMENDED PROCEDURE

Composition and properties of ferrous 1:10-phenanthroline cyanide in chloroform solution

The composition of the chloroform-soluble, ferrous-1:10-phenanthroline compound was determined by direct analysis. A quantity of the material was prepared and extracted into chloroform. The chloroform solution was then washed well with water to remove any excess cyanide and evaporated under vacuum The solid was then extracted in a Soxhlet extractor with petroleum ether (b p 60–70°) for 10 hr to remove any excess of phenanthroline The product was then dried and analysed for the various components in the following manner.

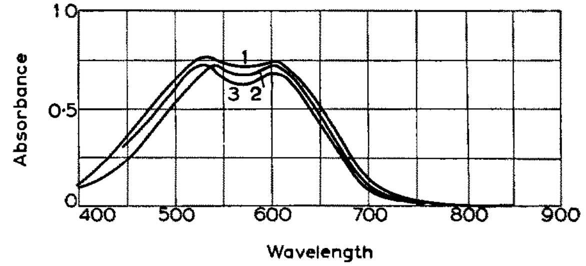

Fig. 1 Absorption spectrum of Fe(4 7-diphenyl-1 10-phenanthroline)$_2$(CN)$_2$ in chloroform (Curve 1); Fe(1 10-phenanthroline)$_2$(CN)$_2$ in chloroform (Curve 2), Fe(1 10-phenanthroline)$_2$ (CN)$_2$ in nitrobenzene (Curve 3)

The cyanide was determined by placing a sample of the compound in a Kjeldahl distillation flask, acidifying with 6*N* sulphuric acid, and steam distilling The distillate, containing the cyanide, was collected in dilute ammonium hydroxide and titrated with silver nitrate to the silver iodide end-point.

The solution remaining behind in the distillation flask was partially neutralized and diluted to 250 ml Iron and phenanthroline were determined on different aliquots of this solution. The iron was determined spectrophotometrically by the 1:10-phenanthroline procedure The 1.10-phenanthroline was determined by treatment with excess ferrous sulphate and comparison of the absorbance of the solution with a series of 1:10-phenanthroline solutions each containing an excess of iron The compound analysed by the above scheme showed a composition of one iron, two cyanides and two phenanthrolines. This is in agreement with the results obtained by Margerum and Banks[1] and by Schilt[2].

By inference the ferrous-bathophenanthroline compound is dicyano-*bis*-(4 7-diphenyl-1·10-phenanthroline)-iron^{II}.

The absorption spectra of each of the complexes in various solvents are given as Fig 1 The spectra were recorded on a Cary Recording Spectrophotometer (variable band width) using 1-cm cells.

Preparation of low-iron copper metal

Inasmuch as the copper wire available was found to contain about 8 p p m. of iron it was necessary to prepare an iron-free copper Purification by electro-deposition in the presence of ethylenediaminetetra-acetic acid as suggested by Kreimer and Tuzhilina[3] was followed Copper wire was dissolved in nitric acid The acid was neutralised and to the slightly acid solution was added 5 g of disodium dihydrogen ethylenediaminetetra-acetate The copper was deposited electrolytically at a slow rate until the deposition was nearly complete. The cathode was then washed and placed in a new solution of disodium dihydrogen ethylenediaminetetra-acetate and the copper plated on a second electrode This process was repeated two more times after which the copper was still contaminated to the extent of 1 p p.m. The copper was stripped from the electrode with nitric acid and the solution evaporated to dryness The residue was treated with a small quantity of hydrochloric acid and diluted to 250 ml. Ten ml of this solution contained 1 g of copper.

Reagents required

1:10-phenanthroline. 0 1% solution. Dissolve 0.10 g of 1:10-phenanthroline monohydrate (G Frederick Smith Chemical Co , Columbus, Ohio) in 100 ml of water.

Bathophenanthroline. 0·1% solution. Dissolve 0·10 g of 4:7-diphenyl-1:10-phenanthroline (G. Frederick Smith Chemical Co., Columbus, Ohio) in 100 ml of ethanol.

Sodium acetate. Iron-free, aqueous solution. Dissolve 50 g of sodium acetate trihydrate in 100 ml of water. Add 10 ml of hydroxylammonium chloride, 5 ml of bathophenanthroline and extract with *iso*amyl alcohol until the iron is completely removed. Extract the iron-free solution three times with chloroform to remove the *iso*amyl alcohol.

Hydroxylammonium chloride. Iron-free, aqueous solution. Dissolve 50 g of hydroxylammonium chloride in 100 ml of water. Add 10 ml of sodium acetate, 5 ml of bathophenanthroline and extract with *iso*amyl alcohol until the iron is completely removed. Extract the iron-free solution three times with chloroform to remove the *iso*amyl alcohol.

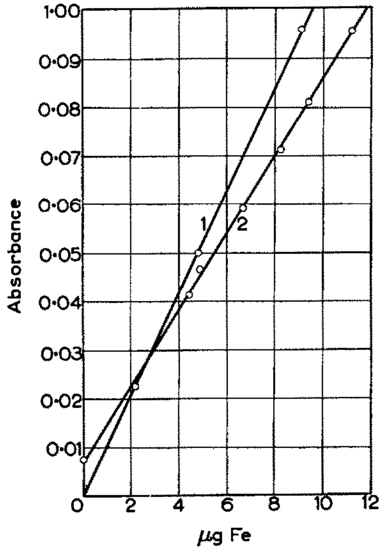

FIG. 2. Calibration curves, Fe(4:7-diphenyl-1:10-phenanthroline)$_2$(CN)$_2$ in chloroform. Curve 1, copper absent, curve 2, 1·0 g of copper present. Intercept of curve 2 presumably represents iron present in the "pure" copper used in making up the standards.

Ammonium thiocyanate. Iron-free, aqueous solution. Dissolve 50 g of ammonium thiocyanate in 100 ml of water. Add 10 ml of hydroxylammonium chloride solution and 10 ml of sodium acetate solution followed by 5 ml of bathophenanthroline solution. Extract with *iso*amyl alcohol until all the iron is removed and then three times with chloroform to remove the *iso*amyl alcohol.

Standard iron solution. Dissolve 1·000 g of electrolytic iron in 30 ml of 6*N* hydrochloric acid. Dilute to one litre. Prepare a secondary standard iron solution by diluting 10·00 ml of the standard solution to one litre.

Procedure for the determination of iron in copper metal

Weigh 1·00 g of the sample into a 125-ml conical flask, add 10 ml of distilled 6*N* hydrochloric acid and 5 ml of 30% hydrogen peroxide. When the vigorous reaction subsides heat the solution to boiling and hold at this temperature until dissolution is complete. (In the case of samples of very large particle size additional hydrogen peroxide may be added to aid dissolution). When the sample is completely dissolved, evaporate the solution to near dryness, take up again in 25 ml of distilled water and transfer to a 125-ml separatory funnel. Add 10 ml of hydroxylammonium chloride solution and sufficient distilled ammonium hydroxide to render the solution neutral or slightly alkaline. Add 10 ml of sodium acetate solution, followed by 10 ml of ammonium thiocyanate solution. If the solution is sufficiently alkaline it will have the colour and consistency of thick cream at this point. Otherwise additional ammonium hydroxide should be added. Add one ml of bathophenanthroline solution and mix well. Add 2 g of potassium cyanide and extract at once with 15 ml of chloroform. Allow the mixture to stand for 5 min and then draw off the lower layer into a 25-ml volumetric flask.

Dilute the solution to the mark with chloroform, add a few crystals of potassium cyanide and mix well. Read the absorbance at 600 mμ within 2 hr and determine the amount of iron present by comparison with the calibration curve.

Preparation of the calibration curve

Using the secondary standard iron solution introduce into a series of 125-ml separatory funnels quantities of iron varying between 1 and 10 μg To each funnel add 10 ml of iron-free copper and treat the solution according to the procedure given above for the determination of iron in copper metal

RESULTS AND DISCUSSION

The presence of copper in the solution analysed affects the observed absorbance of the chloroform solutions of the iron-phenanthroline cyanide. In preparing the calibration curve, therefore, roughly the same weight of copper should be added to each standard as used in the sample for analysis, that is about 1 g. Calibration curves with and without added copper are shown in Fig. 2. Although the system conforms to Beer's law up to concentrations of at least 30 μg of iron, the upper limit is about 14μg in the presence of one gram of copper.

The iron content of National Bureau of Standards Sample No. 45c, Copper, Melting Point Standard, was determined by the above procedure. Slabs of copper were cut from the bar and cleaned by dipping in concentrated hydrochloric acid to remove any iron acquired from the cutting tool. Samples of 1.0 to 1.36 g were taken for the analysis.

Found for NBS No 45c: 2 1, 2.0, 2.3 p.p.m. Fe

Uninsulated electric wire, 1.0 to 1.1 g samples:

Found: 8.2, 8 3, 8 4, 8.1, 8.3, 8.2, p.p.m. Fe

The presence of zinc leads to low results as zinc reacts with phenanthroline and prevents the development of the iron-phenanthroline colour. Various attempts to circumvent this trouble failed and the method is not applicable to brass.

Note—The referee of this paper suggests that the effect of copper on the calibration curve is caused by the co-precipitation of iron with the cuprous thiocyanate Inasmuch as the ferrous-phenanthroline-cyanide complex is not formed in the presence of cyanide, such co-precipitated iron is rendered inactive Thus it is essential that the same amount of copper be present in all determinations and standards Authors agree

Zusammenfassung—*Tris*-(4 7-Diphenyl-1 10-Phenanthrolin)-Eisen-II reagiert mit Cyanid in einer neutralen Losung und bildet einen violett-gefarbten Komplex, Dicyano-*bis*-(4 7-Diphenyl-1 10-Phenanthrolin)-Eisen-II.

Der Gebrauch dieses Komplexes fur die Bestimmung von Eisen in Kupfer wird beschrieben Die Methode ist fur die Bestimmung von 1 bis 10 Teilen/Million des Eisens in Kupfermetall anwendbar.

Résumé—Le *tris*-(4 7-diphényl-1 10-phénanthroline)-fer-II réagit en solution neutre avec le cyanure avec formation d'un complexe violet, le dicyano-*bis*-(4.7-diphényl-1 10-phénanthroline)-fer-II Les auteurs décrivent l'utilisation de ce complexe pour le dosage du fer dans le cuivre. Cette méthode permet de déterminer 1 à 10 parties par million du fer dans le cuivre métallique.

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APPLICATIONS OF PYROHYDROLYTIC CLEAVAGES IN SPOT TEST ANALYSIS

A CONTRIBUTION TO THE CHEMISTRY OF SPECIFIC, SELECTIVE AND SENSITIVE REACTIONS*

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Summary—If organic compounds are heated in contact with hydrates of manganous sulphate or oxalic acid or if they are heated along with succinic or phathlic acid, the water released in the temperature range 100–230° can accomplish hydrolyses that do not occur with boiling water. The term pyrohydrolysis is suggested for those hydrolyses which can be accomplished only at elevated temperatures

Analytical applications of pyrohydrolyses are possible provided brief heating with appropriate water donors yields cleavage products which can be readily detected in the gas phase Examples are given of the detection of. helicin by splitting off salicylaldehyde; anilides of aliphatic carboxylic acids by splitting off aniline; O-acetyl compounds by evolution of acetic acid, aliphatic-bound halogen by splitting off hydrogen halides; aromatic sulphonic acids by generation of sulphur dioxide; N-methyl and N-ethyl groups by production of formaldehyde and acetaldehyde respectively.

All of the tests can be successfully conducted within the bounds of spot test analysis and possess microanalytical limits of detection

ELSEWHERE[1] it has been shown that hydrolytic cleaving of organic compounds by the dry method can be accomplished by heating with hydrates of manganous sulphate or oxalic acid. The solid hydrates function as water donors either directly in solid–solid reactions or indirectly by splitting off quasi-superheated steam, which on contact with the likewise heated organic compound leads to the hydrolytic cleavage of the latter. Hydrolyses can be effected in this way which cannot be brought about at all by the wet method.

The participation of hydrates in dry hydrolyses is a special case of a much more general effect, namely the action of water on hydrolysable compounds at temperatures above the boiling point of water. This type of hydrolysis may be called pyrohydrolysis.[2] Obviously the source of the water accomplishing such hydrolyses is not a relevant factor. It is essential that the water split off at higher temperatures be able to react immediately at the place of its production on hydrolysable compounds, which at the reaction temperature may be solid, or molten, or dissolved in the water donor. This concept of pyrohydrolysis is in accord with the familiar fact that concentrated sulphuric acid, itself a semi-hydrate, can effect hydrolytic cleavings at elevated temperatures.[3] Moreover, dry heating (pyrolysis) of organic compounds, with access of air, often yields hydrolysis products of the starting material, or their definite fission products, because of the action of the water produced in the pyrolysis.

It may be expected that pyrohydrolysis of organic compounds will have analytical applications, provided that the cleavages are rapid and extensive, and yield fission

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* Translated by R. E. OESPER, University of Cincinnati, Ohio, U S.A.

products which are readily detectable in the gas phase. Experiments along this line have already shown certain guiding principles In general, hydrates of metal sulphates are but slightly active, the water release occurs in a rather narrow temperature zone (usually with 200° as upper limit) and the reaction field is limited to the surface of the solid hydrate. In the case of concentrated sulphuric acid it should be noted that this reagent not only serves as water donor but also as dehydrant and oxidant, with the result that other reactions may occur in addition to hydrolysis If organic compounds are subjected to dry heating without an admixed substance, the water required for hydrolysis is obtained at the expense of the material being hydrolysed, and there arise also other than purely hydrolytic cleavage products, which as in the case of concentrated sulphuric acid, cloud the reaction picture of a hydrolysis.

Improved results are given by the use of crystallised oxalic acid, succinic acid, and phthalic acid as water donors. Oxalic acid dihydrate begins to release water at 100° and continues to do so with sintering and melting up to 160°, a temperature region in which hydrolyses can be accomplished Succinic acid melts at 189°, and the production of the anhydride starts at this temperature:

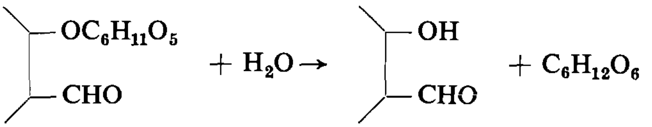
$$(CH_2COOH)_2 \rightarrow (CH_2CO)_2O + H_2O$$

This reaction increases as temperature rises, and consequently the melt can function as water donor in contact with hydrolysable compounds at temperatures exceeding 200°. The same is true of phthalic acid, whose melt undergoes conversion into phthalic anhydride.

The pyrohydrolysis of organic compounds requires the action of water at elevated temperatures. However, this is a necessary but not a sufficient condition There is required also a "reaction readiness" of the particular organic compound within the region of the thermal release of water. No definite predictions can be made with respect to this point; experimental tests are required. Reaction systems will now be described in which new selective tests were reached through the rapid occurrence of pyrolytic hydrolyses.

Detection of helicin

An excellent instance of a pyrohydrolysis, which can be realised with any of the water-donors cited above, is the saponification of helicin, which is the glucoside of salicylaldehyde:



In aqueous solution and in the absence of acid, this hydrolysis can be accomplished only by continuous boiling. In contrast, it occurs quickly if the glucoside is subjected to dry heating, because the water arising from the pyrolysis of the sugar component is hydrolytically active. When helicin is taken to 105–110° along with $MnSO_4 \cdot 4\ H_2O$ or $H_2C_2O_4 \cdot 2\ H_2O$, salicylaldehyde can be detected very soon; actually this aldehyde appears within several minutes even at 100°.

The salicylaldehyde split off in the pyrohydrolysis can be detected by means of its condensation product with hydrazine since this salicylaldazine fluoresces intensely yellow-green under the ultra-violet lamp.[4]

Procedure. A pinch of the solid sample or a drop of an aqueous solution is placed in a micro test tube with several cg of hydrated manganous sulphate or crystallised oxalic acid and gradually taken to dryness. The mouth of the test tube is covered with a disc of filter paper moistened with the reagent solution. The test tube is immersed in a glycerol bath which is heated to 110°. A positive response is indicated by a yellow-green fluorescent fleck on the paper when examined under the ultra-violet lamp

Limit of detection. 0 1 μg helicin

Reagent A cold saturated solution of hydrazine sulphate or chloride plus several grams of sodium acetate (buffer).

Detection of anilides of aliphatic carboxylic acids

Anilides of aliphatic and aromatic carboxylic acids may be saponified by dry heating alone or by heating with oxalic acid dihydrate:

$$R(Ar)CONHC_6H_5 + H_2O \rightarrow R(Ar)COOH + C_6H_5NH_2$$

These are interesting instances of pyrohydrolysis but they have no analytical significance since the release of aniline can be accomplished more simply by boiling with concentrated alkali hydroxide solution.

If the water-donor is $MnSO_4 \cdot 4\,H_2O$ (which loses its water of crystallisation between 110 and 200°), only anilides of aliphatic carboxylic acids will release aniline through pyrohydrolysis at 130°, whereas anilides of aromatic carboxylic acids remain unaltered. The released aniline is transported by the water vapour furnished by the heated manganous sulphate hydrate and may be revealed by contact with *p*-dimethylaminobenzaldehyde with which it yields a yellow Schiff base.[5] This pyrohydrolysis thus provides a convenient means of distinguishing the anilides of aliphatic as contrasted with aromatic carboxylic acids

Procedure. One drop of the test solution in ether is placed in a micro test tube along with several cg of manganous sulphate tetrahydrate and taken to dryness. The mouth of the test tube is covered with a disc of filter paper impregnated with a saturated ether solution of *p*-dimethylaminobenzaldehyde The test tube is placed in a glycerol bath previously heated to 130° A positive response is indicated by the rapid appearance of a yellow stain on the paper.

The test revealed·

25 μg *n*-butyric acid anilide	10 μg formanilide
25 μg adipic acid anilide	10 μg acetanilide
25 μg *p*-bromoacetanilide	10 μg carbanilide
25 μg propionanilide	20 μg oxanilide

Detection of O-*Acetyl compounds*

If one portion of a dry mixture of aliphatic or aromatic O-acetyl compounds with crystalline oxalic acid is heated to 100° by itself and another portion is heated to 100° after adding a little water, only the first portion will undergo hydrolytic cleaving to yield acetic acid.

$$R(Ar)OCOCH_3 + H_2O \rightarrow R(Ar)OH + CH_3COOH$$

Consequently, there is here exhibited the remarkable fact that water of hydration is more active at 100° than boiling water. A pyrohydrolysis of O-acetyl compounds can also be achieved by heating them to 100–140° with manganous sulphate tetrahydrate.

Since N-acetyl compounds remain unaltered when taken to these temperatures with hydrated oxalic acid or manganous sulphate, the procedure described here can serve as a reliable test for o-acetyl compounds, assuming the absence of inorganic or organic salts of acetic acid, because they too release acetic acid on dry heating with oxalic acid.

Procedure. The test is made in a micro test tube. Several cg of pulverised hydrated oxalic acid are mixed with a little of the sample or with a drop of its solution in alcohol or ether. The solvent is volatilised if need be The mouth of the test tube is covered with a disc of acid-base indicator paper and then warmed in a glycerol bath at 110°. If the response is positive, the indicator paper quickly shows the presence of acidic vapours.

The test revealed.

10 μg acetylsalicylic acid
100 μg acetylmethylsalicylate
50 μg acetylcellulose
50 μg acetylacetanilide

Detection of aliphatically-bound halogen

The most usual method for distinguishing between aliphatic and aromatic bound halogens is based on the rapid formation of alkali halide by the former when warmed with alkali hydroxide. Rauscher[6] recommended the use of monoethanolamine, which is not only a strong base but as an amino alcohol has considerable miscibility with or solvent power for many organic compounds. The methods now in use are not completely reliable and apply only to mobile halogen. However, the mobility can be increased by other groups, even in aromatic compounds. For instance, Rauscher points out that chlorodinitrobenzene behaves like an aliphatic chlorine compound toward OH^- ions.

Proceeding on the basis that the transformation of organic bound halogen atoms into halide ions as expressed by

$$\text{R(Ar)Hal} + H_2O \rightarrow \text{R(Ar)OH} + \text{H Hal}$$

is a hydrolysis (which in the case of aliphatic halogen compounds can be accomplished by strong bases) it seemed logical to attempt to split off hydrogen halides from non-volatile organic materials through pyrohydrolysis. The trials showed that hydrated metal sulphates or oxalic acid have no or at most insignificant effect; they lose their water of hydration within a temperature interval (100–200°) where the organic halogen compounds obviously are not yet ready to undergo pyrohydrolysis. In marked contrast, heating with concentrated sulphuric acid (240°) and likewise dry heating (at 400–500°) with no additive present, resulted in the rapid release of halogen hydride (often even of free halogen)* from aliphatic and also aromatic compounds. The efficacy of melts of succinic acid and phthalic acid as water donors lies between the above extremes when the range 200–230° is used. Under these conditions, aliphatic halogen compounds, without exception, undergo pyrohydrolysis, whereas only one compound (bromothymol blue) among the 39 aromatic halogenated materials tried did not follow the general behaviour of non-response. This selectivity is expressively exhibited by chlorodinitrobenzene (noted above) which yields no hydrogen chloride when heated with succinic (phthalic) acid. Accordingly, the detection of the hydrogen halides split off in the succinic acid melt by pyrohydrolysis makes possible a differentiation of aliphatic and aromatic bound halogen. In practice, such differentiation

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* The evolution of elementary halogen (blueing of starch-iodide paper) may well be due to autoxidation of the anhydrous hydrogen halide produced initially. It is noteworthy that aliphatic halogen compounds are particularly prone to yield free halogen on dry heating.

may be a desirable step after the Beilstein test has shown that the specimen contains halogen.

Acid-base indicator paper may be used to reveal the gaseous hydrogen halide produced by pyrohydrolysis only if other acidic volatile products have not arisen. Therefore it is better to employ a specific test for halogen hydracid which is based[7] on the release of ferrocyanide ions by the reaction:

$$Ag_4[Fe(CN)_6] + 4\ Hal^- \rightarrow 4\ AgHal + [Fe(CN)_6]^{-4}$$

which in turn yield Prussian blue with ferric ions. This demasking can be readily seen through the use of paper impregnated with silver ferrocyanide and moistened with ferric sulphate

The test for aliphatic bound halogen described here is not valid in the presence of inorganic or organic salts of hydrohalic acids or organic derivatives of hypohalous acids (Chloramine-T, 2·6-dichloro-quinone 4-chloroimine, etc.) because acidic hydrogen halides or hypohalous acids result when these compounds are melted along with succinic (phthalic) acid Interference likewise is occasioned by organic compounds whose pyrohydrolysis leads to volatile acids which destroy silver ferrocyanide. Such compounds include thiol compounds which yield hydrogen sulphide, and phenoxyacetic acid and its derivatives which hydrolyse to give volatile glycolic acid.

Procedure A micro test tube is used. Several cg of succinic (phthalic) acid, and a little of the solid sample or a drop of its solution in alcohol or ether, etc are brought together and taken to dryness if need be The mouth of the test tube is covered with a disc of reagent paper moistened with 0 1% ferric sulphate solution The test tube is placed in a glycerol bath previously brought to 200° and the temperature raised to 230° If aliphatic halogen is present, a more or less intense blue colour appears on the paper within 1–3 minutes (often sooner)

Reagent paper Silver ferrocyanide is prepared by adding excess silver nitrate to neutral potassium ferrocyanide solution The thoroughly washed precipitate is dissolved in concentrated ammonium hydroxide Quantitative filter paper is bathed in the ammonical solution and dried in a hot air blast. The $Ag_4[Fe(CN)_6]$ remains in the pores of the paper If stored away from the air, the paper will keep

The following were detected 10 μg α-Aminochloroacetophenone (I), 40 μg 1.1:1-Trichloro-2 2′-*bis*-(*p*-chlorophenyl) ethane (II); 30 μg Hexachlorbenzene (III); 100 μg Nitrobenzylchloride (IV); 10 μg Chloromycetin (V), 30 μg Chloral-α-ethylquinoline (VI), 20 μg 1·1 1-Trichloro-2-hydroxy-3-benzamidopropane (VII), 50 μg (*o*-Methoxy-phenoxy) ethylbromide (VIII), 20 μg N-trichloromethyl-mercapto-tetrahydro-phthalimide (IX)

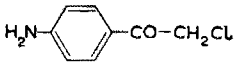
Among the aromatic halogen compounds tested were· 2-chloromandelic acid, 2-bromomandelic acid, 4-iodomandelic acid, *p*-chloroaniline, 7-iodo-8-hydroxyquinoline-5-sulphonic acid, 2-hydroxy-7-chloro-2-quinoline carboxylic acid, 4-bromobenzhydrol, 6 8-dichlorobenzoylenurea, 2:6-dichlorobenzylcyanide, 1 2 4:5-tetrachlorobenzene, tetrachlorohydroquinone, 2 4-dinitrochlorobenzene, 4-bromomandelic acid, tetrabromophthalic anhydride, 3-bromomandelic acid, *p*-chlorobenzophenone, *p*-chloraniline biguanidine, 2-chloro-3-methyl anthraquinone, bromonaphthol, 4-hydroxy-7-chloroquinoline, 2-hydroxy-5-chlorobenzaldehyde, pentachlorophenol, chloranil, dichloro-oxyquinaldine, *o*-bromobenzoic acid, 4-chloro-2-amino anisole, 1-methyl-4-cyano-6-methoxyquinoline iodide, hexachlorobenzene, 2 5-dichlorophenylhydrazine, bromothymol blue

With the exception of bromothymol blue (limit of detection 25 μg) none of these aromatic halogen compounds undergo pyrohydrolysis under the conditions imposed here.

Detection of aromatic sulphonic acids

The standard conversion of aromatic sulphonic acids into phenols by fusion with alkali hydroxide

$$ArSO_3Na + NaOH \rightarrow ArOH + Na_2SO_3$$



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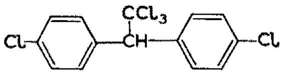

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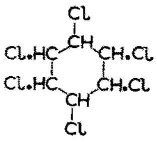

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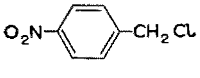

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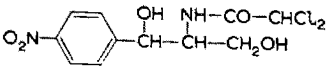

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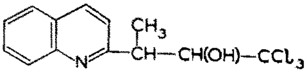

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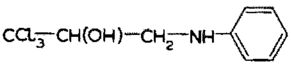

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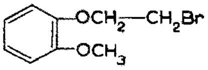

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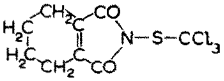


IX

is fundamentally nothing other than the hydrolysis

$$ArSO_3H + H_2O \rightarrow ArOH + H_2SO_3$$

accomplished in an alkaline *milieu.*

Accordingly, the above reaction which leads to the splitting off of sulphur dioxide, may be expected to occur also in the form of a pyrohydrolysis. Actually this is the case when melts of succinic or phthalic acid are used as water donors. On fusion with these acids, the sulphonic acid is first liberated and then yields sulphur dioxide. Since this pyrohydrolysis occurs quickly and since it is easy to detect sulphur dioxide, a very convenient test for sulphonic acid results.

The formation of Prussian blue, as recommended by Heisig and Lerner[8] is used to detect the sulphur dioxide in the tests described here. Care must be taken to insure the absence of compounds which yield reducing materials on pyrohydrolysis. Thio-compounds, in particular, may be mentioned since the SH group is readily substituted by the OH group during pyrohydrolysis. Thio-compounds are readily revealed by holding lead acetate paper above the succinic acid melt; the paper is browned or blackened by the hydrogen sulphide.

Procedure. A little of the solid or 1 drop of its solution is placed in a micro test tube along with several cg of succinic or phthalic acid. After removal of the solvent (if any) the test tube is placed in a glycerol bath previously brought to 200°. A disc of filter paper moistened with ferric ferricyanide solution is placed over the mouth of the tube The temperature is then increased to 250°. A more or less intense blue stain appears on the paper if the test is positive.

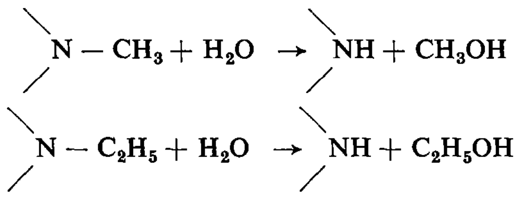
Reagent 0 08 g anhydrous ferric chloride and 0 1 g potassium ferricyanide are dissolved in 100 ml of water

The procedure revealed:

10 μg 1 .4-naphtholsulphonic acid
5 μg 4-aminonaphthalenesulphonic acid
10 μg sulphosalicylic acid
20 μg Congo red

Detection of N-*methyl and* N-*ethyl compounds*

If N-methyl or N-ethyl compounds are heated with succinic or phthalic acid to 200–220°, pyrohydrolysis occurs:



$$>N-CH_3 + H_2O \rightarrow >NH + CH_3OH$$

$$>N-C_2H_5 + H_2O \rightarrow >NH + C_2H_5OH$$

In the presence of air, the hot alcohol vapours are extensively oxidised to formaldehyde or acetaldehyde, respectively. This reaction may be detected if paper moistened with Nessler's solution is held above the melt. The blackening is due to the reaction

$$H(CH_3)CHO + HgI_4^{-2} + 2\,OH^- \rightarrow H(CH_3)COOH + Hg^0 + H_2O + 4\,I^-$$

This redox reaction with Nessler's solution does not however distinguish between formaldehyde and acetaldehyde. If the latter is to be detected, the Lewin colour reaction[9] should be employed. In it, a blue colour is developed in a solution of nitroprusside containing piperidine.

Procedure. A little of the solid or 1 drop of its solution is placed in a micro test tube along with several cg of succinic acid and if need be the solvent is removed The test tube is placed in a glycerol bath previously heated to 200° The mouth of the tube is covered with a disc of filter paper moistened with Nessler or Lewin reagent. The temperature of the bath is then taken to 220°. A black or blue colour on the paper indicates a positive response The intensity of the colour is dependent on the test material

The following gave positive responses (with Nessler's reagent).

25 μg ethyl orange
10 μg methyl orange
5 μg Malachite green
5 μg Tetrabase
10 μg Celestine blue
5 μg *p*-nitrosodiethylaniline
5 μg *p*-dimethylaminobenzaldehyde
5 μg Brilliant green

Zusammenfassung—Werden Hydrate von Mangansulfat oder Oxalsäure, bzw. Bernsteinsaure oder Phthalsaure in Kontakt mit organischen Verbindungen erhitzt, so konnen durch das im Temperaturbereich 100–230° abgespaltene Wasser Hydrolysen bewirkt werden, die mit kochendem Wasser nicht eintreten Fur derartige, nur bei hoherer Temperatur realisierbare Hydrolysen wird die Bezeichnung Pyrohydrolyse vorgeschlagen

Analytische Anwendungen von Pyrohydrolysen sind moglich, wenn bei kurzer Erhitzung mit geeigneten Wasserdonors Spaltprodukte entstehen, die in ihrer Gasphase empfindlich nachweisbar sind Hierfur werden folgende Beispiele angefuhrt:

Nachweis von Helicin durch Abspaltung von Salicylaldehyd

Nachweis von Aniliden alifatischer Carbonsauren durch Abspaltung von Anilin

Nachweis von o-Acetylverbindungen durch Abspaltung von Essigsaure

Nachweis von alifatisch gebundenem Halogen durch Abspaltung von Halogenwasserstoff

Nachweis von-aromatischen Sulfosauren durch Abspaltung von Schwefeldioxyd.

Nachweis von N-methyl u N-athylgruppen durch Abspaltung von Formaldehyd bzw. Acetaldehyd

Samtliche Nachweise konnen in der Arbeitsweise der Tupfelanalyse durchgeführt werden und besitzen mikroanalytische Erfassungsgrezen

Résumé—Si les composés organiques sont chauffés en présence des hydrates du sulfate manganeux ou de l'acide oxalique, ou avec les acides succinique ou phthalique, l'eau libérée à une température de l'ordre de 100°–230° peut effectuer des hydrolyses qui ne se produisent pas avec de l'eau à température d'ebullition On suggère l'emploi du terme "pyrohydrolyse" pour ces hydrolyses qui n'ont lieu qu'à température élevée

Les pyrohydrolyses permettent des applications analytiques à condition que le chauffage rapide avec des donneurs d'eau appropriés cède des produits qu'on peut identifier facilement en phase gaseuse On donne les exemples suivants: la détection de l' hélicine par la formation de l'aldéhyde salicylique, des anilides des acides carboxyliques aliphatiques par la formation de l'aniline, des composés o-acétyl par l'evolution de l'acide acétique, des halogénures aliphatiques par la formation des halogénures d'hydrogène, des acides sulfoniques benzéniques par le dégagement du dioxyde de soufre, des groupes N-methyl et N-ethyl par la formation des aldéhydes formique et acétique respectivement

Toutes ces expériences peuvent s'effectuer dans les limites de l'analyse à la touche, et permettent la détection à l'échelle microanalytique

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ANALYTICAL CHEMISTRY OF COBALT

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(*Received* 5 *March* 1958)

Summary—A critical selection is given of the more original methods for the detection and determination of cobalt, with particular emphasis on developments during the past ten years

ALTHOUGH cobalt compounds were used in very early times for colouring glass, it was not until 1742 that Georg Brandt[13] isolated the metal and gave it its name. At present it is developing extensive industrial applications, particularly as a constituent of "stellites", non-corroding alloys used in the manufacture of high-speed cutting tools. It is also used in the manufacture of catalysts, paint dryers, permanent magnets, and as a colouring agent in the glass and ceramic industries. More recently, ^{60}Co has been used as a substitute for radium in the treatment of cancer.

Cobalt analytical literature is extensive and often controversial. Although some incidental reviews covering limited aspects of the subject have appeared,[29,47,73,172] no concise account embracing the entire subject is available. The present review is an attempt to meet the need for this.

It is not possible to include all the published methods; a critical selection of the more original methods will therefore be given, with particular emphasis on developments during the past ten years.

QUALITATIVE ANALYSIS

The separation of cobalt from other metals for the purpose of identification may be carried out using chromatographic techniques [86,122,152,157,165] An ingenious method which may be used for the detection of cobalt in the presence of other metals has been described by Weisz.[167] By means of his "ring oven" the identification of a dozen or so metals contained in one 1·5-μl drop of solution is possible.

In addition to 1-nitroso-2-naphthol, ammonium thiocyanate, rubeanic acid, phenylthiohydantoic acid, and nitroso-R-salt, many new reagents have been advocated for the detection of cobalt Among these may be mentioned hydroxyiminodimedone,[65] 2-mercapto-acetamido-4-nitrophenol,[16] thiourea,[67] β-mercaptopropionic acid,[96] iodoxine (8-hydroxy-5:7-di-iodoquinoline),[110] alkali pyrophosphates, especially $K_4P_2O_7$,[119] glycerol and conc. NaOH,[112] 5:6-benzoquinoline and ammonium thiocyanate,[68] and the *p*-nitrophenylhydrazone of diacetylmonoxime.[49] In addition, the catalysed oxidation of Mn^{II} to Mn^{IV},[168] the deep blue colour with the monothiophosphate ion,[176] and the characteristic green colour of the Field–Durrant peroxy compound in presence of bicarbonates[36] have been used.

For the spectrographic detection of cobalt, Standen[151] has recommended the 2424·93 and 2521·36 Å lines as the most sensitive.

QUANTITATIVE ANALYSIS

A comprehensive account of earlier methods used in cobalt analysis is given by Rudisüle.[128]

In the analysis of complex materials, removal of interfering substances is a prerequisite of the estimation of cobalt. The difficulties involved have been discussed [25,47,73,133,177] Of the interfering elements, copper, nickel and iron are the most troublesome to remove

Cobalt is tenaciously retained by the hydroxides of iron and aluminium Iron may be removed from nickel and cobalt by ZnO, but separation as ferric phosphate from an acetic acid solution is far more effective:[177]

$$2Na_3PO_4 + Fe_2(SO_4)_3 \rightarrow 2FePO_4 \downarrow + 3Na_2SO_4$$

Standard methods of separating cobalt from nickel include the use of 1-nitroso-2-naphthol, potassium nitrite, or dimethylglyoxime for the removal of nickel. Harris and Sweet[73] found that separation of cobalt as Co-1-nitroso-2-naphtholate was marred by reluctance of this compound to dissolve in acids for the subsequent estimation of cobalt by another method

Torrance[160] effected a separation by anodic deposition of cobalt as oxide

Several new methods have been proposed recently for the separation of cobalt and nickel. Nenadkevich and Saltykova[111] base a method on the ability of cobalt, unlike nickel, to form stable cyanide complexes in acid solution. Another method[57] makes use of the fact that $Co(OH)_3$ is precipitated at a lower pH than $Ni(OH)_3$; Al^{3+} and Ca^{2+} salts are employed as buffers. Ion-exchange methods have also been used.[81,74] Flaschka and Abdine have described the separation of cobalt and nickel from other elements in one precipitation by means of thioacetamide.[52]

Gravimetric methods

The precipitation of cobalt by 1-nitroso-2-naphthol introduced by Ilinski and von Knorre[78] in 1885 was one of the first methods used for determining a metal with the aid of a selective organic reagent. In spite of its many defects, and the large number of other methods proposed for estimating cobalt since then, it remains, in modified form one of the most used methods in cobalt analysis Complexes in which cobalt is bivalent or tervalent are possible; the composition under various conditions has been the subject of several investigations.[10,87,102] Slawik[147] and Eder[44] ignited the complex and weighed the resulting oxide. A difficulty in this procedure was the explosive decomposition at about 270°, a feature clearly indicated in Duval's pyrolysis curve for the material.[43] Doubt was thrown on the composition of the oxide It was assumed to have the composition Co_3O_4; on this assumption Congdon and Chen[29] obtained an accuracy of 1 % when assessing the method. A further modification is reduction of the oxide to metallic cobalt by hydrogen for final weighing; it is in this form that the method is claimed to be most accurate. Conversion of the metal so obtained to sulphate has also been recommended, this being ignited at red heat.

No matter which modification is used the 1-nitroso-2-naphthol method is open to much criticism The precipitate is impure. This is partly due to the two valency states; but in addition the reagent acts as oxidant, and in this process is itself reduced to products which further contaminate the precipitate. The bulky nature of the precipitate and its tendency to stick to glassware make filtration difficult; poisonous fumes are given off on heating; and the solubility of the precipitate in acetic acid solutions remains indeterminate.

Earlier doubts expressed about 1-nitro-2-naphthol as a reagent for cobalt have been confirmed by Blay and Warren,[9] who found that pure 1-nitro-2-naphthol gave no precipitate with cobalt The reagent used by earlier investigators probably contained 1-nitroso-2-naphthol as impurity.

Separation of cobalt as potassium cobaltinitrite, first suggested by Fischer,[51] is the basis of gravimetric and titrimetric methods. Variation in composition of the precipitate and the long time required for complete precipitation are the main drawbacks. Cumbers and Coppock[30] attempted to precipitate cobalt as dipotassium sodium cobaltinitrite, on which much work had been done in connection with the determination of potassium Under strictly controlled conditions they claimed that a precipitate of composition $K_2Na(NO_2)_6 \cdot H_2O$ was obtained. Thermogravimetric studies on both $2K_3[Co(NO_2)_6] \cdot 3\ H_2O$ and $(K,Na)_3[Co(NO_2)_6] \cdot nH_2O$ were made by Duval[43] who showed the former to be a good weighing form but the latter a bad one. As a means of separating cobalt from other metals (including Ni) the cobaltinitrite method is good, especially if carried out in the presence of tartaric acid,[82] but the final determination of cobalt is best done using another method

Anthranilic acid was applied to the estimation of cobalt by Funk and Ditt[61] in 1933. The method consisted of adding excess of a 3% sodium anthranilate solution to a hot neutral or very slightly acid solution of cobalt, and finally weighing as $Co(C_7H_6O_2N)_2$ after drying at 105°–110°. A titrimetric method was also proposed. Goto[69] in studying the effect of pH on the precipitation of cobalt with anthranilic acid found the minimum pH for complete precipitation, and the maximum pH at which no precipitation took place to be 4·41 and 3·36 respectively. These values have been criticised recently and re-determined.[76] Shennan *et al.*[139] also investigated the precipitation of cobalt anthranilate in buffered solutions in order to find whether separations might be effected. Although accurate results were claimed in unbuffered solutions, low results were obtained in the presence of acetates and tartrates These authors concluded that the method was incapable of extension. Harris[72] has recently examined the method; details are not yet available.

The method has several good features. The purity of the reagent can be checked easily, the precipitate is easy to wash and filter, and its thermogravimetric characteristics[43] indicate a good weighing form.

5-Bromoanthranilic acid has also been proposed for cobalt analysis.[138] The method has the good features mentioned above but the precipitate is soluble in acetates and tartrates, although this can be diminished by using a greater excess of the reagent

The phosphate method is analogous to the zinc and magnesium methods, but although much investigated, it has never received similar recognition. This is mainly due to the appreciable solubility of the precipitate. The overall reaction may be represented by the equation

$$CoCl_2 + 2(NH_4)_2HPO_4 + H_2O \rightarrow CoNH_4PO_4 \cdot H_2O + NH_4H_2PO_4 + 2NH_4Cl$$

Ignition of the double ammonium phosphate yields cobalt pyrophosphate as an alternative weighing form:

$$2CoNH_4PO_4 \cdot H_2O \rightarrow Co_2P_2O_7 + 2NH_3 + 3H_2O.$$

The corresponding method for magnesium has an extensive literature; a good account of the difficulties involved is given by Kolthoff and Sandell.[88]

Early work on the cobalt method[20,27,34,40] took no account of residual cobalt in the filtrate. Dufty[42] estimated it by saturating the filtrate with hydrogen sulphide and, after filtering, igniting the cobalt sulphide to Co_3O_4 Schoeller and Powell[134] used 1-nitroso-2-naphthol to determine the filtrate cobalt, although in later work Schoeller[133] employed hydrogen sulphide. The cobalt found by these procedures was added to the major fraction as $Co_2P_2O_7$ to give total cobalt Despite Dufty's results, which showed considerable filtrate cobalt, some later workers[37,91] made no correction for it. In their examination of analytical procedures for cobalt, Willard and Hall[172] invariably obtained high results using the phosphate method. More recently Matsuo[101] has investigated the effect of pH and ammonium ion concentration on the precipitation of cobalt ammonium phosphate. The precipitates produced under various conditions were ignited to pyrophosphate, and the filtrate cobalt added in each case. He obtained low results under all conditions and concluded that the method was incapable of producing a precipitate of satisfactory composition

The pyrolysis curve[43] for $CoNH_4PO_4{\cdot}H_2O$ indicates that the pyrophosphate appears at 580° and that it is a good weighing form.

The pyridine–ammonium thiocyanate method introduced by Spacu and Dick[148] consists of adding pyridine and ammonium thiocyanate to a cobaltous solution to produce the complex $Co[(C_5H_5N)_4(CNS)_2]$. Its thermogravimetric curve[43] indicates stability up to 60°, followed by continuous loss of weight, so that gravimetric procedures involve drying at lower temperatures in a vacuum desiccator. Dobbins and Sanders[41] found the complex to be partially soluble on washing and in the presence of ammonium ion. As this is present under analytical conditions some loss by solubility is inevitable so that the method cannot be seriously considered for accurate work.

8-Hydroxyquinoline ("oxine"), introduced independently by Berg and Hahn in 1926–27, precipitates cobalt quantitatively between pH 4·2 and 11·6 [8] Berg originally suggested 100° for drying the complex as $Co(C_9H_6ON)_2{\cdot}2H_2O$ and also recommended decomposition with oxalic acid for final weighing as oxide. Fleck and Ward[55] and Cumbers and Coppock[30] found uncertainty in the degree of hydration. The latter workers found that between 90° and 95° the water of hydration was equivalent to 1·75 H_2O and became progressively less on further heating. Accordingly, they recommended drying at room temperature and the use of an empirical factor Duval[43] found that loss of water took place up to 115°, followed by a period of almost constant weight to 295°.

Phenylthiohydantoic acid, introduced by Willard and Hall[172] in 1922, precipitates cobalt in ammoniacal solution as a reddish-brown bulky complex; owing to the indefinite nature of the complex, ignition to the oxide "Co_3O_4" was attempted. This invariably gave high results, attributed by Willard and Hall (*loc. cit.*) to conversion of some of the sulphur in the original precipitate to sulphate. A further development was conversion of the oxide to sulphate for final weighing Cuvelier[32] in further investigating the method found it to give errors as low as 0·1–0·2% However, he used electrolytic cobalt, the purity of which is always subject to doubt, as a primary standard. It is questionable whether the method is capable of this degree of accuracy.

In 1947 Garrido[63] recommended diphenylthiohydantoin as a gravimetric reagent, but the thermogravimetric behaviour of the precipitate[43] indicates that the method is incapable of high accuracy.

Ignition to, and final weighing as $CoSO_4$ is the final procedure in many methods, the temperatures recommended ranging from 400° to 600°. The important question is whether this can be carried out without thermal decomposition of the anhydrous sulphate itself:

$$CoSO_4 \rightarrow CoO + SO_3$$

The extensive literature on this breakdown, much of which is reported in Mellor[104] is very conflicting about the temperature at which decomposition starts, the values ranging from 440° to about 900°. Willard and Hall[172] found 550° as the upper limit for ignition without decomposition, although in later work Willard and Fowler[171] prepared anhydrous cobalt sulphate by heating to constant weight at 500°–650°. More recently Baker and McCutcheon[4] claim that $CoSO_4$ ignited at not higher than 550° gives accurate results as a method of analysis Yardley,[175] in assessing the value of $CoSO_4$ as a primary standard, found that ignition at 400°–550° always produced a product containing traces of water or deficient in SO_3 Duval's thermogravimetric study[43] led him to conclude that dissociation took place over the whole range between 350° and 820°, and that results better than 1% accurate could not be obtained using the method For methods where ignition to sulphate is the final procedure, errors due to operations carried out before the ignition, in addition to the above, would also influence the final result

Precipitation of cobalt as sulphide followed by conversion to oxide and then reduction to metal for final weighing is an old method [58] Although precipitation appears to be complete, washing causes some precipitate to pass through the filter, and ammonium salts dissolve it. Thermogravimetric studies[43] indicate that cobalt sulphide is quite unsuitable as a weighing form.

Lamure[93] in 1946 estimated cobalt as $Co[Hg(CNS)_4]$ using mercuric chloride and ammonium thiocyanate, the precipitate being washed with a dilute solution of the precipitants followed by ether, and then dried at 90°. Sierra and Cárceles[143,144,145] investigated further the optimum conditions for precipitation and the effects of other ions present. More recently the mercury thiocyanate method has been investigated by Korenman *et al* [90] It is very doubtful whether the method in its present form is capable of giving accurate results

The method of separating cobalt and nickel based on the ability of cobalt, unlike nickel, to form a stable cyanide complex in acid solution, has been further developed into a gravimetric method for estimating cobalt [111] After decomposition of the $K_2Ni(CN)_4$, silver nitrate solution was added to the $K_3Co(CN)_6$ and the resulting precipitate of $Ag_3Co(CN)_6$ dried at 130° and weighed Duval[43] has shown it to be stable over the range 98°–252°. The procedure, if nickel were present, would need safety precautions.

Dinitroresorcinol has been proposed as a reagent for the estimation of cobalt [117] Tomicek and Komarek[158] later found that both the composition of the precipitate and the amount of residual cobalt depended on the conditions used. Attempts to improve the method were unsuccessful.

Taurins[155] determined cobalt as the complex $[Co(NH_3)_6][HgI_3]_2$ by precipitating with K_2HgI_4 solution from a strongly ammoniacal cobalt solution in a carbon dioxide atmosphere. As the precipitate is decomposed by water and must be prepared in the absence of air, the method cannot be seriously considered.

Benzoquinaldinic acid as a reagent for cobalt estimation was suggested by Majumdar and De[97] in 1953, the complex $Co(C_{14}H_8NO_2)_2{\cdot}2H_2O$ being weighed after drying at 110°–115°, or the anhydrous form after drying at 150°–155°. They used 10-mg quantities of cobalt only in assessing the method, and their primary standards were of doubtful value, so that their results are difficult to judge.

For the micro-estimation of cobalt *iso*-nitrosodimedone has recently been proposed.[65] In addition to the fact that most common ions do not interfere, its investigators find that the precipitate is thermally stable up to 260°, and its solubility low.

Two rather similar methods involving pyridine complexes which, it was claimed, gave rapid and accurate results, appeared in 1955. Spacu and Schiau[150] precipitate cobalt as $[CoPy_4].[(SCN)_2]$, interference by any iron or aluminium present being eliminated by the addition of sodium sulphosalicylate. Both cobalt and nickel may be separated from iron and aluminium in this way; after weighing the mixed complexes, the nickel may be determined using dimethylglyoxime. The second method[121] is based on the precipitation of cobalt as $[Co\,Py_4]\,[Cr_2O_7]$ by the addition of pyridine and potassium dichromate solution. After washing with ethanol and ether, it is dried in a vacuum desiccator. Nickel and cadmium may also be determined in this way.

In another recent method[64] cobalt is precipitated as $Co(C_7H_5N_2)_2$ by a 1% benziminazole solution. Accurate results are claimed when the complex is dried at 105°.

Reduction by hydrogen to the metal, via "Co_3O_4" of uncertain composition, has been recommended as the final procedure in many methods, e.g.,

$$\begin{tikzcd}
 & \text{Co}^{\text{III}}\text{-1-nitroso-2-naphtholate} \arrow[dr] & & \\
 & \text{Co(OH)}_3 \arrow[r] & {} & \\
\text{Co}^{2+} \arrow[uur] \arrow[ur] \arrow[dr] \arrow[ddr] & & \text{“Co}_3\text{O}_4\text{”} \arrow[r] & \text{Co} \\
 & \text{Co phenylthiohydantoate} \arrow[ur] & & \\
 & \text{CoS} \arrow[uur] & &
\end{tikzcd}$$

Although the procedure itself is old, it is exclusively recommended in the 1956 edition of A.S.T.M. (American Society for Testing Materials.) Methods for Chemical Analysis of Metals, for the determination of cobalt, the initial step being precipitation using 1-nitroso-2-naphtholate.

Yardley[175] found the reduced metal very pyrophoric; this appears to depend on the temperature at which the reduction is carried out. The question of whether the oxide is completely reduced is important. Purchased cobalt "sponge" of "99·99% purity" has been shown to contain appreciable quantities of unreduced oxide.[56] Another drawback to the method is that in weighing the metal itself, weighing errors have the maximum effect, and this, no doubt, is a reason why conversion to the sulphate for final weighing has also been recommended.

Titrimetric methods

Many of the older methods are dependent on the oxidation of cobaltous solutions to cobaltic hydroxide with potassium permanganate in the presence of such substances as HgO or ZnO, these serving only to separate the hydroxide mechanically.

Another large group of methods consists of

$$\mathrm{Co^{II}} \xrightarrow[\substack{\textit{sodium hypochlorite}\\ \textit{iodine}\\ \textit{bromine}\\ \textit{sodium perborate}\\ \text{or } \textit{hydrogen peroxide}}]{\textit{oxidation by}} \mathrm{Co^{III}} \quad [\mathrm{Co(OH)_3}\text{ ammine or carbonato complex}]$$

The excess of oxidant is removed, and the $\mathrm{Co^{III}}$ compound is reduced with standard reductant. The earlier methods which utilised potassium permanganate, sodium hypochlorite, and iodine were examined by Harris[71] who concluded that they were empirical and incapable of high accuracy.

Many titrimetric methods are based on the green carbonato complex produced by adding hydrogen peroxide to a cobaltous solution containing excess of sodium or potassium bicarbonate (the Field–Durrant reaction). Excess hydrogen peroxide is catalytically decomposed by the cobalt present; the complex itself is unstable except in the presence of sodium or potassium bicarbonate. Titrimetric procedures consist of converting the cobalt into the complex and reducing the latter using an indirect method Many difficulties are involved The catalytic decomposition of the excess peroxide leads to errors caused by dissolved oxygen. This is reduced by keeping the volume of solution small. The large excess of bicarbonate must be neutralised with care to avoid loss by effervescence. The complex cannot be heated excessively to hasten the decomposition of excess peroxide or it would itself decompose. Therefore sufficient time must be allowed for this process to take place at lower temperatures.

Laitinen and Burdett[92] used an iodometric procedure. They oxidised the cobalt to the carbonato complex, added potassium iodide and carefully acidified. The liberated iodine was titrated with standard thiosulphate.

In using this method for the semi-micro estimation of cobalt, Mori and Shibata[109] find that it gives high results for cobalt alone, but low results in the presence of ferric iron, nickel, copper and manganese. A photometric method based on the carbonato complex is recommended by these workers instead of the iodometric determination.

Metzl[106] developed a method in which the initial step is conversion of the cobalt to cobaltic hydroxide. This is accomplished in one of two ways, either by decomposing the carbonato complex by sodium hydroxide, or by a similar decomposition of the cobaltammine produced by oxidation of cobaltous solutions containing ammonium chloride. In both cases excess hydrogen peroxide was removed by boiling, the trihydroxide dissolved in an acid potassium iodide solution, and the liberated iodine titrated with standard thiosulphate:

$$2\mathrm{Co(OH)_3} + 2\mathrm{KI} + 3\mathrm{H_2SO_4} \rightarrow 2\mathrm{CoSO_4} + \mathrm{I_2} + 6\mathrm{H_2O} + \mathrm{K_2SO_4}$$

In a rather similar method Engle and Gustavson[46] used both hydrogen peroxide and sodium perborate as oxidants:

$$8\mathrm{CoSO_4} + 4\mathrm{NaBO_3} + 14\mathrm{NaOH} + 5\mathrm{H_2O} \rightarrow 8\mathrm{Co(OH)_3} + \mathrm{Na_2B_4O_7} + 8\mathrm{Na_2SO_4}.$$

Other workers using sodium perborate were Willard and Hall,[172] Sarver[131] and more recently Baker and McCutcheon.[5] Excess perborate is easily removed by boiling for ten minutes. The trihydroxide was found to dissolve slowly, especially last traces.[172] Furthermore, sources of error were found which depended on the procedure used. For example, when ferrous sulphate itself was added to the alkaline solution, air-oxidation of the iron took place giving high results. If acid ferrous sulphate were added, loss of free oxygen due to instability of the Co^{3+} ion in acid solution became a source of error.

Sarver (*loc. cit.*) attempted, by careful manipulation of taps, to suck ferrous sulphate solution without air into the alkaline cobaltic hydroxide. Sulphuric acid was similarly introduced and finally the excess of standard ferrous sulphate was back titrated with potassium dichromate. Recently Baker and McCutcheon (*loc. cit.*) have described a modified form of Sarver's method.

The possibility of using reducing agents other than potassium iodide and ferrous sulphate to reduce cobaltic hydroxide was investigated by Willard and Hall Stannous chloride was found to be very good, the trihydroxide dissolving easily, but a carbon dioxide atmosphere was necessary:

$$2Co(OH)_3 + SnCl_2 + 6HCl \rightarrow 2CoCl_2 + SnCl_4 + 6H_2O$$

Reduction by titanous sulphate, sodium arsenite, antimony trichloride, potassium thiocyanate, and hydrazine salts were investigated by the same workers without success.

Methods involving oxidation to cobaltic hydroxide as first step were examined by Evans[47] who concluded that they were incapable of giving accurate results.

Several titrimetric methods have been proposed based on initial precipitation of cobalt as dipotassium sodium cobaltinitrite They are very similar in principle. The cobaltinitrite precipitate is dissolved in excess of standard potassium permanganate and sulphuric acid. Nitrous acid is formed, and the cobalt reduced to the bivalent state. Eleven equivalents of potassium permanganate are used for each mole of cobaltinitrite. The excess of permanganate has been determined in several ways. Karslake[83] and Faleev[48] used oxalic acid; Vassiliev[164] and Nikolow[114] used potassium iodide in acid solution, titrating the liberated iodine with standard thiosulphate.

In addition to the gravimetric procedure, Funk and Ditt[61] also proposed a titrimetric anthranilate method This consisted of dissolving the washed anthranilate precipitate in $4N$ hydrochloric acid and titrating with a potassium bromate–bromide solution; the slight excess of bromine was determined by adding a small quantity of potassium iodide and titrating the liberated iodine with thiosulphate·

$$Co[C_6H_4(NH_2)COO]_2 + 2HCl \rightarrow CoCl_2 + 2C_6H_4(NH_2)COOH$$

$$C_6H_4(NH_2)COOH + 2Br_2 \rightarrow C_6H_2(NH_2)Br_2COOH + 2HBr$$

The titrimetric modification of the 8-hydroxyquinoline method[8] is well known It consists of liberating the 8-hydroxyquinoline by adding dilute hydrochloric acid to the washed precipitate and then brominating to 5:7-dibromo-8-hydroxyquinoline with a standard potassium bromate–bromide solution. Owing to difficulty in detecting the end-point, Fleck and Ward[55] recommended an iodometric procedure as in the anthranilate end-point.

The cobaltinitrite, anthranilate, and 8-hydroxyquinoline titrimetric methods each possess the unsatisfactory feature of precipitation, followed by filtration and washing an as integral part of the determination. The possibility of errors, particularly due to the solubility of the precipitates, detracts considerably from the value of these methods in accurate work.

Almost simultaneously, Spacu and Kuras[149] and Dobbins and Sanders[41] developed titrimetric procedures based on the precipitation of cobalt with pyridine and ammonium thiocyanate. In each case, excess of standard thiocyanate was added, and this was back titrated with standard silver nitrate solution

The cyanide method developed by Evans[47] is based on earlier work by Rupp and Pfenning[129] and Glasstone and Speakman.[66] It is a result of combining the reaction of cobalt and potassium cyanide, to form a complex of 1:5 Co : CN ratio, with the Liebig method for titrating cyanides with silver nitrate The procedure recommended by Evans is difficult to carry out in practice and contains several unsatisfactory features. For example, one step involves bubbling a stream of air through the solution for exactly six minutes, low results being obtained for five minutes and high results for seven minutes. The method has been examined by Hall and Young who find its accuracy to be 1–3%.

A titrimetric method based on oxidation of cobalt in ammoniacal solution by potassium ferricyanide was introduced in 1935 by Dickens and Maassen[38] and Tomicek and Freiberger.[159] The end-point is determined potentiometrically. Results using the direct method were found to be low; the procedure then adopted was to add the cobaltous solution to excess of standard ferricyanide containing ammonia and ammonium chloride, and to back titrate the excess with a standard cobaltous solution. The standard potentials of the individual couples are

$$[Fe(CN)_6]^{4-} = [Fe(CN)_6]^{3-} + e^- \qquad E_0 = -0{\cdot}36 \text{ volt.}$$

$$[Co(NH_3)_6]^{2+} = [Co(NH_3)_6]^{3+} + e^- \qquad E_0 = -0{\cdot}10 \text{ volt.}$$

Bagshaw and Hobson[3] raised doubts as to whether all the cobalt was oxidised at the point of inflection, owing to the closeness of the two potentials Later, Yardley[175] using changed conditions found no "overlap" of the two systems and obtained titration curves which could only be explained if the equilibrium constant for the reaction was about 2×10^6. Recently Cassy[19] has found that in a citrate–sulphate solution the equilibrium constant is $9{\cdot}8 \times 10^4$, indicating that 0·34% of the Co^{II} remains unoxidised. A method employing the "dead stop" technique has been described.[59]

Diehl and Butler[39] have recently recommended replacing the ammonia by ethylenediamine, the Co^{II} ethylenediamine complex being a stronger reducing agent by some 0·5 volt. The potential break at the equivalence point is augmented by a similar amount, although dissolved oxygen now becomes an interfering factor and must be removed. More recently Kopanica and Doležal[89] have described a direct titration of cobalt with standard potassium ferricyanide in the presence of glycine. The latter forms a more stable complex with cobalt than either ammonia or ethylenediamine and no inert atmosphere is needed.

There is little doubt that the ferricyanide method is excellent for the routine determination of cobalt, especially in the presence of other cations (only manganese interferes) and where high accuracy is not required.

In a recent paper Kawagaki[84] has attempted to improve the oxalate method by the precipitation of cobalt oxalate in the presence of acetic acid. It is washed, dissolved in sulphuric acid, and titrated with standard potassium permanganate.

Dakin[33] and later Schoeller and Powell[134] developed a titrimetric method based on cobalt ammonium phosphate. The precipitate was dissolved in excess of standard sulphuric acid and a back titration made with standard alkali, the end point being indicated by disappearance of the lilac colour.

A ferrocyanide method[60] for the semi-micro estimation of cobalt has recently made its appearance Unlike an older form of the method which employed an external indicator, the new one uses a starch–iodine end-point

Coetzee[28] has developed a method for titrating cobalt with 0·1*N* alkali using thymolphthalein as indicator. Conversion of the blue hydroxide to the rose-coloured form enabled the indicator change to be observed. Accurate results have been claimed for this method, but previous separation of the cobalt is necessary.

EDTA forms both bivalent and tervalent complexes with cobalt, the latter being more stable than the former:

$$Co^{2+} + H_2Y^{2-} \rightarrow CoY^{2-} + 2H^+$$

$$Co^{3+} + H_2Y^{2-} \rightarrow CoY^{-} + 2H^+$$

The redox potential of the system Co^{3+}/Co^{2+} with EDTA was found by Přibil[123] to be —0·6 V, which meant that oxidation to the tervalent state was possible using ceric sulphate. A method based on this was subsequently developed,[126] the end-point being determined potentiometrically The oxidation was found to be very slow, a considerable time-lag occurring between addition of the reagent and constant potentiometric readings.

The most direct titration between cobalt and EDTA was proposed by Flaschka in 1952.[54] Murexide was used as indicator, the maximum amount of cobalt which could be determined was 0·38 mg. In 1954 Harris and Sweet[73] utilised the zinc-EDTA method for estimating cobalt. Excess of standard EDTA was added to an acid solution of cobalt, the excess being determined by back titration with a standard zinc solution using Eriochrome Black-T as indicator For quantities of cobalt above 50 mg the end point was difficult to detect

Subsequent work has been mainly concerned with a search for better indicators. Catechol violet,[98] 1-(2-pyridylazo)-2-naphthol,[53] potassium thiocyanate and acetone[154] and pyrogallol red[153] have been proposed Kinnunen and Wennerstrand[85] find that carrying out the back titration with standard manganous sulphate gives an improved end point with Eriochrome Black-T as indicator Hara and West[70] have described the semi-micro estimation of cobalt using high frequency conductimetric titrimetry. For simultaneous estimation of cobalt and nickel, Přibil[124] uses the fact that the nickel-EDTA complex, unlike the cobalt complex, reacts with potassium cyanide with the liberation of EDTA itself

Yalman[174] has recently proposed an entirely new titrimetric method for cobalt based on the formation of iodopentammine cobalt^{II} nitrate when iodine is added to an ammoniacal cobalt solution containing ammonium nitrate Standard iodine is used, the excess being determined by titration with tervalent arsenic using a starch–iodine or potentiometric end-point. The main reaction may be represented as follows:

$$2Co^{2+} + 10NH_3 + I_3^- \rightarrow 2Co(NH_3)_5I^{2+} + I^-$$

Sodium metavanadate has been applied to the determination of cobalt.[146] The cobalt is precipitated as the complex mercury thiocyanate, and this is dissolved in hydrochloric acid. The solution is titrated against standard sodium metavanadate in the presence of iodine monochloride, which acts as catalyst and oxidiser. Chloroform is used as indicator.

A new iodometric method[137] has been described in which the complex $Co_6(NH_4)_3(AsO_4)_5$ is titrated with standard thiosulphate after adding potassium iodide.

Finally, in the field of non-aqueous titrimetry, Brummet and Hollweg[15] have developed a method in which either dithizone or 1-nitroso-2-naphthol may be used.

Electrolytic method

The electrolytic method is probably the most important in cobalt analysis and is recommended by many sources as the best method where large amounts of cobalt are involved and high accuracy is desired. Electrolytic cobalt has been used by many workers as a primary standard and the electrolytic method is often used to standardise stock solutions for use in assessing other cobalt methods of analysis.

In order to prevent the slight anodic deposit of cobalt which sometimes occurred in ammoniacal solution, Wagenmann[166] added small amounts of hydrazine sulphate to the electrolyte. Lundell and Hoffman[94] used sodium bisulphate for the same purpose. The addition of reducing agents also helped to prevent rough deposits said to be due to oxidation of the cobaltous-ammine ion.

In 1931 Brophy[14] by using a high rate of stirring (>800 r p.m) and a high current density (4–7 A/dm^2) claimed complete deposition of substantial quantities of cobalt in 30 min. Later, doubts were held as to the completeness of deposition, and procedures were recommended by which residual cobalt in the spent electrolyte could be estimated by means of hydrogen sulphide as in the phosphate method.[75,162] Many variations of the electrolytic method are to be found in the literature Scott and Furman[135] recommended a low current density over a period of 12–15 hr. Young and Hall[177] carry out the deposition rapidly at 90°, testing for absence of cobalt with nitroso-R-salt In a more recent method Kallman,[82] using the procedure for final determination of cobalt following the cobaltinitrite separation, used a low current density and 6–8 hr for deposition. Because sodium bisulphite was used, he found the cobalt deposit contaminated with sulphur; this he estimated gravimetrically as $BaSO_4$ and corrected the weight of deposit accordingly. In this form of the method, the time factor is a serious drawback.

A new form of the electrolytic method was proposed by Torrance[160] in 1939. He deposited the cobalt as Co_2O_3 on the anode at pH 5. The deposit was found to adhere badly for quantities of cobalt greater than 40 mg. Very recently, Salyer and Sweet[130] deposit hydrated cobaltic oxide on an anode, from a solution containing a known weight of ^{60}Co After a short electrolysis the deposit is weighed and is examined with a Geiger counter; the cobalt concentration is then deduced using the isotope dilution principle. Internal electrolysis has been described by Schleicher,[132] and electrolysis using a rotating mercury electrode by Tutundžić and Stojković.[163] Some of the unsatisfactory features of the electrolytic method are.

(*i*) incomplete deposition,
(*ii*) an occasional slight anode deposit in the absence of a reducing agent,
(*iii*) a contaminated deposit in the presence of a reducing agent,
(*iv*) a tendency for solution of the platinum anode during prolonged electrolysis.

In (*iv*) it is assumed that any platinum lost from the anode in this way is deposited on the cathode.

The electrolytic method has been carried out with a greater diversity of procedure than any other method. Chemical composition of the electrolyte, time of electrolysis, current density, temperature, type of electrode, rate of stirring and the pH of the solution may be varied

Recently, the electrochemical behaviour of the system Co–H_2O has been studied[35] by establishing the diagram of electrode potential versus pH, and the conditions necessary for producing electrolytic cobalt free from cobaltous hydroxide have been established. Similar information for the electrolysis of cobalt solutions containing ammonium sulphate and ammonia would involve a knowledge of the system Co–NH_3–H_2O.

Colorimetric and absorptiometric methods

As might be expected for a transitional element, a large number of colorimetric and absorptiometric methods are available for estimating cobalt. Some which have been published since 1950 are given in Table I.

Not all are new; several deal with applications or modifications of existing methods.

The nitroso-R-salt method is particularly good and continues to be improved further. A great advantage is that although the reagent forms coloured complexes with most of the common metals, all except the cobalt complex are destroyed by nitric acid Claassen and Westerveld[26] gave the transmission minimum for the Co–NRS complex as 415 mμ, but they recommended measurement at 550 mμ since at this wave length the reagent itself absorbed least Recent work has improved the sensitivity of the method by destroying the excess nitroso-R-salt with sodium perborate in hydrochloric acid[116] or with potassium bromate.[141] A five-fold increase in sensitivity is claimed and the estimation of a cobalt concentration as low as 0·05 μg ml^{-1} is possible

It is interesting to note that the trioxalato-cobalt^{III} method is claimed by Mehlig and Zeagas[103] to be suitable for the accurate estimation of macro quantities of cobalt.

Miscellaneous methods

Protiva[127] has recently introduced a polarographic method which is suitable for steels of high cobalt and nickel content It is claimed to be more rapid than older methods; the accuracy is given as ±0·3%.

Small amounts of cobalt in nickel salts (0·005–0·1%) may be determined with a ±6% accuracy by means of a spectrographic method introduced recently by Čůta and Rauscher [31]

PRIMARY STANDARDS

A survey of cobalt analytical literature reveals that a very wide selection of primary standards has been used, many of doubtful value. Furthermore, many workers, for the purpose of assessing particular methods, have standardised cobalt stock solutions of arbitrary strength by using a wide range of existing methods. Consequently, their final results only relate to these methods. Many of the published methods do not specify the particular standard used.

In the survey of gravimetric procedures, reference was made several times to

TABLE 1

Method or reagent	Reference
Tartrate	(11)
Diphenylthiocarbazone	(105)
o-Nitroso-*p*-cresol	(7)
Tetraphenylarsonium cobaltothiocyanate	(1)
Direct colour	(62) (178)
Trioxalato-cobalt^{III}	(103)
Thiocyanate	(18) (77) (95)
Peroxy-bicarbonate	(156) (109)
iso-Nitrosomalonylguanidine	(79) (80)
EDTA	(79) (99)
EDTA and hydrogen peroxide	(21)
4-Nitro-2-mercapto-acetamidophenol	(16)
2-Nitroso-1-naphthol	(2) (6)
Triphenylmethylarsonium thiocyanate	(45)
Diethyldithiocarbamate	(23) (24) (12) (125)
2·6-[*bis*-2′-Pyridyl]-pyridine	(170)
2-Nitroso-1-naphthol-4-sulphonic acid	(173)
Diacetylmonoxime	(17)
α-Benzilmonoxime	(17)
Nitrilotriacetic acid	(113)
Nitrilotriacetic acid and hydrogen peroxide	(21)
β-Mercaptopropionic acid	(96)
1-(2-Pyridylazo)-2-naphthol	(22)
2.2′.2″-Terpyridine	(108)
m-Methoxy-*o*-nitrosophenol	(161)
1-Nitroso-2-naphthol	(115) (95)
Ethyl xanthate	(120)
3-Methoxy-5-nitrosophenol	(118)
Alkali thiocyanate and tri-*n*-butylamine	(179)
Alkali cyanate and tri-*n*-butylamine	(179)
Tetraphenylphosphonium cobaltothiocyanate	(140)
Thiocyanate and tri-*n*-butylammonium acetate	(180)
Diethylenetriamine	(169)
Furil-α-monoxime	(100)
Nitroso-R-salt*	(116) (50) (141) (136)
2-Methyl-2-thiopseudourea	(142)
Ethylenediamine	(107)

* Sodium-1-nitroso-2-hydroxynaphthalene-3 6-disulphonate

inaccurate methods resulting from cobalt compounds of uncertain composition. This state of affairs should be borne in mind as a critical consideration in assessing the value of primary standards Very little attention has been given to this aspect of cobalt analysis; the only recent worker to discuss it is Yardley[175] who finally adopted purified potassium cobalticyanide as standard.

Apart from relatively few cases where standards containing no obvious unsatisfactory features have been used, it is doubtful whether great importance can be attached to the degreees of accuracy claimed in the published results on cobalt analytical methods.

Zusammenfassung—Eine kritische Auswahl der ursprunglicheren Methoden fur die Nachweis und die Bestimmung von Kobalt, mit insbesonders Nachdrock uber Entwicklungen wahrend der letzten zehn Jahre wird gegeben

Résumé—L'auteur présente une sélection critique des méthodes les plus originales pour la detection et la détermination du cobalt, et plus particulièrement les développements pendant les dix dernières années.

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DETERMINATION OF POLYMER CONCENTRATIONS IN VERY DILUTE SOLUTIONS BY A CLOUD POINT METHOD

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Summary—A method is described for measuring the concentration of polymeric materials in extremely dilute solution (down to 1 p p m or less) by mixed solvent precipitation The method is characterised by precision and ease of performance but requires initial calibration for the particular material being investigated At the lowest concentrations, a rapid rise of slope of the calibration curve compensates for the increasing difficulty in measuring end points Sample curves are given for poly(methyl methacrylate) and polystyrene

THE accurate determination of very small concentrations of polymer dissolved in a suitable solvent has received little discussion in the literature. Nevertheless, such extremely dilute polymer solutions exhibit a number of interesting properties. Jenckel and Rumbach[1] have shown that the adsorption of polymeric substances from solution, while relatively constant at the usual concentration ranges, drops sharply to zero when, for nonmetallic adsorbends such as glass, quartz, and carbon, the concentration is as low as from one to three mg of polymer per 10 ml of solvent. Weissberger, Simha and Rothman[2] and Streeter and Boyer[3] have studied the viscosity of very dilute solutions and have found effects ascribed to changes in the adsorption on the glass walls of the viscometer. In a study of adsorption equilibrium at low concentrations, of the kinetics of desorption, or of the boundary lubrication of metallic plates by small amounts of polymeric materials, it is desirable to measure conveniently and accurately the concentration of polymer in a very dilute solution.

When, therefore, in connection with a study of lubrication, it was necessary to use a large quantity of solvent with a minute amount of polymer, suitable techniques had to be developed for concentration measurements. Viscosity methods were found unsuitable for the reasons just mentioned,[3] and because of the erratic flow of dilute polymer solutions[4,5,6,7] which is observed unless excessive precautions are incorporated into the measuring methods. Other analytical methods investigated included infrared absorption, saponification and subsequent neutralization, fluorescence, turbidimetry, nefluorometry, and mixed solvent precipitation. The last consists of titrating, with a nonsolvent, a solution of the polymer in a mixture of solvent and different nonsolvent, until the appearance of a trace of cloudiness. With this technique, a considerable order of precision was obtained while at the same time retaining procedural convenience.

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EXPERIMENTAL PROCEDURE

A number of solutions of known concentration were prepared, employing the same batch of polymer which had been used for the lubrication experiments. This was done to retain the same average molecular weight of the polymer in solution, and thus avoid introducing an additional parameter.

The standard solutions were prepared by dilution from a master solution formulated by dissolving an accurately weighed amount of polymer (at least 0 2500 g) in a known quantity (at least 250 ml) of thiophene-free benzene. Subsequent dilution permitted elimination of weighing and transfer errors, leaving only the relatively small error in measuring volumes. These standard solutions, stored in volumetric flasks, together with all solvents, titrants, and lubrication samples were kept in a constant temperature room at 72°F for at least 24 hours before titration was performed

Both poly-(methyl methacrylate) and polystyrene were investigated.

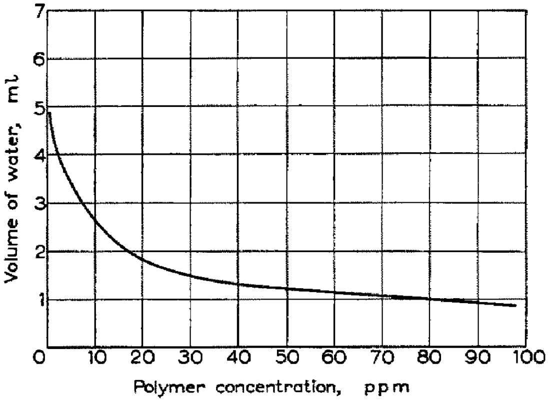

FIG. 1. Calibration curve for poly(methylmethacrylate) Plot of volume of water (ml) vs polymer concentration in benzene (p p m) Temperature = 72°F

The concentration determinations, in the case of poly-(methyl methacrylate), were made in the following manner: ten ml aliquots of each standard concentration were measured into 125 ml Erlenmeyer flasks, and 25 ml methanol added. The solution, clear at this point, was then titrated with distilled H_2O until a cloudiness just appeared in the thoroughly mixed material This was taken as the end-point. The titrations were run in the same constant temperature room at 72°F, and time was allowed for temperature equilibrium after titration before comparison with the blank The end-point is determined visually with the aid of a clear solution used as a blank, and a strong white, heat-filtered light

Precipitation with a single nonsolvent was not effective For example, with poly-(methyl methacrylate), precipitation could not be obtained with methyl alcohol addition alone, at concentrations below 50 p p m , and at higher concentrations a sufficient volume of alcohol (more than used in the procedure below) precipitated essentially the whole concentration, so that no titration curve was obtainable.

RESULTS AND DISCUSSION

Precipitation with distilled water in the presence of methyl alcohol yielded smooth reproducible data, *e g.*, as that of Table I and Fig. 1, which show the result for the procedure described above. Different volumes of methyl alcohol produced similar curves which were shifted to the right or the left, according as the volume of methyl alcohol was less or greater Thus concentrations below 1 p p.m are similarly measurable In addition, changing to different alcohols also shifted the curves to right or left.

The difficulty of measuring end-points in the range below 10–15 p.p.m. is, fortunately, compensated for by the fact that the rise of the curve in this region makes the effect of slight errors in H_2O volume less important. In polymer concentrations below 10 p.p.m., the error in H_2O volume due to error in end-point is ±0·05 ml. This causes the resultant error in concentration to be approximately 0·04 p.p.m below 10 p.p.m. In concentrations above 15 p.p.m. the end-points are sharp, and reproducible to ±0·01 ml. This corresponds to an error from 0·1 to 1·2 p.p m. The method is accurate therefore to between 1 and 2%, with slightly higher precision in the lower range.

TABLE I

Conc of standard solutions (p p m)	Volume of distilled H_2O added to mixture of 25 ml methanol + 10 ml standard solution (ml)
1.62	4 2
3.76	3 6
10 00	2 7
20 0	1 7
40 0	1 3
94 1	0 9

The most convenient concentration-differential in which to titrate is that in which the slope of the curve is large and the onset of turbidity still easily determinable. In the present instance, the range 0–40 p p.m. was the desired region, and the position of the curve was so adjusted.

Instrumental measurement of the end-point by turbidity light transmission, and right angle scattering were also performed in an effort to improve the accuracy of the end-point. The methods are suitable, but unless precautions are taken, the instruments affect the temperature of the solution, so that the end-point becomes a function of the time required to complete a titration. Temperature sensitivity is to be expected from the theory,[8,9,10] although quaternary systems have not been treated in sufficient detail. Instrumental measurements require, for example, a heat-filtered light source, a gas photocell and d.c. power source, and either a high-gain cathode ray oscilloscope or a high-gain amplifier and d.c. voltmeter; the accuracy of the visual results was so great that such an expenditure was unnecessary.

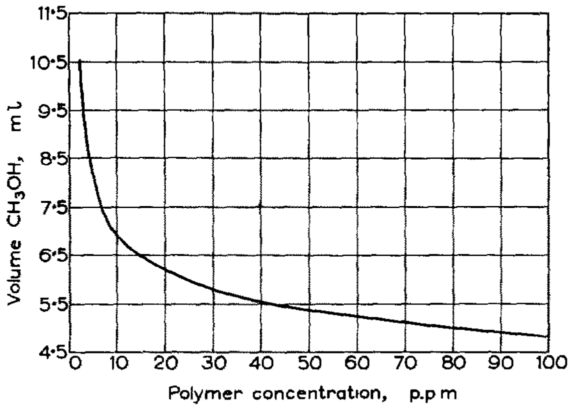

FIG 2 Calibration curve for polystyrene. Plot of CH_3OH (ml) vs concentration of polymer in benzene (p p m) Temperature = 73°F
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In Table II and Fig. 2 are shown the results for polystyrene in thiophene-free benzene. In this case it was necessary to use acetone as the initial additive and titrate with methyl alcohol. Similar precision is obtained, and the techniques are entirely similar. It appears that the method is applicable to a variety of polymers with suitable reagents.

Because of the dependence of the exact curve upon the quantity and type of materials used and on the temperature, calibration with standard solutions should be performed in the laboratory, and the range of desired concentrations and working conditions selected. As previously intimated, the average molecular weight of the polymer will affect the curves. Some experimental evidence to this effect has been obtained, but since it represents a problem diverging from the purpose of the supported investigation, it is not our intention to proceed further into this phase of the investigation.

TABLE II

Concentration of polystyrene (p.p.m.)	Volume of CH_3OH added to mixture of 25 ml acetone + 10 ml standard solution (ml)
100	4.83
90	5.05
80	5.11
70	5.13
60	5.24
50	5.36
40	5.52
30	5.80
20	6.25
10	6.83
8	6.99
7	7.60
6	7.84
5	8.82
4	9.24
2	10.53

Acknowledgement—The authors are grateful to Prof. E. G. Bobalek for discussions concerning the method and results, and to George W. Sohl for his assistance in performing the titrations. This research has been carried out with the support of the Office of Ordnance Research, U. S. Army.

Zusammenfassung—Es wird über eine Methode zur Messung der Konzentration hochpolymerer Substanzen in sehr verdünnten Lösungssystemen berichtet, die auf Präzipitation durch gemischte Lösungsmittel beruht. Das Verfahren ist einfach und genau, verlangt aber Eichung für jede Kombination von Substanz und Lösungsmittel. Die Schwierigkeit, bei kleinsten Konzentrationen den Endpunkt festzustellen, wird durch den schnellen Anstieg der Eichkurve kompensiert. Für Poly-(methyl methacrylat) und Poly-styrol werden Beispielkurven für die experimentellen Resultate angegeben.

Résumé—On décrit une méthode de mesure de la concentration des matières polymériques en solution fort diluée (à 1 partie par million au moins) en précipitant par des solvants mixtes. Cette méthode

est caractérisée par la précision et la facilité de la technique, mais demande un étalonnage initial pour la matière particulière qu'on étudie Aux concentrations les plus faibles la pente rapide de la courbe d'étalonnage compense la difficulté croissante à mesurer la fin des réactions On donne à titre d'exemple des courbes pour le poly-(méthyl méthacrylate) et le polystyrène

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Talanta, 1958, Vol 1, pp 110-116, Pergamon Press Ltd, London.

COULOMETRIC TITRATION OF DYESTUFFS WITH ELECTROLYTICALLY GENERATED DITHIONITE

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(*Received* 27 *January* 1958)

Summary—Dithionite was electrolytically generated at a mercury pool cathode in an electrolytic cell containing bisulphite. The generated reagent was successfully used to titrate methylene blue and indigo carmine By titrating at room temperature, equilibrium was quickly established, and the end point was determined by a photometric technique The optimum pH range for the titration was 3–5 and the concentration of bisulphite was 0 01*M*. Milligram amounts of dyestuffs were determined with an average error of 0 5%

INTRODUCTION

BY the electrolytic or chemical reduction of bisulphite dithionite (hyposulphite) is produced.[1,2] Dithionite is a powerful reducing agent. The instability of dithionite with respect to decomposition, and its rapid air oxidation have, however, prevented its use as an ordinary titrimetric reagent. Since coulometric titration is especially valuable when the titrant is unstable, the present investigation was undertaken to determine the feasibility of titrating oxidants with electrolytically generated dithionite. In the work described here the method was tested by titrating dyestuffs, using photometric end-point detection.

Electrolytically generated titanium^{III}[3] and uranium^{V}[4] ions have been used for coulometric titrations, but the use of dithionite, which is a more powerful reducing agent, has not heretofore been described.

POTENTIAL–pH DIAGRAM

The oxidation–reduction reaction of the dithionous acid-sulphurous acid system is represented as,

$$HS_2O_4^- + 2H_2O = 2H_2SO_3 + H^+ + 2e^-, \quad E_0 = -0\,08 \text{ V vs N H.E.} \qquad (1)$$

where E_0 is the standard oxidation–reduction potential of this system. The potential–pH diagram was constructed from a combination of equation (1) and the reported dissociation constants of dithionous acid[5] and sulphurous acid,[6] and is shown in Fig 1 (Curve I).

On the other hand, sulphite exerts a reducing action upon strongly oxidizing systems, with the formation of sulphate or dithionate. The standard oxidation–reduction potential of the sulphite–sulphate system is calculated to be 0·17 Volt vs. N.H.E. However, Charlot[7] pointed out that the sulphite–sulphate or –dithionate system is irreversible, and in practice sulphite is not so powerful a reducing agent as expected from its thermodynamically calculated potential. He showed that the irreversible potential, which is expressed by equation (2), is of practical importance in predicting the oxidation–reduction reaction. The potential–pH diagram for 0·1*M* sulphite solution[8] is shown in Fig 1 (Curve II) Equation (2) shows that the

$$E = 0{\cdot}33 - 0{\cdot}036 \log [SO_3^{2-}] \qquad (2)$$

potential is independent of the concentration of oxidant, and shifts to more positive values as the concentration of sulphite decreases

Curve III in Fig. 1 is the potential–pH diagram for the hydrogen–hydrogen ion system for a pressure of one atmosphere of hydrogen

It is apparent from Fig. 1 that (i) a mercury cathode, which has a high hydrogen overvoltage, should be employed; otherwise the evolution of hydrogen will interfere with the generation of dithionite; and (ii) the oxidation potential of the substance to be titrated should lie between curves I and II.

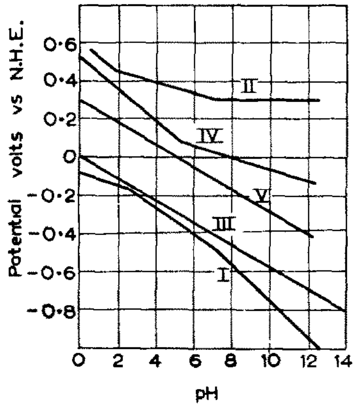

FIG. 1 Potential–pH diagram (I) dithionite–sulphite system (II) sulphite–sulphate or –dithionate system (III) hydrogen–hydrogen ion system (IV) leuco–methylene blue–methylene blue system (V) leuco–indigo carmine–indigo carmine system

In the present work the titration of methylene blue and of indigo carmine were investigated. Both of these dyestuffs undergo two-electron reduction and their reduction products are colourless leuco-compounds. The potential–pH diagrams for the leuco-methylene blue (methylene white)–methylene blue and leuco-indigo carmine–indigo carmine systems[9] are shown in Fig 1 by Curves IV and V, respectively.

EXPERIMENTAL

Apparatus The specially constructed titration cell shown in Fig 2 was used The cell was placed in the cell compartment of a Yanagimoto photometric titrator The cell had a capacity of 100 ml and the total volume of solution was about 50 ml The surface area of the mercury pool cathode was about 7 cm² The cathode mercury, which was purified by distillation, could be used repeatedly without the special precautions described by Lingane and Iwamoto [10] A zinc rod served as an anode The anode compartment, filled with 1*M* zinc sulphate solution, was isolated from the bulk of the solution in the titration cell by means of a semipermeable membrane which was secured with a short piece of vinyl resin tube of the appropriate diameter around the edge of the glass tube During the titration the solution was stirred by a nitrogen stream and, at the same time, the surface of the cathode mercury was stirred by a floating magnetic stirrer with a stirring bar Vigorous stirring with the magnetic stirrer should be avoided, to prevent the platinum wire used for electrical connection from being exposed to the solution When the absorbancy measurements were being made, the stream of nitrogen was temporarily interrupted The nitrogen, from a cylinder, was freed from oxygen by passing it through vanadium^{II} sulphate solution

The constant current supply was similar to that described by Myers and Swift [11] The generating current was determined by measuring the voltage drop across a standard resistor through which the current was passed. Because of current fluctuations, it was sometimes necessary to average several current measurements made during a run.

A stop-watch, which had been checked against a standard clock, was used to measure the generating time.

Reagents. All the solutions except buffer solutions were prepared from chemically-pure-grade chemicals and distilled water. Buffer solutions were prepared from reagent-grade chemicals. Bisulphite solution, approximately 0.05*M*, was prepared by dissolving 0.5 g of sodium metabisulphite in 100 ml of water. This solution was prepared daily. The standard methylene blue solution was prepared by dissolving 3.2 g of methylene blue in 1 litre of water and standardizing this solution against standard picric acid solution, using a titrimetric-extraction method[12]. Standard indigo carmine solution was prepared by dissolving 4.7 g of indigo carmine in 1 litre of water and standardizing the solution against standard chromium$^{\mathrm{II}}$ sulphate solution[13], using a potentiometric method.

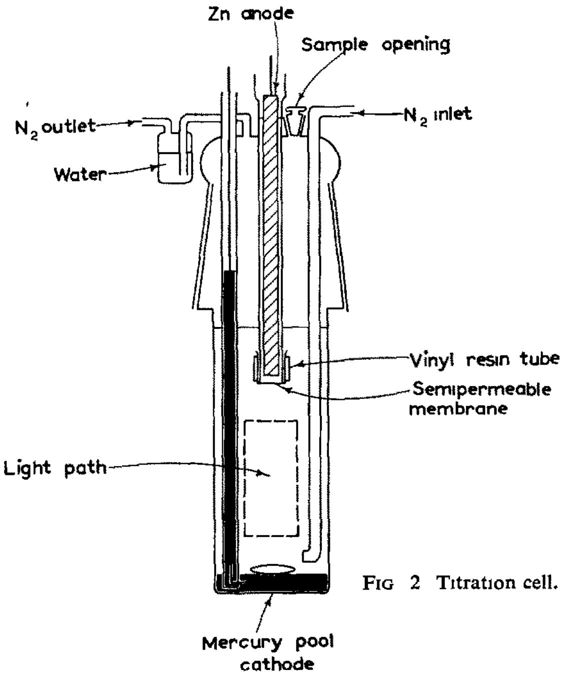

FIG. 2. Titration cell.

Procedure. 10 ml of 0.05*M* bisulphite solution, 20 ml of acetic acid–acetate buffer solution (pH 4.0) and 20 ml of distilled water were placed in the titration cell. Nitrogen was turned on to mix and de-aerate the contents of the cell, and the magnetic stirrer was set in operation. The wave length was set at 610 mμ and the slit opening was adjusted to give an absorbancy of zero. A pre-titration was carried out after the addition of a small but unmeasured amount of the dyestuff solution to be titrated. When an appropriate absorbancy (approximately 0.4) was reached, the pre-titration was stopped. The absorbancy was measured and noted. A 1- or 2-ml sample was then transferred by a calibrated pipette into the titration cell with nitrogen passing. The titration was started, and continued at constant current until the end-point was approached. When the change in absorbancy revealed an approaching end-point, the titration was stopped at 3- or 5-sec intervals and the absorbancies were measured. The absorbancy measurement could be made immediately after stopping titration, as the reaction between dyestuff and dithionite is rapid. Only four or five readings near the end-point were necessary. By plotting these absorbancy values against time, a straight line was obtained. The end point was given on this line by the point which showed the same absorbancy value* as the end of the pre-titration.

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* The effect of dilution on the absorbancy value was neglected, as the volume of the sample solution was very small as compared with the total volume of the titration solution.

It was possible to make five or six titrations using the same generating medium without introducing an appreciable error

Oxygen dissolved in the sample solution causes a high result. To correct this error, a blank titration was carried out as follows: after the completion of the sample titration, a volume of distilled water equal to that of the sample solution was placed in the titration cell. Part of the reduction product of the dyestuff produced in the sample titration was oxidized by the oxygen dissolved in the distilled water, and a blue colour gradually reappeared The solution was allowed to stand for several minutes with passage of nitrogen, until the absorbancy reading ceased to increase. The dyestuff thus restored was then titrated in the same way as described above.

The amount of electricity required for the titration of the sample was obtained by subtracting the product of current and time in the blank titration from that in the sample titration

All titrations were performed at room temperature. Fig 3 shows part of a typical run for methylene blue.

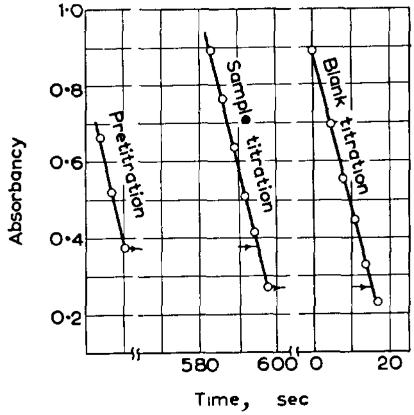

FIG. 3 Titration graph for 5 69 mg of methylene blue The concentration of bisulphite was 0 01M and the pH was 4 0.

RESULTS AND DISCUSSION

Effect of pH. It is known that in the electrolytic generation of dithionite the solution employed must not be too acidic or too basic and that many substances may catalyse the formation of dithionite. Therefore a series of experiments using various buffer solutions was carried out in order to establish the optimum pH range for the coulometric titration.

Methylene blue was titrated. The end-point correction and titration procedure used were as described above, with the exception that the pH of the system was varied. At pH values higher than 7 dithionite could not be generated. On the other hand, in 0·1N nitric acid solution dithionite could be generated but titration efficiencies were not greater than 75% and, moreover, reproducibility was very poor. This result may be explained by the rapid decomposition of dithionite in the strong acid medium. The results of a series of titrations in which the pH was varied between 2 and 5 are shown in Table 1. It can be seen that the optimum pH range was 3–5 However, a system at a pH 5 is not convenient, because the reduction product of methylene blue is somewhat difficult to dissolve at this pH value, and when more than 5 mg of sample were taken the resulting insoluble product interfered with the photometric detection of the end-point. At pH 6 the reduction product became even more difficult to dissolve.

Kolthoff and Miller[14] reported that sulphurous acid (sulphur dioxide) is reduced at the dropping mercury electrode and at pH values smaller than 4 the reduction product is not dithionous acid, $H_2S_2O_4$, but sulphoxylic acid, H_2SO_2. In the present work, no effort was made experimentally to confirm this conclusion. However, it may be noted that the half-wave potentials of —0·37 V vs S.C.E. at pH 1 and —0·67 V vs. S.C.E. at pH 6 given by them are in fairly good agreement with the oxidation-reduction potentials of a dithionous acid–sulphurous acid system obtained from curve I in Fig. 1, namely, the values of —0·36 V vs. S.C.E. at pH 1 and —0·65 V vs. S.C.E. at pH 6. At any rate, the present method of coulometric titration gives the same results, irrespective of whether the intermediate is dithionous acid or sulphoxylic acid.

TABLE I EFFECT OF pH ON DETERMINATION OF METHYLENE BLUE

The generating medium (volume *ca* 50 ml) was 0·01*M* in bisulphite and 0·08*M* in buffer component. The generating current was about 3·1 mA and the titration time was about 480 sec

pH	Buffer solution	No of detns	Amount of methylene blue		Average dev (*mg*)
			taken (*mg*)	found (*mg*)	
2·0	Monochloroacetic acid	4	2·801	2·841	0·007
3·0	Monochloroacetic acid	5	2·801	2·795	0·005
3·0	Biphthalate	5	2·801	2·796	0·007
3·0	Citrate	4	2·801	2·809	0·017
4·0	Acetate	5	2·801	2·805	0·006
5·0	Biphthalate	2	2·801	2·806	0·007

Effect of concentration of bisulphite. As described above, sulphite may function irreversibly as a reducing agent. Therefore the effect of concentration of bisulphite on the coulometric titration of dyestuff was examined experimentally. Titrations were performed in 0·1 and 0·01*M* bisulphite solutions whose pH values were adjusted to 3 with monochloroacetic acid buffer solutions. The results of the titration of methylene blue are shown in Table II. It can be seen that the negative errors are fairly large in 0·1*M* bisulphite solution. This fact may be explained by assuming that the reduction of methylene blue by bisulphite takes place when the concentration of bisulphite is increased. This assumption is further confirmed by spectrophotometric measurement. Solutions containing methylene blue were prepared in the same manner as in the above experiment. These solutions were diluted appropriately and absorbancy measurements were made at 610 mμ over a period of time. During

TABLE II. EFFECT OF CONCENTRATION OF BISULPHITE

The generating medium (volume *ca* 50 ml) was buffered at pH 3·0 with monochloroacetic acid.

Conc of bisulphite, *M*	Current (*mA*)	Titration time (*sec*)	Amount of methylene blue		Error (%)
			taken (*mg*)	found (*mg*)	
0·1	3·107	450·6	2·801	2·712	−3·1
0·1	3·107	449·7	2·801	2·706	−3·3
0·01	3·066	482·3	2·801	2·790	−0·4
0·01	3·059	488·3	2·801	2·801	+0·3

a period of 8 min the absorbancy reading decreased by about 3 % when the concentration of bisulphite was 0·1*M*, while the absorbancy reading was almost constant when the concentration of bisulphite was 0·01*M*.

Titrations of Methylene Blue and Indigo Carmine. Methylene blue and indigo carmine were titrated by the procedure described above. The results are summarized in Table III. Externally generated titanous ion has been used to determine dyestuffs coulometrically.[15] In this method the temperature of the titration solution has to be kept just below boiling point. In the method described here, however, the reactions between dithionite and dyestuffs are rapid and the titrations were performed satisfactorily at room temperature (about 15°).

TABLE III. COULOMETRIC TITRATION OF DYESTUFFS WITH DITHIONITE
The generating medium (volume *ca* 50 ml) was 0 01*M* in bisulphite and was buffered at pH 4 0 with sodium acetate.

Dyestuff	Current (*mA*)	Titration time (*sec*)	Amount of dyestuff		Error (%)
			taken (*mg*)	found (*mg*)	
Methylene blue	3 075	475 4	2 801	2 785	−0 6
	3 087	477 8	2 801	2 810	+0 3
	3 086	476 5	2 801	2 801	±0
	5 075	575 0	5 687	5 645	−0 7
	5 053	580 9	5 687	5 678	−0 2
	5 051	579 7	5 687	5 664	−0 3
	5 030	597 2	5 687	5 684	−0 1
	3 087	951 4	5 687	5 623	−1 1
	3 076	961 2	5 687	5 662	−0 4
	3 100	952 5	5 687	5 654	−0 6
Indigo carmine	3 114	483 5	3 395	3 402	+0 2
	3 115	480 0	3 395	3 377	−0 5
	3 112	480 5	3 395	3 377	−0 5
	3 111	484 0	3 395	3 406	+0 3

Acknowledgement—The author wishes to express his sincere thanks to Professor Sôichirô Musha for his kind guidance and helpful advice throughout this work

Zusammenfassung—Es wird electrolytisch Dithionit an der Quecksilberskathode in einem Bisulfit erhaltenden electrolytischen Gefass entwickelt Dieser Substanz wird erfolgreich benutzt um Methylenblau und Indigocarmin zu titern Durch Titrage bei gewohnlicher Temperatur wird Gleichgewicht schnell erreicht, und der End-punkt wird photometrisch bestimmt

Das optimale Gebiet der Titrage behauft sich auf pH 3 bis 5, und die Konzentration des Bisulfits auf 0,01*M* Milligram-mengen von Farbstoffen werden mit einem durchschnittlichen Fehler von 0,5 % bestimmt

Résumé—On a produit de la dithionite par électrolyse avec cathode de mercure dans une cellule à électrolyse contenant du bisulfite Le réactif dégagé a été utilisé avec succès pour titrer du bleu de méthylène et du carmin d'indigo En titrant a température ordinaire, l'équilibre est vite établi, et la fin du titrage a été determinée par une technique photométrique La zone de pH optimum pour le titrage était 3–5, la concentration du bisulfite 0,01*M* On a pu déterminer ainsi des colorants à l'echelle du milligramme avec une erreur moyenne de 0,5 %.

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THE SPECTROPHOTOMETRIC DETERMINATION OF ALKALINE EARTH METALS AFTER SEPARATION BY PAPER CHROMATOGRAPHY

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(*Received* 14 *January* 1958)

Summary—The spectrophotometric titration of magnesium, calcium, strontium, and barium, in the visible and ultra-violet regions of the spectrum, has been investigated and a method is presented for the determination of small amounts of these elements by spectrophotometric titration using Eriochrome Black T as indicator, after separation by paper chromatography and removal from the paper with dilute hydrochloric acid. The minimum amount of each cation determined was 0 5μM and the procedure was applied successfully to the analysis of a dolomite, a strontianite, and a barytocalcite.

SEVERAL procedures have been reported for the determination of the alkaline-earth metals after the separation by paper chromatography.[1–3] In two of these procedures[1,2] the elements are estimated semi-quantitatively, and, in another[3] the elements are determined indirectly by microtitration. An interesting method is that by Pollard, McOmie, and Martin[4] who have determined the alkaline-earth metals spectrophotometrically using *o*-cresolphthaleincomplexone for barium, strontium, and calcium, and Eriochrome Black T for magnesium. In an earlier work,[5] we ourselves have described a separation by paper chromatography of these elements and beryllium in which the elements are estimated semi-quantitatively by visual comparison. Although this method of estimation was found suitable for many purposes, it became necessary to investigate methods which would permit a more accurate determination of the separated elements. A spectrophotometric titration of the elements after their removal from the chromatographic paper was found to be very satisfactory and the development of this procedure is now reported.

REMOVAL OF SEPARATED CATIONS FROM THE CHROMATOGRAM

The solvent-mixture used was methanol-*n*-butanol-*sym*-collidine-6N acetic acid (40 : 20 : 20 : 20% v/v) and the separated cations were detected by spraying with sodium rhodizonate solution for barium and strontium, and 8-hydroxyquinoline for calcium and magnesium.

Three methods of removing the separated salts from the chromatogram were investigated:

(1) dissolving the material from the chromatogram with concentrated acid after development with the detecting reagent,

(2) cutting out the separated bands from the sprayed paper and destroying the organic matter by a wet or dry oxidation process;

(3) separating two identical amounts of the mixture on the same paper, spraying only the control to find the position of the bands, and dissolving out the separated salts from the unsprayed chromatogram with water or dilute acid

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Of these procedures, the most satisfactory was the third, and this was therefore used throughout.

Initially Whatman 3 MM paper was used as supporting medium but, because of the relatively high calcium content of this paper, it was replaced by the double-acid-washed Whatman No. 41 for quantitative work.

SPECTROPHOTOMETRIC TITRATIONS WITH DI-SODIUM ETHYLENEDIAMINETETRA-ACETATE

Several methods were tried for the determination of the salts after separation from the chromatogram. Although some were satisfactory for one or two of the elements, none was capable of use for all four: it was, therefore, decided to search for a method that could be used for all the cations and, to this end, titrations of the solutions with ethylenediaminetetra-acetate (EDTA) were investigated.

Magnesium and the alkaline earths form stable water-soluble complexes with EDTA. The stability constants of these complexes have been determined;[6] pK values are: magnesium 8·7, calcium 10·6, strontium 8·6 and barium 7·8. Biedermann and Schwarzenbach[7] have suggested that magnesium should be titrated with EDTA in a solution buffered at about pH 10, using Eriochrome Black T as indicator. The colour-change is from wine-red to blue. Calcium, strontium and barium do not form very stable complexes with this indicator. Murexide forms a stable complex with calcium[8,9] and can be used to detect the end-point when a solution of that metal is titrated at pH 12. Any magnesium in the solution is precipitated as the hydroxide at that pH and is not titrated. Strontium and barium may also be titrated with the reagent using Eriochrome Black T as indicator, if a known quantity of magnesium is added.[7,10–12] In visual titrations there is a limit below which the indicator concentration must not fall, if a colour-change is to be detected. When this minimum amount of indicator is added to microgram quantities of magnesium, the end-point is very unsatisfactory. For this reason a spectrophotometric titration was necessary for the determination of the salts removed from the paper.

A spectrophotometric titration has been used by Sweetser and Bricker[13] for the quantitative determination of iron, cobalt and nickel, and Karsten *et al.*[14] have found that a plot of optical density against wavelength for the free dye (Eriochrome Black T) and the magnesium complex, shows the greatest differences in absorption at 530 and 630 mμ. If titrations of magnesium with EDTA are made at 630 mμ, the light absorption increases, *i.e.* the optical density rises as the end-point is approached until a constant value is obtained. At 530 mμ, a decrease in optical density occurs. Under optimum titration conditions a sharp break in the optical density–volume of titrant curve occurs at the end-point Fortuin *et al.*[15] have developed a theory of the spectrophotometric titration and shown that a sharp break in the above curve is obtained if·

(1) $K_C \gg K_I$ (numerically, log K_C/K_I should be at least 4).

(2) K_I is large (numerically, 10^{4-5}), where K_C is the complex-forming capacity of the titrant substance and K_I is the complex-forming capacity of the indicator. The first of these criteria is the more important. The end-point of the titration becomes less sharp as the value of log K_C/K_I decreases. However, satisfactory end-points may still be obtained provided that the value exceeds 3.

For magnesium ions and Eriochrome Black T indicator at pH 9–10 a value of

$10^{4\cdot 5-5\cdot 5}$ for K_I has been given.[14] Since the K_I values for calcium, strontium and barium are small it is necessary to add magnesium ions to a solution of these ions, to get a detectable end-point when the solution is titrated with EDTA. The K_I value for magnesium should therefore be compared with the K_c values for calcium, strontium and barium in a solution buffered at pH 10. Such a comparison is made in the following table. $K_I(\mathrm{Mg})$ is taken as $10^{5\cdot 0}$.

TABLE I STABILITY CONSTANTS OF ALKALINE EARTH COMPLEXES

Cation	K_c	$K_c/K_I(\mathrm{Mg})$
Mg	$10^{8\cdot 2}$	$10^{3\cdot 2}$
Ca	$10^{10\cdot 1}$	$10^{5\cdot 1}$
Sr	$10^{8\cdot 2}$	$10^{3\cdot 2}$
Ba	$10^{7\cdot 3}$	$10^{2\cdot 3}$

These figures suggest that titration curves would be satisfactory for magnesium, calcium and strontium, but less satisfactory for barium.

APPARATUS

The arrangement of the apparatus for the spectrophotometric titrations on the UNICAM SP 500 spectrophotometer was similar to that employed by Hunter and Miller.[16] The apparatus is shown in Fig. 1. The titration cell which completely fills the cell compartment of the spectrophotometer was constructed from 3-mm PERSPEX sheet and had external dimensions 9·9 × 4·7 × 6·2 cm. The cell compartment was closed by a PERSPEX cover which had two openings in it for a 5-ml burette and a microstirrer. The stirrer (supplied by Voss Instruments Ltd.) was suitably driven by a 2-volt accumulator in series with a variable resistance. Opaque paper was stuck to the cover by means of chloroform to make it light proof.

As PERSPEX is opaque to ultra-violet light, a special cell with quartz windows was constructed for use in the region 200–400 mμ. This cell, a diagram of which is shown in Fig. 2, had the same dimensions as the ordinary cell but contained two quartz windows of dimensions, 3·4 × 2·5 × 0·1 cm. These were constructed from a 3 in × 1 in. fused silica microscope slide of 1 mm thickness (supplied by Thermal Syndicate Ltd.) and were sealed to the PERSPEX with ARALDITE 101 cold-setting resin mixed with Hardener 951 (supplied by Aero Research Ltd.). The windows were inserted in such a way that the beam of monochromatic light passed through the centre of them to the photoelectric cell.

REAGENTS

Disodium dihydrogen ethylenediaminetetra-acetate dihydrate. An approximately 0·0025*M* aqueous solution.

Magnesium, calcium, strontium, and barium chloride solutions. Exactly molar. Other standards were prepared from these by dilution.

Ammonia–ammonium chloride, solution A. 6·75 g ammonium chloride and 57 ml of 0·88 ammonia diluted to 100 ml with water.

Ammonia–ammonium chloride, solution B. 5·40 g ammonium chloride and 57 ml of 0·88 ammonia diluted to 100 ml with water.

Ammonia, solution C. 57 ml of 0·88 ammonia diluted to 100 ml with water.

Indicator solution. A centrifuged solution of 50 mg of Eriochrome Black T and 450 mg of hydroxylamine hydrochloride in 10 ml of anhydrous methyl alcohol.

Ascorbic acid. A 1% w/v aqueous solution freshly prepared.

Potassium cyanide. A 0·4% w/v aqueous solution.

Ammonium tartrate. A 0·2% w/v aqueous solution.

As far as possible, all reagents were of ANALAR grade.

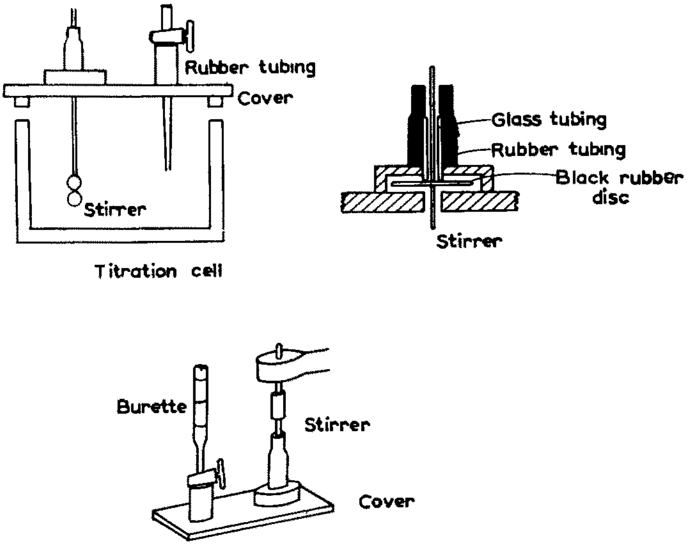

FIG. 1.

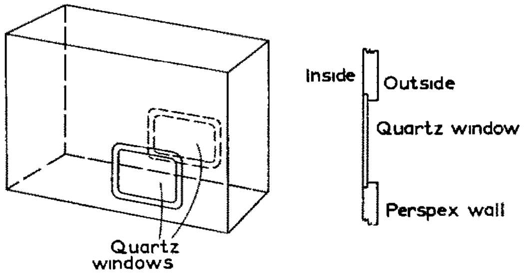

FIG. 2

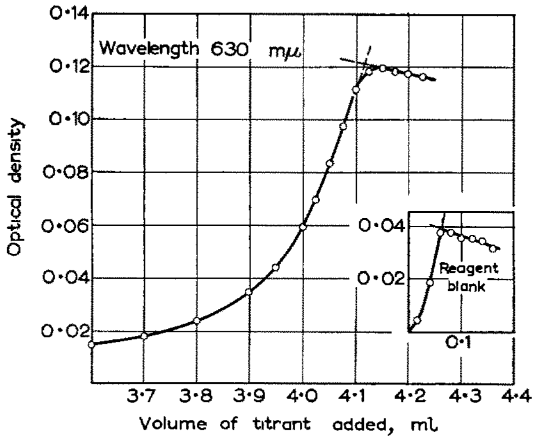

FIG 3

TITRATIONS IN SIMPLE BUFFERED SOLUTIONS

Approximately 0 0025*M* EDTA solution was standardized at 630 mμ by titrations with 10 *μM* amounts of magnesium chloride contained in 100 ml of solution buffered at pH 10 with ammonia-ammonium chloride Solution A and containing 0 1 ml of Eriochrome Black T indicator solution Corrections were made for the indicator blank Titres were concordant to 3 parts in 1000 Typical titration curves for 10 *μM* of magnesium chloride and blank are shown in Fig 3

Titrations in simple buffered solutions had one particular defect; fading of the indicator occurred which was troublesome if the titration was not completed within 15 min

Using this technique, mixtures of 2 5 *μM* amounts of each of the elements were separated on a chromatogram, removed from the paper by means of 0 05*N* hydrochloric acid, and titrated with EDTA Recoveries for each cation (after correction for the blank) are shown in Table 2.

TABLE 2

Cation	Amount in the mixture (*μM*)	Amount recovered (*μM*)
Magnesium	2 50	2 49
Calcium	2 50	2 43
Stronium	2 50	2 38
Barium	2 50	2 25

The results, especially for barium, appeared to indicate that 0 05*N* hydrochloric acid did not remove all of the cations from the paper In later work *N* hydrochloric acid was employed

TITRATIONS IN THE ULTRA-VIOLET RANGE

Because of the trouble from the fading of the indicator in the above titrations, attention was turned to the possibility of carrying out titrations in the ultra-violet region without the use of an indicator

Sweetser and Bricker[17] have stated that the X^{4-} and MX^{2-} ions have different absorption curves in the short ultra-violet region of the spectrum (H_4X represents ethylenediaminetetra-acetic acid and M^{2-} a bivalent cation) For magnesium and calcium the greatest difference in absorption takes place at 222 mμ Using 1-cm quartz cells on the UNICAM SP500 spectrophotometer and solutions of $2\ 4 \times 10^{-3}M$ EDTA, graphs of optical density as a function of wave-length were drawn for solutions of the X^{4-}, MgX^{2-}, CaX^{2-}, SrX^{2-}, and BaX^{2-} ions The curves of the last four ions were very similar A plot of the difference between the optical density readings for X^{4-} and MX^{2-} ions gave a maximum at 218 mμ, a value in good agreement with that of Sweetser and Bricker

With water in the PERSPEX cell with quartz windows it was not possible to balance the spectrophotometer at wavelengths less than 220 mμ so that titrations were carried out at 225 mμ Information concerning increases in optical density during titration was obtained by adding a 0 0025*M* solution of EDTA in 0 5-ml increments to (1) 100 ml of solution at pH 10 containing 50 *μM* of magnesium chloride and (2) 100 ml of water, buffered at pH 10, with ammonia and ammonium chloride The results are shown in Fig 4. The graphs are linear indicating the suitability of 0 0025*M* reagent for titrating magnesium

Using EDTA solution previously standardized at 630 mμ, 5 *μM* amounts of magnesium chloride were titrated at 225 mμ The result is reproduced in Fig 5 The end-point occurs at 2 03 ml compared with 2 07 ml for the titration of the same amount at 630 mμ (no blank corrections were made in either case) Similar results were obtained for barium

Generally, titrations at 225 mμ gave less concordant results than those at 630 mμ, possibly due to the fact that a very wide slit width (1 5 mm–2 0 mm) is required at 225 mμ and this results in slight unsteadiness in galvanometer readings It is also difficult to get accurate readings for blanks in this region

TITRATIONS OF SOLUTIONS TREATED WITH CYANIDE

The main drawback to titrations in simple buffered solutions was the fading of the indicator during titration This is attributed to a reaction between traces of iron and the indicator Hunter

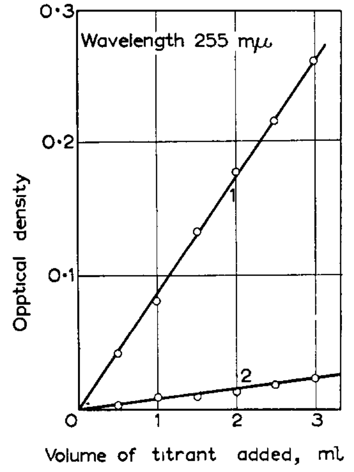

FIG. 4.

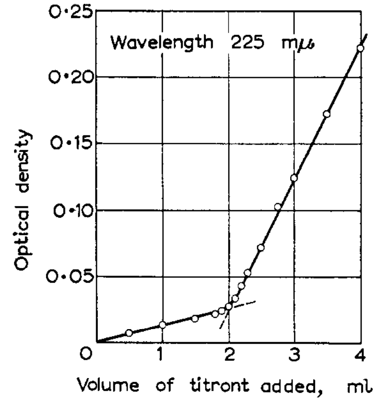

FIG. 5.

and Miller[16] were able to eliminate interference from iron, copper and certain other elements in the titration of zinc with EDTA by reducing the iron to the ferrous state with ascorbic acid and complexing with potassium cyanide in alkaline solution.

Following this procedure, 2 mg of ammonium tartrate and 4 mg of potassium cyanide were added per 100 ml of solution. These quantities were calculated to be about ten times any likely impurities present. 10 μM amounts of magnesium chloride in a solution buffered at pH 10 were titrated using this procedure. Titres, corrected for the blanks, agreed to within 2 parts in 1000. With cyanide present there was no fading of the indicator. The graphs of optical density plotted against volume of titrant are similar to those with no cyanide present but the slopes are less steep. Typical graphs for 10 μM amounts of magnesium, calcium, strontium and barium are shown in Fig. 6. those for magnesium and calcium are the best. For amounts of strontium less than 2.5 μM, the graph resembles those of magnesium and calcium very closely. The titrations of solutions with cyanide present were considered to be very satisfactory.

PROCEDURE

The standardisation of EDTA solution

Add 10 ml of exactly 0.001M magnesium chloride solution, *i.e.* 10 μM, to a conical flask and dilute to about 40 ml with water. Add 0.05 ml of concentrated hydrochloric acid solution, 1 ml of 0.2% w/v ammonium tartrate solution and 0.05 ml of a freshly prepared 1% w/v solution of ascorbic acid to the flask. Add 2 ml of the ammonia–ammonium chloride solution B and 1 ml of 0.4% w/v potassium cyanide solution, heat the solution to 80° and allow to cool in the air for 10 min. Cool to room temperature by immersing the flask in cold water and add 0.1 ml of the indicator solution, *i.e.*

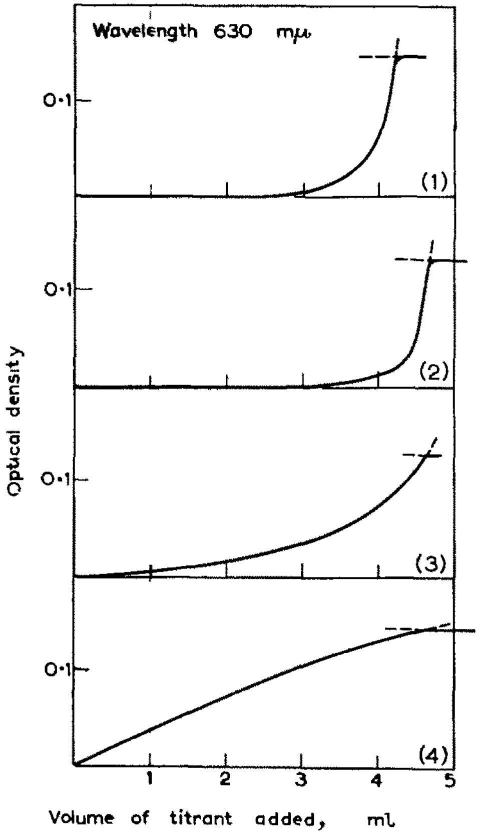

FIG 6 (1) 10 μM magnesium chloride + reagent blank, (2) 10 μM calcium chloride + 1 μM strontium chloride + 1 μM magnesium chloride + reagent blank, (4) 10 μM barium chloride + 1 μM magnesium chloride + reagent blank.

enough indicator to give a rise in optical density of 0 1 to 0 2 divisions Transfer the solution to the PERSPEX titration cell, making the volume up to 100 ml

Balance the UNICAM SP 500 Spectrophotometer with the switch in position '1' and optical density at zero. Set to an optical density of 0 01 and with the dark current shutter open add the titrant slowly from a 5-ml burette until the galvanometer balances Close the dark current shutter, and after adjusting the dark current if necessary, proceed with the addition of the titrant in small increments making sure that the optical density is steady after each addition Near the end-point, add the solution in 0 025-ml increments and allow an interval of 1 minute before reading the optical density. Continue the titration until the readings are the same for four consecutive additions of titrant Determine the end-point from the (optical density–volume of titrant) curve A reagent blank is determined in the same way.

The complete analysis

Prepare a 16-cm wide sheet of Whatman No 41 filter paper Mark the paper along the 7-cm line at point 2 cm, 6 cm, 10 cm, and 14 cm from one edge Place an exact volume of solution containing 2 5 μM each of the four chlorides on the 2-cm position from an AGLA micrometer syringe Apply identical quantities of the chlorides on the 6- and 10-cm positions, leaving the 14-cm position blank. Place the paper in the chromatographic vessel.[5] After removal of the developed chromatogram, dry the paper in an oven Detect the positions of the separated salts on the control (the outside strip) Mark out the unsprayed position of the sheet into areas containing the separated cations. In a similar manner, mark out the blank strip into four areas, corresponding to the four elements

Extract the inorganic material from each of the twelve positions of paper (4 positions are for blanks) with 2 ml of *N* hydrochloric acid The acid should be left in contact with the paper for 10 minutes. Collect the solutions in conical flasks and wash the papers with 25 ml of 0 02*N* hydrochloric acid followed by 10 ml of water

To each solution add 1 ml of 0 001*M* magnesium chloride and 1 ml of 0 2% w/v ammonium tartrate solution. Add 0 05 ml of a freshly prepared 1 % w/v solution of ascorbic acid, 2 ml of ammonia solution C and 1 ml of 0 4% w/v potassium cyanide solution Heat the flasks to 80°, cool in air for 10 min, and then cool to room temperature by immersing the flasks in cold water Add 0 1 ml of indicator solution to each flask and transfer the solutions to the titration cell making the volume up to 100 ml Titrate each solution with EDTA solution by the method outlined above for the standardisation of the titrant.

The results for the analysis of mixtures of 2 5 μM and 0 5 μM of the four cations are given in Table 3.

TABLE 3. ANALYSES FOR ALKALINE EARTH CATIONS

Cation	Amount present (μM)	Corrected recovery (μM)	Error (μM)
Magnesium	2 50	2 30	−0 20
	2 50	2 50	0
	0 50	0 54	−0 04
	0 50	0 35	−0 15
Calcium	2 50	2 45	−0 05
	2 50	2 70	−0 20
	0 50	0 30	−0 20
	0 50	0 48	−0 02
Strontium	2 50	2 36	−0 14
	2 50	2 52	−0 02
	0 50	0 50	0
	0 50	0 57	−0 07
Barium	2 50	2 60	−0 10
	2 50	2 64	−0 14
	2 50	0 58	−0 08
	0 50	0 59	−0 09

For a solution containing a particular element, the titratable inorganic material originated from four sources, *viz* (*a*) the salt extracted from a portion of the chromatogram, (*b*) the foreign cations extracted from the paper at the same time, (*c*) the added magnesium chloride (1 μM) and (*d*) the titratable cations from the reagents, *i e* the reagent blank

For the corresponding blank solution, the titratable inorganic material originated from three sources, *viz.* (1) the foreign cations extracted from the paper blank, *i e.* the portion of paper equal in area to the portion from which the salt was extracted, both portions being taken from the chromatogram at the same distance from the starting line, (2) the added magnesium chloride (1 μM) and (3) the titratable cations from the reagents Quantities (*b*), (*c*), and (*d*) are the same as (1), (2), and (3) respectively

The foreign titratable material from the paper (*b*) and (1) were found to vary from 0 11 μM for barium to 0 42 μM for magnesium (40 cm^2 of paper in both cases). The reagent blank (*d*) and (3) was 0 34 μM

Recoveries are correct to $\pm 0\ 20\ \mu M$.

The analysis of carbonate rocks

The above method was applied to the analysis of a dolomite, a strontianite, and a barytocalcite as follows.

Place a weighed 50-mg portion of the rock in a porcelain basin and cover with a clock glass. Moisten the powder with a little water and introduce through the spout of the basin 2 ml of concentrated hydrochloric acid. When the reaction has ceased, rinse the cover glass and sides of the basin with water and evaporate the solution to dryness on a gently heated sand bath. Add 1 ml of concentrated hydrochloric acid and, after about 1 min, dilute with 4 ml of water. Warm and filter through a 7-cm Whatman No. 4 paper receiving the filtrates in a 30-ml beaker. Add 2 or 3 drops of dilute hydrochloric acid to the basin and rinse the insoluble residue with 8 ml of hot water added in small portions.

Evaporate the solution in the beaker to 1 ml and transfer the solution to a 5-ml graduated flask. Make up to the mark with water. On a sheet of Whatman No. 41 paper 12 cm wide, mark points along the 7-cm line at 2 cm, 6 cm, and 10 cm from one edge. To each of the 2-cm and 6-cm marks apply 0.04 ml of solution in volumes of 0.005 ml, drying the spots between each addition with an electric hair dryer. The 10-cm position is left blank. Develop the chromatogram and determine the separated cations as outlined above.

The results for three rocks are given in Table 4.

TABLE 4. ANALYSIS OF MINERALS

	Analysis by described method (%)	Previous analysis (%)
Dolomite	MgO 20.2 ; CaO 29.5	MgO 21.5 , CaO 30.5
Strontianite	CaO 4.1 ; SrO 60.2	—
Barytocalcite	CaO 19.1 , BaO 42.6	CaO 18.4 ; BaO 44.5

The Dolomite was No. 88 supplied by the Bureau of Standards, Washington, U.S.A.

The Barytocalcite was from Alston, Northumberland, England and was previously analysed for calcium oxide and barium oxide by a classical method.[18]

Much smaller quantities of rock could be analysed if the cations were obtained in a volume of 0.05 ml for application to the paper. It is suggested, in this connection, that the solution should be evaporated to dryness in a micro-crucible, the residue taken up in 0.05 ml of water, the resulting solution drawn up into a fine capillary and applied to the paper. The crucible should be rinsed with 2 × 0.05-ml portions of water and the washings also applied to the paper. Approximately the same weight of rock should be similarly treated for the control. In this way, 1 mg of a dolomite and 3 mg of a strontianite or barytocalcite could be analysed with an accuracy for each oxide of ±1% of the total contents for amounts of oxide up to 20%; and with an accuracy of ±2% where the amount of oxide was greater than 20%.

The procedure has been applied successfully to the determination of microgram amounts of magnesium in copper-stabilised chlorophyll,[19] 3-mg samples being analysed.

Zusammenfassung—Die spektrophotometrische Titrage des Magnesiums, Calciums, Strontiums und Baryums wird auf sichtbarem und ultra-violettem Gebiet untersucht, und ein Verfahren fur die Bestimmung geringer Mengen dieser Elemente durch spektrometrische Titrage nach papier-chromatographischer Trennung wird beschrieben.

Der Minimalbetrag jedes Kations belauft sich auf 0,5 μM und das Verfahren wurde zur Analyse von Dolomit, Strontianit und Barytocalzit erfolgreich benutzt.

Résumé—Après examen du titrage spectrophotométrique du magnésium, du calcium, du strontium et du baryum dans les régions visibles et ultra-violettes du spectre, on présente une méthode pour effectuer le dosage de petites quantités de ces éléments par titrage spectrophotométrique, utilisant

comme indicateur le noir ériochrome T, après séparation chromatographique sur papier et déplacement par l'acide chlorhydrique dilué. La quantité minimum dosée de chaque cation a été 0,5 μM On a appliqué avec succès ce processus à l'analyse d'une dolomie, d'une strontianite et d'une barytocalcite.

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Talanta, 1958, Vol 1, pp 127-137, Pergamon Press Ltd, London

SELECTIVE POTENTIOMETRIC TITRATION OF METAL IONS WITH TRIETHYLENETETRAMINE*

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(*Received* 11 *March* 1958)

Summary—The theoretical conditions necessary for the potentiometric titration of metal ions with triethylenetetramine ("trien") and for the selective titration of mixtures of ions with this reagent, alone or in conjunction with EDTA, are discussed It is shown that it is possible to choose conditions suitable for selective titrations, and this is illustrated by titrations of Cu, Zn, Ni, Cd and Hg, singly and in two-component mixtures Alkaline earths do not interfere in the titrations.

INTRODUCTION

CERTAIN metal ions (such as cobalt, nickel, copper, zinc, cadmium, and mercury) form more stable co-ordination bonds with nitrogen than with oxygen.[13] In ammoniacal solutions such metal ions form stable ammine complexes. In contrast, other metal ions (such as alkaline and rare earths, aluminium, bismuth, lead and scandium) either do not react or form hydrous oxide precipitates. Thus, reagents such as polyamines (which have only nitrogen atoms as co-ordinating atoms) complex with a more restricted set of metal ions than reagents such as EDTA and consequently are extremely useful as selective titrants. Although the limited complexing nature of the polyamines was recognised early by Schwarzenbach,[14] only recently has practical use been made of these reagents. Triethylenetetramine, "trien",

$$H_2N—CH_2\,CH_2—NH—CH_2\,CH_2—NH—CH_2\,CH_2—NH_2$$

was first employed for practical titrations by Reilley and Sheldon,[9] who found that copper, zinc, mercury, and cadmium may be selectively titrated in the presence of calcium, magnesium, strontium, and barium using metallochromic indicators More recently Flaschka and Soliman[2] described the photometric titration of copper. Undoubtedly the lack of a source of purified trien attributed to the delay in its application; an easy purification method proposed by Reilley and Sheldon[9] alleviates this difficulty to some extent

Comparison of trien and EDTA

A cursory examination of the stability constants of trien and EDTA (Table I) indicates that trien often forms complexes considerably more stable than EDTA for some bivalent metal ions, yet weaker for other metal ions This is summarised in periodic chart form·

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf						

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* Presented at the XV Congress of the International Union of Pure and Applied Chemistry, Lisbon, 1956

One must be cautious, for comparisons according to the log K values alone can be quite misleading. Of greatest importance are *effective* formation constants which take into account the competitive equilibria of metal ion hydrolysis, the complexing action of the buffer, and the effect of acid.

TABLE I STABILITY CONSTANTS OF TRIEN, AND EDTA COMPLEXES
(25.0° = 0.1)

Metal	Log K, trien[7]	Log K, EDTA[1,11]
Hg^{2+}	25.0	22.1
Cu^{2+}	20.1	18.7
Ni^{2+}	14.1	18.6
Zn^{2+}	11.9	16.4
Cd^{2+}	10.8	16.4
Pb^{2+}	10.4	17.9
Mn^{2+}	—	13.8
Mg^{2+}	negligible	8.9
Ca^{2+}	negligible	10.7
Sr^{2+}	negligible	8.9
Ba^{2+}	negligible	7.9
Bi^{3+}	negligible	>20
La^{3+}	negligible	15.1[a]
Al^{3+}	negligible	16.1[a]

[a] 20°

$$\begin{array}{ccc} \multicolumn{2}{c}{\overbrace{\qquad\qquad M \qquad\qquad}} & + \quad Y \longrightarrow MY \\ + & + & + \\ xOH^- & yZ & nH^+ \\ \downarrow & \downarrow & \downarrow \\ M(OH)_x & MZ_y & H_nY \\ (\textit{Hydrolysis Effect}) & (\textit{Complex Effect}) & (\textit{pH Effect}) \end{array} \tag{1}$$

Each of these effects will be compared in the following sections:

pH *effect:* As seen in equation (1), the hydronium ion competes with the metal ion for the titrant. For this reason, metal ions which form weak complexes can be titrated effectively only in more alkaline solutions. On the other hand, metal ions which form very stable complexes can be titrated even in acid solutions. The pH at which a metal ion of given complex stability can be effectively titrated can be calculated from the acidity constants of the complexing agent and from the stability constant of the metal complex. For the titrants under consideration, the acidity constants[1] are given in Table II.

TABLE II

Titrant	Acidity constants (Log K_{n-i})			
	K_1	K_2	K_3	K_4
EDTA	2.0	2.76	6.16	10.26
trien	3.32	6.67	9.20	9.92

The *effective* stability constant K_E is then given by

$$K_E = \frac{[\mathrm{MY}]}{[\mathrm{M}][\mathrm{H}_n\mathrm{Y} + \mathrm{H}_{n-1}\mathrm{Y} + \cdots \mathrm{Y}]} = \frac{K}{\alpha} \tag{2}$$

where K is the stability constant of the metal complex (Table I) and

$$\alpha = 1 + \frac{[\mathrm{H}^+]}{K_n} + \frac{[\mathrm{H}^+]^2}{K_n \cdot K_{n-1}} + \cdots + \frac{[\mathrm{H}^+]^n}{K_n \cdot K_{n-1} \cdots K} \tag{3}$$

where K_n, K_{n-1}, etc. are the acidity constants of the titrant. Thus,

$$\log K_E = \log K - \log \alpha \tag{4}$$

The values of log α for the trien and EDTA as a function of pH are plotted in Fig. 1. From consideration of the pH effect alone, the effective stability constants of the metal–EDTA and metal–trien complexes both decrease with decreasing pH *but at different rates* For example, at pH 5 the log K_E values of Cu–EDTA and Cu–trien, are 12.3 and 9.3 respectively, while at pH 8 the values are 16.4, and 16.9 respectively. Obviously one cannot then judge the relative complexing action of two *complexing* reagents solely from the log K values because, as seen in the example above, the pH effect not only exerts considerable influence but also may even change the *order* of stability.

Because of the relatively large magnitude of the pH effect in the case of trien, only mercury and copper ions may be titrated effectively in acid solution

As a general rule the minimum log K_E for a satisfactory titration is 4-log C where C is the concentration of the metal ion to be titrated This corresponds to the quality of the end-point in the acidimetric titration of $3 \times 10^{-3}M$ sodium bicarbonate.

Effect of hydrolysis: While the "pH effect" points to the use of alkaline conditions for the most effective titration, the hydrolysis of metal ions under such conditions has the opposite effect and lowers the effective stability constants as seen from equation (1). Consequently, an optimum pH value (where log K_E is maximum) exists for the titration of a given metal ion, this pH depending upon the stability of the metal complex, the ease of hydrolysis of the metal ion, and upon the pH–log α relationships of the titrant. The resulting effect of these competitive equilibria is readily estimated from Figure 1 where the effect of formation of metallic hydroxide precipitates is given. The straight lines marked Hg, Cu, Ni, Zn, Cd and Pb indicate the change in activity (expressed as pM) of the metal ions in question caused by hydrolysis This pM value is given, for bivalent metal ions, by

$$\mathrm{pM} = \mathrm{p}K_{\mathrm{sp}} + 2\,\mathrm{pH} - 28 \tag{5}$$

where K_{sp} is the solubility product constant of the metal hydroxide, shown in Table III. The corresponding effective equilibrium constant for the reaction between the metal hydroxide and titrant becomes

$$\log K_E = \log K - \log \alpha - \mathrm{pM} \tag{6}$$

Thus for copper at pH 7, where log $\alpha = 5\ 3$ and pM $= 4\ 9$, log $K_E = 9.9$ indicating a feasible titration condition using trien. In the case of lead at pH 9, where log α = 1.3 and pM = 7.4, log K_E = 1.7 indicating an unfavourable titration condition using trien. If EDTA were employed for lead at pH 9, log α = 1.2, pM = 7.4, and log K_E = 9.3 and a very satisfactory titration condition exists.

TABLE III

Metal hydroxide	K_{sp}
HgO	3×10^{-26} *a*
$Ni(OH)_2$	1.6×10^{-16} *a*
$Cu(OH)_2$	1.6×10^{-19} *a*
$Zn(OH)_2$	6.3×10^{-17} *b*
$Cd(OH)_4$	1.0×10^{-13} *b*
$Pb(OH)_2$	8.7×10^{-16} *a*

a Latimer, *loc. cit.*[3] *b*. Reilley and Holloway, *loc cit.*[5]

The complex effect: A detailed analysis of Figure 1 shows that the optimum log K_E value occurs for each metal ion at a pH condition where the metal ion precipitates. Direct titration of such metal precipitates however is undesirable, because titration reactions involving precipitates are extremely slow. In practice this is avoided by the addition of a complexing agent to bring the metal ion into homogeneous solution. The complexing agent employed for this purpose must increase pM to a value greater than that caused by hydrolysis. Consequently the log K_E value will be even further diminished by the addition of the complexing agent and only a minimum quantity should be added.

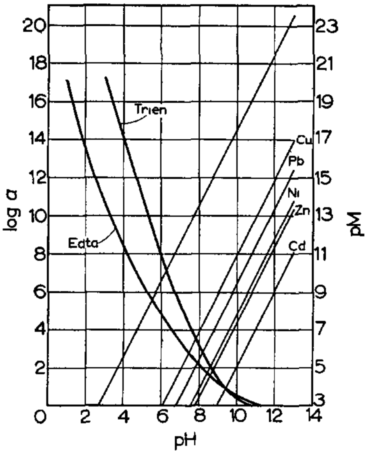

FIG. 1. Hydrolysis and pH effects for EDTA and trien and several metal ions.

Frequently the complexing agent serves also as a buffering agent, maintaining the pH at a desired value during the course of the titration. In these cases one must avoid the temptation of adding more buffer than is necessary. Sometimes best results are obtained by the trick of adding two reagents: *one*, a poor complexing agent which can be added in ample quantity to serve as buffer and *two*, an effective complexing agent which is added in a quantity just sufficient to dissolve the hydrous oxide precipitate.

Factors influencing the end-point response

The above section describes the various parameters which govern the reaction between the metal ion and the titrant in solution. Such conditions also affect the end-point response exhibited by the mercury indicator electrode. In fact the mercury electrode itself is extremely useful in detecting the effect of such conditions. On the other hand the mercury electrode does impose certain limitations of its own in detecting all the pertinent conditions. For these reasons a discussion of the equilibrium problem from viewpoint of the mercury indicator electrode, while overlapping the previous discussion somewhat, is nevertheless informative.

The mercury electrode in contact with a solution containing metal ions to be titrated together with a small added quantity of mercury trien complex will exhibit a potential corresponding to the following half-cell·

$$\text{Hg} \mid \text{Hg Trien, M-Trien}^{n+}, \text{M}^{n+}$$

A combination of the Nernst equation for a mercury electrode

$$E = E^{\circ}_{\text{Hg}} + 0.0296 \log [\text{Hg}^{2+}]$$

with the equations for the stability constants of the 1·1 mercury trien complex

$$K_{\text{HgZ}} = \frac{[\text{HgZ}^{2+}]}{[\text{Hg}^{2+}][\text{Z}]}$$

and a 1:1 metal (Me^{n+}) trien complex

$$K_{\text{MeZ}} = \frac{[\text{MeZ}^{n+}]}{[\text{Me}^{n+}][\text{Z}]}$$

gives at 25°

$$E_{\text{Hg}} = E^{\circ}_{\text{Hg}} + 0.0296 \log \frac{[\text{Me}^{n+}][\text{HgZ}^{2+}]}{[\text{MeZ}^{n+}]\, K_{\text{HgZ}}} + 0.0296 \log K_{\text{MeZ}} \qquad (7)$$

the potential is directly proportional to log [M^{n+}] and *consequently directly proportional to pM*. The mercury electrode is therefore analogous to the glass electrode, which exhibits a potential proportional to pH. Just as acids may be titrated with a base using a glass electrode, metal ions may be titrated with trien using a mercury electrode.

From equation (7), the potential of the mercury electrode is seen to depend *linearly* on log K of the particular metal chelate involved, provided that the concentrations of the mercury chelate, the metal ion, and the metal chelate are kept constant. The log K of the metal chelate complex can be calculated readily from experimental data provided the value of the stability constant for the mercury complex, K_{HgZ}, is known.

The latter can also be determined experimentally from potential measurements with the mercury electrode. The potential of a mercury electrode in a solution containing free trien and mercuric trien chelate is given at 25° by

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log \frac{[\mathrm{HgZ}^{2+}]\,\alpha}{[\mathrm{Z}]_{\mathrm{t}} K_{\mathrm{HgZ}}} \tag{8}$$

where $[\mathrm{Z}]_{\mathrm{t}}$ corresponds to the stoichiometric concentration of trien.

With a knowledge of α, K_{HgZ} can then be calculated from the measured potential–pH function and the concentrations involved. Curve I in Fig. 2 shows this experimentally determined potential as a function of pH for a solution which contains equal amounts of free chelating agent (trien) and the corresponding mercury–trien complex.

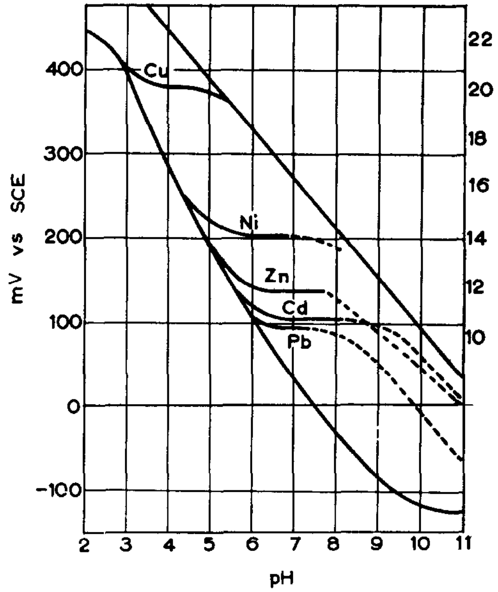

FIG 2 Potential–pH diagram for metal trien complexes. 25° and ionic strength of 0.1 (KNO_3) I 0.001M HgZ^{2+} + 0.001 Z II Calculated (3) potential for $Hg + 2\,OH^- \rightarrow HgO + H_2O + 2\,e^-$ Other lines, 0.001M HgZ^{2+} + 0.001M MeZ^{2+} + 0.001M Me^{2+} Note line I is obtained in the case of Mg, Ca, Sr, Ba, La, Al, and Bi

Alternatively, K_{HgZ} can be determined from the potential of curve I at high pH values (>11) where trien exists only in the free base form and $\alpha = 1$. In this manner the stability constant of HgZ can be obtained without a knowledge of the acidity constants of the trien.

With the help of this constant, K_{HgZ}, a log K scale was calculated from equation 1 and plotted at the right hand side of Fig. 2. Next, a potential–pH diagram was constructed from experimental data for each of several metal ions in such a way that, for definite concentrations of the chemicals involved in equation (7), the log K value for the metal chelate could then be read directly from the measured potential of the mercury electrode, in its pH-independent region (Fig. 2). These log K values are given in Table I A difference in log K of one unit corresponds to a difference of 29.6 mV in potential.

Because curve I is obtained in the presence of Mg, Ca, Sr, Ba, La, Al and Bi, no stable trien complex with these metals exists. The dotted lines, in the cases of metals which do complex, represents the hydrolysis of these metal ions.

An excellent way of presenting the information concerning conditions for the titration of the various metal ions from the mercury electrode viewpoint is in a potential–pH diagram. Because an extensive treatment of the practical determination and application of such diagrams has appeared elsewhere,[6,7,8,10,11] only an abbreviated discussion is given here.

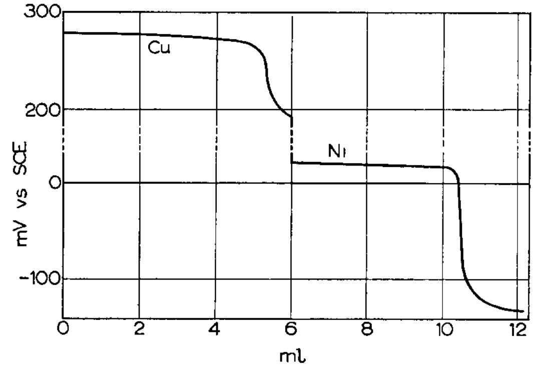

Fig 3. Titration of copper–nickel mixture.

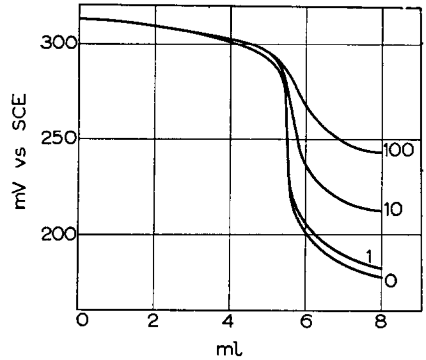

Fig. 4 Titration of copper in the presence of 0-, 1-, 10-, and 100-fold excess of nickel.

The first step in characterising a given chelating titrant is to construct experimentally a potential–pH diagram. This diagram allows immediate prediction of not only the ability of the chelating titrant to complex various metal ions under a wide variety of conditions but also the potentials and effectiveness of the potentiometric end-point detection.

From this diagram for trien several useful applications can be seen immediately.

First, copper may be selectively titrated in the presence of nickel at a pH of approximately 5. On the assumption that 120 mV difference is necessary for a satisfactory selective titration, one may calculate from the data in Fig. 2 that copper may be selectively titrated in the presence of a 100-fold excess of nickel ion. Furthermore, one may predict that, after the titration of copper, the pH can be increased to 8 or above, and the titration continued to a second break corresponding to the titration of nickel. Fig. 3 illustrates the complete analysis of a two-component mixture of copper and nickel where both are present in approximately equal quantities. A sketch, Fig. 4, is also included illustrating the titration of copper in the presence of a 0-, 1-, 10-, and 100-fold excess of nickel.

Table IV gives some typical data for the analysis of certain individual metal ions and Table V for some metal ion mixtures.

TABLE IV. TITRATION OF METAL IONS WITH TRIETHYLENETETRAMINE (TRIEN)

Ion	*M* moles of metal ion in 5.0 ml solution determined by titration with 0.1*M* EDTA	*M* moles of metal ion in 5.0 ml solution determined by titration with 0.1*M* N_4	Error in *M* moles	% Error	*M* moles of metal ion in 0.5 ml solution determined by titration with 0.01*M* N_4	Error in *M* moles	% error
Cu^{2+} (Sulphate)	0.495	0.494	−0.001	−0.20	0.0499	+0.0002	+0.60
		0.494	−0.001	−0.20	0.0498	+0.0003	+0.40
		0.494	−0.001	−0.20	0.0495	0.0000	0.00
Zn^{2+} (Sulphate)	0.523	0.524	+0.001	+0.19	0.0519	+0.0004	+0.76
		0.524	+0.001	+0.19	0.0521	−0.0002	−0.38
		0.522	−0.001	−0.19	0.0521	−0.0002	−0.38
Hg^{2+} (Nitrate)	0.495	0.495	0.000	0.00	0.0497	+0.0002	+0.40
		0.496	+0.001	+0.20	0.0495	0.0000	0.00
		0.495	0.000	0.00	0.0494	−0.0001	−0.20
Ni^{2+} (Sulphate)	0.470	0.470	0.000	0.00	0.0470	0.0000	0.00
		0.471	+0.001	+0.21	0.0470	0.0000	0.00
		0.470	0.000	0.00	0.0473	+0.0003	+0.03
Cd^{2+} (Nitrate)	0.485	0.488	+0.003	+0.61			
		0.488	+0.003	+0.61			
		0.488	+0.003	+0.61			

The alkaline earths and rare earths give data falling on line I throughout the pH range studied and consequently any of the metals, Hg, Cu, Ni, Zn or Cd can be selectively titrated in the presence of the alkaline earths and rare earths. If EDTA is used as a titrant, conditions may be selected so that the alkaline earths and rare earths may be titrated along with the other metal ions. Consequently, through the combined use of two titrants—EDTA and trien—a complete multicomponent analysis may be obtained in many cases.

THE MERCURY ELECTRODE

The mercury electrode employed in this work was of the design proposed by one author (E. H. Sargent and Company, Chicago, Illinois, Catalog No. 5-30413). Amalgamated gold wires or electrodes also work well. Clean the mercury cups with dilute nitric acid and rinse thoroughly with distilled water. Fill the cup with *clean* mercury. Mercury often contains a surface coating of metal

TABLE V. TITRATION OF MIXTURES OF METAL IONS WITH TRIEN

Mixture		*M* moles of metal ion in 5.0 ml solution determined by titration with 0.1*M* N_4	Error in *M* moles	% error	*M* moles of metal ion in 0.5 ml solution determined by titration with 0.01*M* N_4	Error in *M* moles	% error
$Cu^{2+} + Zn^{2+}$	Cu	0.494	−0.001	−0.20	0.0491	−0.0004	−0.80
	Zn	0.523	0.000	0.00	0.0528	+0.0005	+0.95
	Cu	0.494	−0.001	−0.20	0.0492	−0.0003	−0.60
	Zn	0.522	+0.001	+0.19	0.0527	+0.0004	+0.46
	Cu	0.493	−0.002	−0.40	0.0493	−0.0002	−0.40
	Zn	0.522	−0.001	−0.19	0.0519	−0.0004	−0.76
$Cu^{2+} + Zn^{2+}$ (in presence of $Ca^{2+} + Mg^{2+}$)	Cu	0.493	−0.002	−0.40	0.0497	+0.0002	+0.40
	Zn	0.525	+0.002	+0.38	0.0526	+0.0003	−0.57
$Hg^{2+} + Cd^{2+}$	Hg	0.495	0.000	0.00			
	Cd	0.487	+0.002	+0.40			
	Hg	0.490	−0.005	−1.00			
	Cd	0.490	+0.005	+1.02			
	Hg	0.490	−0.005	−1.00			
	Cd	0.487	+0.002	+0.40			
$Cu^{2+} + Ni^{2+}$	Cu	0.490	−0.005	−1.00	0.0492	−0.0003	−0.60
	Ni	0.470	0.000	0.00	0.0472	+0.0002	+0.42
	Cu	0.490	−0.005	−1.00	0.0493	−0.0002	−0.40
	Ni	0.468	−0.002	−0.42	0.0470	0.0000	0.00
	Cu	0.490	−0.005	−1.00	0.0493	−0.0002	−0.40
	Ni	0.469	−0.001	−0.21	0.0473	+0.0003	+0.63

oxides which will not only interfere with the electrode response but which may dissolve and react with the titrant, leading therefore to erroneous results. In case of doubt mercury can be washed briefly with dilute nitric acid or alkaline (pH 10) EDTA solution and then rinsed thoroughly with distilled water The mercury is allowed to remain in the electrode cups after each titration (being rinsed with distilled water before the next titration).

Solutions to be titrated must be free of materials which react with mercury^{II} or mercury^{I} ions such as cyanide, sulphide, iodide, bromide, and large amounts of chloride This is especially important for titrations carried out in acid solution

The electrode system (mercury indicator and calomel reference) are dipped into the solution to be titrated and a drop of indicator solution (mercury–trien complex) is added The titrant is then added until the potentiometric break is obtained Trien may be added as a titrant for direct titration of metal ions or a standard solution of an appropriate metal ion may be used for back titration in cases where an excess of trien is added first

REAGENTS

Metal ions

Approximately 0 1*M* solutions of $CuSO_4$, $ZnSO_4$, $NiSO_4$, $Cd(NO_3)_2$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$, and $Ba(NO_3)_2$ were prepared by dissolving 0 25 mole of the salt in water and making the volume up to 250 ml The solution of 0 1*M* $Hg(NO_3)_2$ was prepared by dissolving 0 25 mole of the salt in the minimum quantity of dilute nitric acid, and increasing the volume to 250 ml with distilled water The concentration of these solutions was determined by titration with a standard solution of EDTA, the end-point being determined potentiometrically The EDTA itself was standardized by potentiometric titration with a standard copper solution, prepared from a weighed quantity of pure copper foil

The 0 01*M* solutions of metal ions were prepared by dilution

Triethylenetetramine ("trien")

The triethylenetetramine was obtained in crude form from Carbide and Carbon Chemicals Company, Charleston, West Virginia For sharp end-points, it was absolutely necessary to purify the commercial trien. Recrystallisation of the bisulphate or tetranitrate was found to be satisfactory. The following procedure was used for the bisulphate, and that for the tetranitrate is similar

Sixty millilitres of crude trien, 400 ml distilled water and 100 ml 95% ethanol were mixed together, and 276 ml H_2SO_4 (46 ml concentrated H_2SO_4, 230 ml water) were added slowly with stirring. (The pH at this stage should be less than 2, if not, more acid should be added) Crystals of the impure bisulphate now separate out The mixture was cooled in an ice bath, and the crystals filtered and washed twice with 80 ml of a 1.1 mixture of ethanol and water They were redissolved in 550 ml hot water, the hot solution was filtered, and 185 ml hot ethanol were added slowly and with stirring to the filtrate The mixture was cooled in an ice-bath and the crystals which separated out were filtered, washed 3 times with 80 ml of 1 1 ethanol and water, and dried at 80–100° under reduced pressure (water pump) Yield 55–65% For use at 0 01*M* concentration, a further recrystallisation is desirable.

To prepare a 0.1*M* solution, approximately 34 g were dissolved in 1 litre of distilled water containing 0 4 moles sodium hydroxide The solution was standardised by potentiometric titration with standard $Cu(NO_4)$ solution, prepared from pure copper foil The solution is stable for at least two months

Buffers

Ammonia–ammonium nitrate buffer was prepared by mixing equal quantities of 0 5 molar solutions of ammonium hydroxide and ammonium nitrate

Triethanolamine buffer consists of a 0.5*M* solution of triethanolamine in water, the acidity being adjusted to pH 7 5 by addition of the necessary quantity of nitric acid

Acetate buffer is a mixture of equal quantities of 0 5*M* acetic acid and 0 5*M* sodium acetate The pH is adjusted to 5 2 by the addition of nitric acid or sodium hydroxide

Mercury–trien complex is prepared by mixing exactly equivalent quantities of 0 1*M* $Hg(NO_3)_2$ and 0 1*M* trien as determined by a separate potentiometric titration.

PROCEDURES

Titration of single metal ions

Copper, zinc, cadmium, and nickel titration were carried out in ammonia–ammonium nitrate buffer at pH 9.3 Because the mercuric ion precipitates in the ammonia buffer, triethanolamine buffer at pH 7.5 was used for this titration

The titrations were carried out in a 250-ml beaker stirred by a magnetic stirrer Two indicator electrodes were used a glass electrode for checking the pH and a mercury one for determination of the end-point, a calomel electrode was used as the reference electrode in each case

Ten ml of buffer (1 ml for titration of 0 01*M* solutions) were pipetted into the beaker containing approximately 50 ml water and 5 0 ml of metal ion solution, and 1 drop of mercury–trien complex were added The pH was checked, and if necessary adjusted by addition of small quantities of sodium hydroxide or nitric acid The glass electrode was then exchanged for the mercury one, and the titration carried out until a sharp break was obtained

Titration of mixtures of copper and zinc

Owing to the widely differing stability constants of these two metal complexes, selective titrations can be carried out by employing the "pH effect " The copper ion is first titrated at pH 5 2 (acetate buffer) because zinc ion does not complex with triethylenetetramine at this pH After the copper ion is titrated, the pH is then increased to 9 3 (ammonia–ammonium nitrate) and the zinc ion is titrated

Ten ml of acetate buffer, 5 0 ml of copper sulphate and 5 0 ml zinc sulphate were pipetted into a beaker containing 50 ml of water and 1 drop of mercury trien was added The pH was adjusted to 5 2 (if necessary), and the titration carried out until a break occurred Ammonium hydroxide was then added until the pH reached 9 3–9 5, and the titration continued until a further break occurred.

Addition of a large excess of acetate was avoided, as this competes with the trien for the metal ion

Copper and zinc in the presence of magnesium, calcium, strontium and barium

The alkaline earths do not complex trien and should therefore not interfere in the above titration. Copper and zinc were successfully titrated under the same conditons as above in the presence of 50 ml each of 0 1M magnesium, calcium, strontium, and barium

Copper and nickel, mercury and cadmium mixtures

Two component mixtures of copper and nickel, or mercury and cadmium were titrated under the same two step conditions as in the case of copper and zinc described above

Acknowledgements—The authors express their appreciation to Dr R W Schmid who collected the data for Figs 2 and 4

This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No AF 18(600)–1160

Zusammenfassung—Es wird die theoretischen Bedingungen, die fur die potentiometrische Titration der Metall-Ionen mit Triathylenetetramin („Trien"), und fur die selektive Titrationen der Ionen-Gemengen mit diesem Reagens, allein oder zusammen mit ADTA wichtig sind, erortet

Es wird bewiesen, dass es moglich ist, Bedingungen die fur selektive Titrationen geeignet sind zu wahlen, und dies wird durch Titrationen von Cu, Zn, Ni, Cd und Hg, allein und in 2-Bestandteil-Gemengen illustriert

Die alkalinischen Erden storen die Titration nicht

Résumé—Discussion des conditions théoriques nécessaires pour le titrage potentiométrique des ions métalliques utilisant le triéthylènetétramine ("trien") et pour le titrage sélectif des mélanges d'ions à l'aide de ce réactif, seul ou avec l'EDTA On démontre qu'il est possible de choisir des conditions permettant d'effectuer des titrages sélectifs, ceci a été illustré par les titrages de Cu, Zn, Ni, Cd et Hg, soit seuls, soit dans des mélanges à deux composants Les alcalino-terreux ne gênent pas

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BEITRAG ZUR CHARAKTERISIERUNG DES FLUORESCEINKOMPLEXONS

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(*Received* 27 *February* 1958)

Zusammenfassung—Es wurde gezeigt, dass das reine Fluoresceinkomplexon im Gegenteil zu dem kommerziellen Calcein in der alkalischen Losung nur eine ganz geringe Restfluorescenz aufweist. In einem Gemisch von Fluoresceinkomplexon mit Fluorescein findet eine innere Absorption der Fluorescenz teilweise statt, jedoch nicht bei einem Calciumuberschuss. Dies konnte zu den Fehlschlussen bei der Beurteilung der Fluorescenzeigenschaften von verschiedenen Calcein-Praparaten fuhren

Das Lichtabsorptionsmaximum des Calceins liegt zwischen den Maxima von Fluorescein und Fluoresceinkomplexon

Im Jahre 1956 beschrieben Diehl und Ellingboe[1] einen neuen komplexometrischen Indikator, das sog "Calcein". Sie stellten Calcein durch ähnliches Verfahren dar, das vorher Anderegg, Flaschka, Sallmann und Schwarzenbach[2] zur Herstellung *o*-Kresolphtaleinkomplexons benutzt hatten. Calcein stellt einen, für die komplexometrische Bestimmung von Calcium, Strontium und Barium in einer stark alkalischen Lösung sehr geeigneten Indikator dar.[1] Dieser neue Indikator weist gegen Murexid und dem oben erwähnten *o*-Kresolphtaleinkomplexon viele Vorteile auf (siehe z B.[3]).

Diehl und Ellingboe beschrieben ihren Stoff als einen Farbindikator mit dem Umschlag von grün zu braun. Das nach unserem Verfahren hergestellte Fluoresceinkomplexon zeigte dagegen Fluorescenzumschläge.[4] Die eigene Fluorescenz unseres Präparates loscht in alkalischem Medium, oberhalb der Laugenkonzentration von 0,025N. Die Erdalkaliionen, auch das Magnesium, rufen in solchen Lösungen eine gelbgrüne Fluorescenz hervor. Der Storeffekt des Magnesiums wird bei einer höheren Laugenkonzentration stark herabgesetzt, sodass es in 0,1N KOH-Lösung möglich ist, die Calciumbestimmung auch neben kleineren Mengen (bis 30 mg) Magnesium durchzufuhren.[1,4] Das Fluoresceinkomplexon wurde vor kurzer Zeit auch fur Calciumbestimmung im Blut[5] und für indirekte Sulfatbestimmung im Wasser[6] vorgeschlagen. Es scheint, dass durch Einführung dieses Indikators das letztgenannte Problem endlich zufriedenstellend gelöst wurde.

Vor kurzem haben wir eine kleine Probe von kommerziellem Calcein erhalten, das höhstwahrscheinlich nach der Vorschrift von Diehl und Ellingboe[1] hergestellt worden war. Da es uns inzwischen auch gelang, Fluoresceinkomplexon (*bis*-N·N-di-(karboxymethyl)-(aminomethyl-fluorescein) in ganz reinem Zustande herzustellen,[7] konnten wir beide Präparate vergleichen

Durch Orientierungsversuche wurde festgestellt, dass sich das Calcein gegenüber den Angaben von Diehl und Ellingboe, ahnlich wie unser Präparat, als ein metallofluorescenter Indikator verhalt. Das Ausloschen der Fluorescenz bei der Titration der Erdalkaliionen war jedoch nur unvollkommen; es blieb immer eine ziemlich starke Restfluorescenz übrig. In dieser Arbeit werden beide Stoffe auf dem fluorimetrischen und spektrofotometrischen Wege charakterisiert.

EXPERIMENTELLER TEIL UND ERGEBNISSE

Apparate

Die fluorimetrischen Messungen wurden mit Hilfe eines einfachen Fluorimeters durchgefuhrt Als Quelle der Excitationsstrahlung wurde Philora "Philips" benutzt mit blauem Filter Die Intensitat der Emission wurde als Fotostrom der Selenzelle mittels eines empfindlichen Galvanometers gemessen Die Messungen wurden in Quarzkuvetten zylindrischer Form immer mit 25 ml Losung durchgefuhrt Alle Ergebnisse der Messungen wurden in Prozenten der Fluorescenz einer 6 $10^{-6}M$ Fluoresceinlosung ausgedruckt

Zu den optischen Messungen wurde das Universalspektrofotometer Zeiss in Zurichtung fur das Messen im Sichtbaren benutzt Die Messschicht betrug 0,5 cm

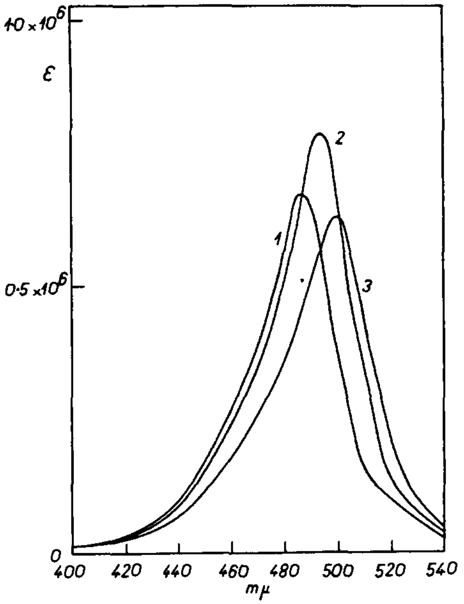

Abb 1 Extinktionskurven von Fluorescein 1, Calcein 2 und Fluoresceinkomplexon 3 in 0,1*N* KOH

Reagenzien

Standardpraparat von Fluorescein (freie Saure) p a

Standardpraparat von Fluoresceinkomplexon Fur $C_{30}H_{26}N_2O_{13}$ (622,5) errechnet. 57,89 % C, 4,21 % H, 4,51 % N, gefunden· 57,99 % C, 4,42 % H, 4,76 % N [7]

Calcein der Fa G F Smith Chem Co , Columbus, Ohio, U S A

Die Vorratslosungen wurden in 0,1*N* KOH zubereitet, das auf 1 l immer 5 ml 0,05*M* Dinatriumsalz der ADTA zur Bindung eventueller Spuren von Kationen enthielt

0,5*M* $CaCl_2$ wurde aus einem p a Praparat vorbereitet

Lichtabsorption von Fluoresceinkomplexon und Calcein

Die Messungen wurden in 3 $10^{-5}M$ Losungen durchgefuhrt Als Molekulargewicht des Calceins wurde das Gewicht des reinen Fluoresceinkomplexons genommen (622,5) Die Extinktionskurven der beiden Praparate wurden mit der Kurve des Fluoresceins verglichen, die in einer Losung derselben molaren Konzentration aufgenommen wurde (Abb 1)

Die Absorptionsmaxima aller drei untersuchten Stoffe in 0,1*N* KOH liegen dicht aneinander. Fluorescein (Kurve 1) absorbiert bei der kurzesten Wellenlange (487 mμ), Fluoresceinkomplexon (Kurve 3) bei der langsten (500 mμ) Das Maximum des Calceins (Kurve 2) befindet sich zwischen diesen beiden (496 mμ)

Der Extinktionskoeffizient des Fluoresceinkomplexons ist etwas niedriger als beim Fluorescein. Mit diesen zwei Stoffen kann die Absorption des Calceins, wegen Schwierigkeiten bei der Wahl des richtigen Molekulargewichtes, nicht unmittelbar verglichen werden Es handelt sich offensichtlich um ein Gemisch von disubstituiertem und monosubstituiertem Derivat des Fluoresceins und vielleicht auch von freiem Fluorescein,[1] was sich auch in der Mittelstellung des Absorptionsmaximums spiegelt. Das Molekulargewicht des Fluoresceinkomplexons ist beinahe doppelt so gross, als das des Fluoresceins, sodass eine Verunreinigung des Calceins durch dieses, oder auch durch das monosubstituierte Derivat zur scheinbaren Erhohung des Extinktionskoeffizientes fuhrt Anderseits kann diese Erhohung zur Beurteilung der Reinheit des Praparates dienen.

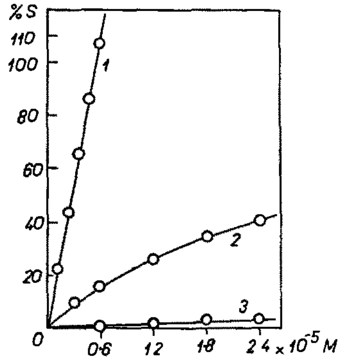

Abb 2. Relative Intensitat der Fluorescenz von Fluorescein 1, Calcein 2 und Fluoresceinkomplexon 3 in der Abhangigkeit von der Konzentration, in 0,1N KOH

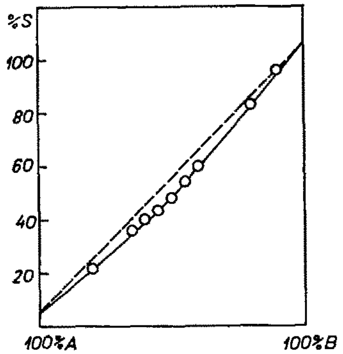

Abb. 3. Relative Fluorescenz der isomolaren Gemischen von Fluoresceinkomplexon und Fluorescein in 0,1N KOH (A = 6 . 10^{-6}M Fluoresceinkomplexon; B = 6 . 10^{-6}M Fluorescein)

Fluorescenzeigenschaften von Fluoresceinkomplexon und Calcein

Die Restfluorescenz der beiden Praparate wurde bei ihren steigenden Konzentrationen in 0,1N KOH gemessen, und mit Fluorescein verglichen. Die Ergebnisse sind in Abb. 2 wiedergegeben Fluoresceinkomplexon weist eine ganz winzige Restfluorescenz auf Dagegen ist die Restfluorescenz des Calceins betrachtlich Wenn auch im Vergleich mit dem linearen Verlauf der Fluorescenz des Fluoresceins in der Abhangigkeit von der Konzentration, die Werte der Restfluorescenz des Calceins viel niedriger sind, ist in diesem Falle die Linearitat nicht erfullt. Deshalb konnten wir zu irrtumlichen Schlussen gelangen, wenn wir die Restfluorescenz bei verschiedenen Konzentrationen beurteilen wurden Es kommt hier offensichtlich eine Selbstabsorption der Fluorescenz zum Vorschein. Ähnlicher Selbstabsorption begegnen wir auch beim Mischen des Fluoresceinkomplexons mit Fluorescein, wie aus der nachsten Abbildung hervorgeht In der Abb 3 ist die Abweichung von der Additivitat in den isomolaren Gemischen von Fluorescein und Fluoresceinkomplexon gegeben. Solche Abweichung wurde nicht in der Anwesenheit des Calciumuberschusses beobachtet (Abb. 4) Daraus folgt, dass wir bei hoheren Konzentrationen eines durch Fluorescein verunreinigten Fluoresceinkomplexons, bei der Reaktion mit Erdalkaliionen eine grossere Fluorescenzausbeute erwarten konnen als bei einem reinen Praparat Bei niedrigen Konzentrationen, bei denen die Selbstabsorption vernachlassigt werden kann, kommt diese Erscheinung nicht vor In der Abb 5 ist die Fluorescenz kleiner Konzentrationen des Fluoresceinkomplexons und des Calceins vor und nach der Zugabe des Calciumuberschusses wiedergegeben. Die Einwagen der beiden Stoffe wurden so gewahlt, dass die Hohen ihre Lichtabsorptionsmaxima genau gleich sind Die Fluorescenzen dieser Losungen sind wieder mit der Fluorescenz des Fluoresceins verglichen Dieser Versuch erlaubt uns auch, die Verunreinigung des Calceins abzuschatzen Dies ist allerdings nur als eine Fluoresceinbeimengung ausdruckbar, da zur Zeit die Licht- und Fluorescenzeigenschaften des monosubstituierten Derivates unbekannt sind Eine einfache Rechnung ergibt 6,6% Fluorescein im Calcein

Summary—Pure fluorescein-complexone, in contrast to commercial Calcein, shows in alkaline solution only a small residual fluorescence In a mixture of fluorescein-complexone and fluorescein, an inner absorption of fluorescence partially occurs, but not, however, in the presence of excess calcium ions This can lead to erroneous conclusions when appraising the fluorescence properties of different preparations of Calcein

The absorption maximum of Calcein lies between those of fluorescein and fluorescein-complexone.

Résumé—Le complexon-fluorescéine, contrairement à la calcéine commerciale, ne montre en milieu alcalin qu'une faible fluorescence résiduelle Dans un mélange du complexon-fluorescéine avec la fluorescéine, il se produit une absorption interne partielle de la fluorescence, mais non, cependant, en présence d'un excès d'ions de calcium Ceci pourrait conduire à des conclusions erronées en évaluant les propriétés fluorescentes de différentes préparations de la calcéine

Le maximum d'absorption de la calcéine se situe entre ceux de la fluorescéine et du complexon-fluorescéine.

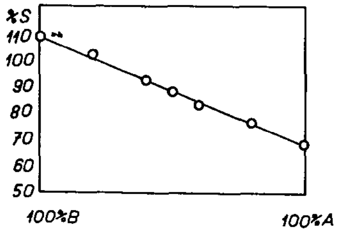

Abb. 4 Relative Fluorescenz der isomolaren Gemischen von Fluoresceinkomplexon und Fluorescein in 0,1N KOH und $10^{-2}M$ $CaCl_2$ Losung, 0,5 ml 0,5M $CaCl_2$ in 25 ml der Messlosung (A = 6 $10^{-6}M$ Fluoresceinkomplexon, B = 6 . $10^{-6}M$ Fluorescein)

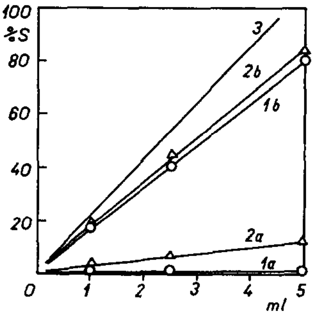

Abb 5. Relative Fluorescenz von Fluoresceinkomplexon und Calcein in 0,1N KOH vor (1*a* und 2*a*) und nach (1*b* und 2*b*) der Zugabe des Calciumuberschusses, im Vergleich mit dem Fluorescein (3). (20 mg Fluoresceinkomplexon, resp 17 mg Calcein, resp. 10 mg Fluorescein in 1 L der Vorratslosung Die auf der Abscisenaxe angegebenen Mengen der Vorratslosungen wurden auf 25 ml verdunnt, eventuell nach der Zugabe von 0,5 ml 0,5M $CaCl_2$)

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A METHOD FOR THE DETERMINATION OF MILLIGRAM AMOUNTS OF SULPHUR WITH 4-AMINO-4′-CHLORODIPHENYL

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(*Received* 17 *February* 1958)

Summary—A method for the determination of milligram amounts of sulphur is described in which 4-amino-4′-chlorodiphenyl is used to precipitate the sulphate resulting from preliminary digestion of organic samples with nitric acid. The consumption of reagent is determined by spectrophotometric measurement of the excess remaining in solution. The method has been applied to the analysis of coals and humic acids

In the course of an examination of certain high-sulphur coals a convenient method was needed for the routine determination of milligram amounts of organic sulphur. The new reagent proposed by Belcher, Nutten, Parry and Stephen[1] for the precipitation of inorganic sulphate, 4-amino-4′-chlorodiphenyl (CAD) was attractive as a basis for such a method, particularly because of its freedom from sensitivity to nitrate ion. Jones and Letham[2] showed that this reagent possessed a well-defined ultra-violet absorption maximum at 254 mμ, and used this property in developing an indirect method for determination of sub-micro quantities of sulphur The method, which was applied to certain mercaptals, involved conversion of sulphur to inorganic sulphate, precipitation with an excess of CAD, and spectrophotometric measurement of the excess, thus avoiding the troublesome separation, washing and weighing of precipitates In the present work the method of Jones and Letham has been adapted to the milligram scale, and a procedure developed which employs only apparatus which is to be found in most laboratories The method has been found to be applicable to coals and related products.

The procedure used by Jones and Letham for the removal of phosphate, which interferes with the determination of sulphate, has not been incorporated in the new method because phosphorus occurs only in very small amounts in the substances under investigation. However, there appears no reason why the phosphate separation step should not readily be included when necessary

The analysis procedure was examined in three steps, namely, oxidation of the organic sulphur with nitric acid to sulphate; evaporation of excess nitric acid; and precipitation of sulphate with CAD and dilution of the excess CAD to a concentration suitable for spectrophotometric measurement

The Carius tube (nitric acid oxidation) procedure used by Jones and Letham proved satisfactory for coal products and for some standard aromatic substances, the oxidation products having only a small ultra-violet absorption at 254 mμ. The sealed tubes were heated by placing in holes in an aluminium block heated electrically to 280°; by means of a simple loading device the tubes could safely be loaded into and removed from the hot block, thus saving the time normally necessary for preliminary heating and final cooling of the Carius furnace.

Excess nitric acid was removed from the digest solution by warming in a current of dry air. The apparatus used is shown in Fig. 1. The use of a dry air stream greatly increases the speed of evaporation, and a digest may be evaporated to dryness in less than one hour. The apparatus is heated by a boiling water bath, and the air inlet is adjusted periodically to keep it about 1 cm above the liquid level in the Carius tube. The stopper at the top of the air inlet tube is removed to facilitate washing when evaporation is complete. A bubbler in the pump line contains water to absorb acid vapours, and serves to indicate the air flow, which should be sufficient just to disturb the surface of the evaporating liquid.

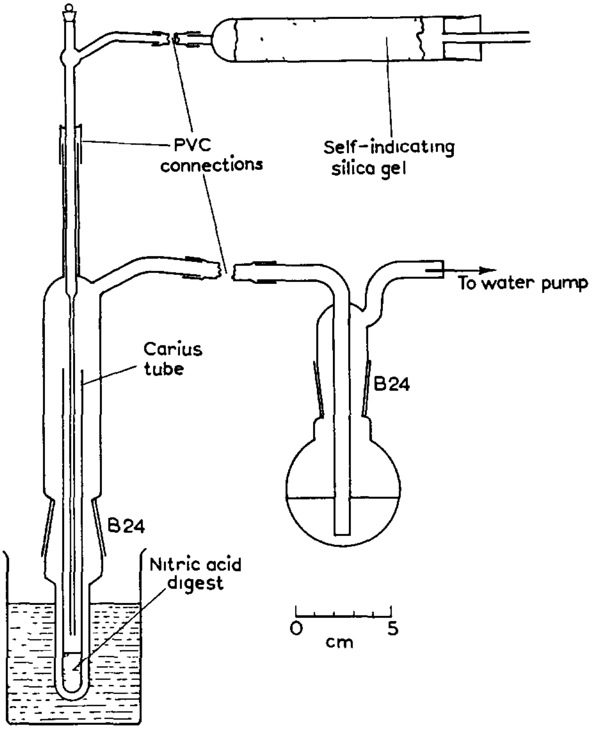

FIG. 1 —Apparatus for evaporation of digests

In elaborating the procedure for precipitation of the sulphate and subsequent dilution of the supernatant liquor, it was necessary to observe the recommendations of Belcher *et al.*[1] regarding the final concentration of reagent necessary for complete precipitation, and also to ensure that the excess of reagent was not too great to allow the difference corresponding to the sulphate to be measured with sufficient accuracy. It was also desirable that the dilution procedure should require only normal titrimetric apparatus.

In the first system investigated a sample containing 0·5–1 mg of sulphur was oxidised and the resulting sulphate precipitated in a final volume of 25 ml with 15 ml of an approximately saturated solution of CAD in 0·1*N* hydrochloric acid. The supernatant liquid containing the excess reagent was diluted 200 times for spectrophotometric measurement, which was made at 254 mμ using a 1-cm cell in a Unicam S.P. 500 spectrophotometer Although this system gave satisfactory results, it was necessary to carry out a separate blank experiment to determine the ultra-violet absorption of the oxidised product. Accordingly, a second system was examined in which the digest was dissolved in 0·1*N* hydrochloric acid to a total volume of 10 ml, and a 5-ml aliquot of the solution treated with 5 ml of CAD solution; the supernatant liquor was diluted 100 times. A separate 2-ml aliquot was diluted 200 times to provide a blank. This second system however gave low results because the excess of CAD was insufficient; increasing the volume of CAD to the next convenient volume, 10 ml, reduced the accuracy of determination of the amount of CAD consumed in the precipitation.

For the third system, the size of the sample was increased so that it contained 1–2 mg of sulphur, and the oxidised material was dissolved in 0·1*N* hydrochloric acid and made up to 25 ml. A 10-ml aliquot was now precipitated with CAD as in the first system, and the blank was obtained by direct dilution of a 1-ml aliquot to 500 ml. The smaller accuracy inherent in a 1-ml pipette could be tolerated here because the low blank values were relatively insensitive to error. This system gave satisfactory results and has been adopted as the recommended procedure.

In addition to the general desirability of obtaining both "blank" and "live" measurements on one and the same solution, a considerable saving in time is achieved since it is necessary to evaporate only one digest, and also the capacity of the Carius furnace is effectively doubled.

EXPERIMENTAL

Reagents

Concentrated nitric acid (d 1·42) containing 25 mg per ml of sodium chloride. Hydrochloric acid, approximately 0·1*N*. 4-amino-4′-chlorodiphenyl, approximately 0·18% in 0·1*N* hydrochloric acid. Cetavlon (cetyltrimethylammonium bromide).

Recommended procedure

A sample of the substance to be analysed, containing 1–2 mg of sulphur, is oxidised by heating with the nitric acid–sodium chloride solution (1·25 ml) in a small sealed tube at 280° for 3 hours. The resulting solution is evaporated to dryness in the opened tube by heating in a current of dry air, and the residue is dissolved out and made up to 25 ml with 0·1*N* hydrochloric acid (Solution A).

To a 10-ml portion of this solution is added 15 ml of CAD solution and a trace of Cetavlon, after shaking, the mixture is allowed to stand for 2 hours, and about 10 ml of the supernatant liquor is centrifuged for 10 minutes at 2000 rev/min to ensure deposition of all precipitate. A 5-ml portion of the clear supernatant is now quantitatively diluted to 100 ml, and 5 ml of this solution are in turn diluted to 50 ml (Solution B). The optical density (I') of Solution B is then measured in a 1-cm cell at 254 mμ against a blank solution prepared by diluting 1 ml of Solution A directly to 500 ml. All dilutions are made with distilled water.

The percentage of sulphur in the sample is calculated from the formula

$$S = \frac{(I - I') \times 32 \times 6250}{\epsilon \times (\text{Wt. of sample in mg})} \times 100\%$$

where I is the "sulphate blank" value determined for each batch of reagent solutions by means of a separate blank experiment, and ϵ is the molar extinction coefficient of CAD at 254 mμ.

In the case of substances, such as some coals, which contain only small amounts of sulphur, it may be necessary to use more nitric acid in the digestion in order to oxidise the greater amount of carbonaceous material in the sample.

The reagent CAD was prepared according to Belcher, Nutten and Stephen[3] and was purified by crystallisation from light petroleum and by vacuum sublimation. M.p. 129° (uncorrected). Found $\lambda_{max} = 254$ mμ and $\epsilon_{254} = 22{,}370$. The difference between this value and that observed by Jones and Letham has been shown to be due to variation between the spectrophotometers used

The recommended procedure was tested using various amounts of potassium sulphate as a standard, the recoveries of sulphate obtained are shown in Table I Recovery of the largest amount of sulphate was not quite complete because the excess of CAD was insufficient. Table II lists the results obtained for a standard sulphonic acid and a sulphonic ester, and compares the values found for certain coals and humic acids with those obtained by the standard (macro) Eschka method The "ultra-violet blank" values are included to show the effectiveness of the oxidation procedure Sulphonic acids were chosen as standards because the sulphonic group was that most likely to occur in the products investigated in this laboratory

TABLE I. RECOVERY OF SULPHATE BY RECOMMENDED PROCEDURE

Potassium sulphate taken (mg)	Optical density at 254 mμ (I')	$I - I'$	Sulphate found (mg)	Sulphate calculated (mg)
0·00	0·534 (I)	—	—	—
2·705	0·479	0·055	1·47	1·49
5·32	0·425	0·109	2·92	2·93
8·34	0·364	0·170	4·55	4·59
10·67	0·314	0·220	5·88	5·87
13·46	0·258	0·276	7·39	7·41
17·24	0·188	0·346	9·26	9·51

DISCUSSION OF RESULTS

The method described above gave recoveries within 1 % of theoretical for amounts of sulphate in the range 3–7·5 mg (1–2·5 mg sulphur). Sulphur analyses of similar accuracy were obtained for standard aromatic substances, which have been shown to be decomposed satisfactorily by digestion with nitric acid. Application to coals and humic acids gave results which agreed satisfactorily with those obtained by the standard macro-method, which requires more time and manipulation than the semi-micro technique The speed of the new method compares favourably with that of existing methods; also, the two most time-consuming operations, digestion and evaporation of the digest, require relatively little supervision by the analyst.

TABLE II DETERMINATION OF SULPHUR IN COALS AND RELATED MATERIALS

Sample	UV blank	Found S (%)	Found S (%) (Eschka)	Calculated S (%)
Sulphanilic acid	0·000	18·50, 18·38	—	18·49
Phenyl *p*-toluene-sulphonate	0·000	12·89, 12·80	—	12·90
Coal C 70	0·003	7·37, 7·40	7·24	—
Coal C 69	0·001	4·12, 4·30	3·96	—
Coal P 126	0·001	0·79, 0·76	0·74	—
Humic acid C 70	0·000	6·17, 6·45	6·15	—
Humic acid C 69	0·000	3·41, 3·21	3·22	—
Humic acid D 355	0·006	0·46, 0·53	0·46	—

Acknowledgements—The authors thank Professor S. G Ward for his interest in this work, and Dr. R. Belcher and Dr. A S. Jones for helpful discussions.

Zusammenfassung—Es wird eine Methode fur die Bestimmung kleiner Mengen von Schwefel beschrieben, vorin 4-Amino-4′-Chlorodiphenyl benutzt wird, um das Sulphat, das von vorlaufiger Zersetzung der organischen Proben mit Salpetersaure resultiert, niederzuschlagen. Der Verbrauch des Reagens wird durch spektrophotometrische Messung des zuruckbleibenden Überschuss in Losung bestimmt

Die Methode wird zur Analyse von Steinkohlen und Humus-sauren angewandt.

Résumé—Description d'une méthode de dosage de petites quantités de soufre, utilisant le 4-amino-4′chlorodiphényl pour précipiter le sulfate résultant de la digestion préliminaire des échantillons organiques avec l'acide nitrique. Le volume du réactif consommé est déterminé par une mesure spectrophotométrique de l'excès qui reste en solution On a appliqué cette méthode à l'analyse des charbons et des acides humiques

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SUBSTITUTIVE HALOGENATION OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTIONS BY INTERHALOIDS—I

HALOGENATING EFFECT OF IODINE MONOCHLORIDE, IODINE MONOBROMIDE AND BROMINE MONOCHLORIDE

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(*Received* 14 *February* 1958)

Summary—The reactions of iodine monobromide and bromine monochloride with certain aromatic compounds in aqueous solution have been examined.

It was found that in halogen substitution reactions, bromine monochloride acts exclusively as a brominating agent Formation of chloro-derivatives or bromide ions could not be detected

Iodine monobromide, on the contrary, proved to act partly as an iodinating, and partly as a brominating agent, even in aqueous solutions containing bromide

IODINE MONOCHLORIDE AS A HALOGENATING AGENT

Iodine monochloride has been used as an iodinating agent for more than a century.[1–10] It has been pointed out by Bennett and Sharpe[11] that in many reactions iodine monochloride acts not only as an iodinating but also as a chlorinating agent Iodine monochloride in the vapour phase chlorinates salicylic acid, and when, dissolved in carbon tetrachloride acts mainly as chlorinating agent although, during the reaction, iodine derivatives form to a smaller extent On allowing anisole in chlorobenzene solution to react with iodine monochloride, iodine derivatives form in 50% and chlorine derivatives similarly in 50% yield, whereas in an acetic acid medium only 20% of anisole is chlorinated.[12] In a nitrobenzene solution, iodine monochloride acts exclusively as an iodinating agent. Hughes and Ingold,[13] and also Waters[14] disclosed a correlation between the dielectric constant of various solvents and the nature of the favoured reaction. Solvents of high dielectric constant encourage a heterolytic mechanism (forming I^+ and Cl^- ions), whereas solvents of low dielectric constant promote a homolytic dissociation (forming I_2 and Cl_2 molecules). In the vapour phase, in almost every case, homolytic dissociation takes place. The energy required for the dissociation of iodine monochloride into I^+ and Cl^- ions (6·69 eV, 155 cal mole^{-1}) has been calculated by Bennett and Sharpe[11] from the first ionization potential of iodine (10·44 eV) and the electron affinity of chlorine (3·75 eV). It was found that ionic dissociation requires more energy than the atomic one. According to the calculations of these authors[11] iodine monochloride dissociates to I^+ and Cl^- ions only in solvents of dielectric constant above 3·8 This also explains the observations of Sandonnini and Borghelo,[15] and of Bruner and Galicki,[16] who state that iodine monochloride is an electric conductor of second order in a chlorobenzene solution ($E = 5{\cdot}8$), in an acetic acid solution ($E = 7{\cdot}1$) and in a nitrobenzene solution

($E = 36$). These solutions, especially the last, are exclusively iodinating agents whereas iodine chlorine dissolved in carbon tetrachloride ($E = 2{\cdot}2$) is mainly a chlorinating agent This presumption is supported by the experience of Grillam and Morton[17] who found that the solution of iodine monochloride in a solvent of low dielectric constant is dark brown, whereas its solution in a solvent of high dielectric constant shows a yellow (orange) colour.

It follows that iodine monochloride (and interhaloids, in general) may dissociate in two ways, depending on the nature of the solvent:

$$2\,ICl \rightleftharpoons I_2 + Cl_2 \tag{1}$$

$$ICl \rightleftharpoons I^+ + Cl^- \tag{2}$$

In a solvent of low dielectric constant dissociation occurs according to equation (1), whilst in a solvent of high dielectric constant dissociation takes place mainly according to equation (2). Since, of the elementary halogens other than fluorine, chlorine represents the strongest halogenating agent, iodine monochlorine acts in a solvent of low dielectric constant (and in the vapour phase also) as a chlorinating agent. The iodizing action of iodine monochloride will, however, prevail under conditions when dissociation follows equation (2).

Considering that water possesses a high dielectric constant[18] ($E = 81{\cdot}7$) and that in a haloid-containing aqueous solution iodine monochloride is present as a complex[19] the dissociation of which yields I^+ and Cl^- ions, it is quite obvious that iodine monochloride is exclusively an iodinating agent in a solution containing hydrochloric acid. On the basis of this rule, the hydrochloric acid solution of iodine monochloride has been applied as titrant by Gengrinovich, Fialkov and co-workers.[20] The aromatic compound to be determined was allowed to react with excess iodine monochloride, and, on allowing the mixture to stand for a period required for iodination, the unreacted amount of reagent was measured by iodimetry. It was found in these experiments that reaction products never contained chlorine. Many aromatic compounds have been determined by this method.[20–26]

IODINE MONOBROMIDE AS A HALOGENATING AGENT

It is more difficult to apply the Bennett and Sharpe theory[11] when interpreting the halogenating action of iodine monobromide, for iodine monobromide proved to be a brominating agent both in carbon tetrachloride and in acetic acid or nitrobenzene solution[27] (although the nitrobenzene solution of iodine monobromide is a conductor of the second order)

The anomalous behaviour of iodine monobromide has been interpreted by Bennett and Sharpe[11,28] as follows: since bromine possesses an electron affinity below that of chlorine, more energy is required for the formation of the haloid ion. Therefore, homolytic dissociation takes place to an appreciable extent in the dissociation of iodine monobromide even in solvents of high dielectric constant; *e.g.* in a nitrobenzene solution of phenol and iodine monobromide, there is competition between elementary bromine and I^+ ions for the phenol molecule. As the reaction between phenol and bromine is an extremely rapid one, whilst iodination by I^+ ions is a "time" reaction,[22] halogenation results in a bromine derivative and elementary iodine.

Pearson and Ross[29] are of the opinion that the solution of iodine monobromide possesses primarily an iodinating action. The iodine derivative formed primarily reacts then with hydrogen bromide present in the solution. In the course of the reaction, a bromine derivative and elementary iodine are formed.

In the present experiments, an examination was made to determine which type of haloid derivatives form in aqueous solution in a substitution reaction, during halogenation by iodine monobromide, and which derivatives predominate. For this purpose, an aqueous solution of the reagent was first prepared.

Preparation of a solution of iodine monobromide

The solution of iodine monobromide was prepared by the following reaction

$$KIO_3 + 2\,KI + 6\,HBr \rightarrow 3\,IBr + 3\,KBr + 3\,H_2O \qquad (3)$$

Potassium hydrogen iodate (3.2495 g) analytical grade, and potassium iodide (5.534 g) analytical grade, were quantitatively transferred into a 1,000-ml measuring flask, acidified by about 400 ml of a 10% solution of hydrogen bromide of analytical grade and diluted to 1 l. The $0.1N$ iodine monobromide solution prepared in this way was about $0.5N$ referred to hydrogen bromide. This solution contained iodine monobromide in the form of a bromide complex, the physico-chemical properties of which will be discussed elsewhere in detail.

It was proved by analytical investigations that the reaction in question proceeds quantitatively according to equation (3). No iodate could be detected in the reaction mixture after its preparation. The method evolved for the determination of bromate in a solution of bromine monochloride was applied for the detection of iodate in the solution of iodine monobromide. When excess iodate was used in the preparation of the reagent, the solution obtained was contaminated by elementary bromine, whereas contamination by elementary iodine appeared only when excess iodide was used.

Reaction with antipyrine

On treating 10 ml of a nearly $0.1N$ solution of antipyrine with 20 ml of $0.1N$ solution of iodine monobromide, part of the latter was reduced to elementary iodine. The excess of iodine monobromide and the iodine developed during the reaction were back titrated by sodium thiosulphate in a sodium acetate medium. The solution with precipitate was shaken three times with 20-ml portions of chloroform, the major part of the chloroform was removed by distillation and the residual solution was evaporated to dryness on the water-bath. The residue was recrystallised from hot water, and proved to be a mixture of iodo-antipyrine and bromo-antipyrine.

Reaction with phenol

The reaction between phenol and iodine monobromide proceeds at an extremely slow rate (in contrast to the reactions of phenol and bromine monochloride, and of phenol and iodine monochloride). Investigations were carried out in the way previously described, except that, before reducing the excess of iodine monobromide, the solution was allowed to stand for 24 hr.

It was found that during the reaction phenol was partly iodinated and partly brominated, in the same way as antipyrine. In this case the ratio of iodine to bromine taken up was *ca.* 2:3. Therefore the action of iodine monobromide is partly iodinating and partly brominating, even in an aqueous solution containing excess bromide ions (*i.e.* in a solvent of high dielectric constant).

BROMINE MONOCHLORIDE AS A HALOGENATING AGENT

No data were found on the use of a solution of bromine monochloride as a halogenation agent for aromatic compounds.

The chemical behaviour and analytical application of interhaloids and cyanogen halides have been described elsewhere.[30–37] It was found,[36] on studying some reactions of interhaloids in aqueous solutions, that in reactions of interhaloids leading to the formation of halide ions, the more electronegative halogen is invariably converted to halide ion. Considering the high dielectric constant of water, this statement is in complete accordance with the theory of Bennett and Sharpe, and suggested the following reactions.

$$ICl + H_2O \rightarrow IO^- + Cl^- + 2\,H^+ : \; ICl + CN^- \rightarrow ICN + Cl^- \qquad (4)$$

$$BrCl + H_2O \rightarrow BrO^- + Cl^- + 2\,H^+ : \; BrCl + CN^- \rightarrow BrCN^- + Cl^- \qquad (5)$$

Knowledge of the above reactions made it possible to resolve a number of analytical problems.

We decided to examine the behaviour in an aqueous solution with aromatic compounds of bromide monochloride.

Preparation of a solution of bromine monochloride

An aqueous solution of bromine monochloride was prepared as described elsewhere [34] In addition, a hydrochloric acid solution of bromine monochloride was prepared from potassium bromate and potassium bromide in a hydrochloric acid medium, according to the reaction:

$$KBrO_3 + 2\,KBr + 6\,HCl \rightarrow 3\,BrCl + 3\,KCl + 3\,H_2O \qquad (6)$$

The preparation, examination and physico-chemical properties of the solution will be discussed elsewhere

Reaction with antipyrine

On adding a quantity of antipyrine equivalent to bromine monochloride, the reaction mixture became colourless Subsequently, the solution was made alkaline with some drops of ammonia, using litmus paper as indicator, and shaken in a separating funnel with 3 × 20-ml portions of chloroform The combined chloroform extracts were shaken with 20 ml of water made alkaline by some drops of ammonia Then the major part of the chloroform was removed by distillation, and the residue was evaporated to dryness on the water bath The dry residue was dissolved in a large volume of boiling water On cooling, 4-bromo-antipyrine crystallised in form of white needles, which, on filtering and drying, were readily identified (m p 117°)

The aqueous phase obtained in the chloroform extraction was also analysed but no bromide ions could be detected by the cyanogen bromide method [32]

Reaction with phenol

This reaction was examined by the same method, except that the residue obtained on removal of the chloroform by distillation was recrystallised from ethanol.

The reaction of phenol with bromine monochloride in nearly equivalent amount afforded tribromophenol (m p 96°), whereas with excess of the reagent tribromophenol–bromide (m p 120°) was obtained In the latter case, the reaction product was filtered off and the excess of bromine monochloride was removed by washing

The analysis of the aqueous phase obtained after the chloroform extraction showed no trace of bromide ions

The reactions of phenol and of *p*-nitrophenol with excess of a hydrochloric acid solution of bromine chlorine, have also been examined On allowing the reaction mixture to stand for a minute (phenol) and for $\frac{1}{2}$ min (*p*-nitrophenol), the excess reagent was measured by iodometry It was found that phenol was completely converted into tribromophenol (m p 96°), and *p*-nitrophenol, in turn, to dibromo-*p*-nitrophenol (m p 142°) Actually the products of bromination are tribromophenol-bromide (with phenol) or the appropriate labile bromo-compound (with *p*-nitrophenol) These are converted to tribromophenol and dibromo-*p*-nitrophenol, respectively, when the excess of bromine monochloride is back titrated

Reaction with fluorescein

An ethanolic solution of 5–10 mg of fluorescein was diluted with water until no precipitate appeared, and an equivalent quantity of bromine monochloride was then added The red precipitate thus obtained was filtered and recrystallised from ethanol. Since eosin, has no well defined melting point, the reaction product was identified by the absorption spectrum of its aqueous solution (Fig. 1)

The investigation of the reactions of antipyrine, phenol, *p*-nitrophenol and fluorescein with bromine monochloride proved that in an aqueous solution it acts as a brominating agent. The results of our investigations, whilst confirming our earlier statements on the chemical behaviour of interhaloids, are also in full accordance with the theory of Bennett and Sharpe

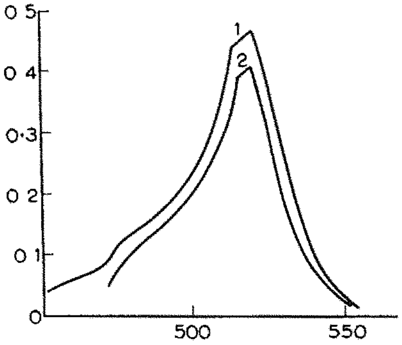

FIG. 1. Absorption spectra of eosin Curve 1. Absorption spectrum of product obtained with bromine monochloride Curve 2 Absorption spectrum of product obtained by direct bromination.

CONCLUSIONS

A solution of bromide monochloride, provided it possesses an appropriate stability, may serve for preparative purposes in organic chemistry or as a standard titrant in analytical chemistry.

For similar purposes, an aqueous solution of iodine monobromide proved to be unsuited since it acted in the same reaction both as an iodinating and as a brominating agent: thus the course of the reaction could not be defined.

Zusammenfassung—Es wird die Reaktionen von Jod-bromid und Brom-chlorid mit gewissen aromatischen Verbindungen in wasserigen Losungen untersucht

In halogen-substuierten Reaktionen wirkt Brom-chlorid exklusiv als bromierender Agent Bildung von Chlor-Derivaten oder Bromid-Ionen konnte nicht nachgewiesen werden

In Gegenteil wirkt Jod-bromid teils als iodierender Agent und teils als bromierender Agent sogar in wasseriger bromidhaltiger Losung

Résumé—On a examiné les réactions du bromure d'iode et du chlorure de brome sur certains composés benzéniques, opérant en solution aqueuse

On a trouvé que dans une solution aqueuse dans des réactions où l'on substitue les halogènes le chlorure de brome agit très nettement, étant exclusivement un agent de bromuration La formation d'ions, soit des dérivés chlorhydriques, soit du bromure, n'a pu être décelée

Le bromure d'iode, au contraire, s'est révélé en partie comme un agent iodurant, en partie comme un agent de bromuration, même dans une solution contenant du bromure.

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ULTRAVIOLET SPECTROPHOTOMETRIC PROPERTIES OF FERRIC COMPLEXES OF 2:2′-DIPYRIDINES IN GLACIAL ACETIC ACID

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(*Received* 14 *February* 1958)

Summary—2:2′-Dipyridine forms a stable, yellow-green complex with iron^{III} in glacial acetic acid with a ligand to iron mole ratio of 1.60 to 1 (3 to 2). The 4.4′-disubstituted derivatives also form a yellow-green complex. Solutions of these complexes are characterised by a strong absorption maximum in the 250–350 mμ region of the spectrum. The spectrophotometric constants of the iron^{III} complexes were evaluated at this maximum. The iron^{III} complex of the diphenyl derivative has the largest molar absorptivity of all the 2:2′-dipyridines studied.

INTRODUCTION

THE direct chelation of Fe^{III} with 1:10-phenanthroline and its derivatives in aqueous solution is in general not possible over a pH range of 1 to 12. An exception to this condition is that of Fe^{III} with 1:10-phenanthroline to form a complex with a ligand to metal mole-ratio of 3 to 2 as employed by Manning and Harvey[1] in the simultaneous spectrophotometric determination of ferrous and ferric iron. Brandt and Howsmon[2] studied the Fe^{III}-1:10-phenanthroline system in glacial acetic acid and found the complex to have a ligand to metal ratio of 1 to 1. They isolated an orange-yellow salt which was of the composition Fe(phen)Cl_3.

The study has been made[3] of 2:2′-dipyridine and eleven 4:4′-disubstituted dipyridines as their Fe^{II} complexes by Smith and Banick in aqueous solutions at pH 1 to 12 and in glacial acetic acid by the authors[4] of the present study. The reaction of Fe^{III} in direct chelation with a group of the same ligands in glacial acetic acid is the subject of the present work. The ligands included are unsubstituted 2:2′-dipyridine and the 4:4′-substituted dipyridines of the following types: ethyl, bromo, chloro, ethoxy, phenoxy, dicarbethoxy and phenyl groups.

PREPARATION OF REAGENT SOLUTIONS

Solutions of 2:2′-*dipyridine and derivatives.* 0.010F solution in glacial acetic acid. The 4:4′-dicarboxy and -dicarboxamide-2,2′-dipyridines are quite insoluble in glacial acetic acid and were not investigated as in the previously cited[3,4] studies. The procedures involved in this study required 0.0020F and 0.0010F solutions of the various ligands in glacial acetic acid.

Ferric chloride solutions. A weighed amount of reagent grade ferric chloride hexahydrate was dissolved in glacial acetic acid to give 0.0020F solutions.

IDENTIFICATION OF THE IRON^{III}-2:2′-DIPYRIDINE COMPLEX

Since 2:2′-dipyridine and its 4:4′-disubstituted derivatives all reacted with iron^{III} to give the same yellow-green coloured complex in glacial acetic acid, stable over a period of at least 48 hours, it was reasonable to assume that the nature of the complex in each case was the same. Hence, identification of the 2:2′-dipyridine complex would serve to identify the nature of the iron^{III} complex with its derivatives.

The first step in the identification of the iron^{III} complex of 2:2′-dipyridine in glacial acetic acid was to obtain a spectrum of a solution of the complex, a solution of 2:2′-dipyridine, and a solution of ferric chloride in order to select a suitable wavelength for spectrophotometric examination of the complex.

The 2:2′-dipyridine solution was prepared by diluting 0.50 ml of the 0.00200*F* 2:2′-dipyridine solution to 25 ml in a glass-stoppered volumetric flask with glacial acetic acid. The ferric chloride solution was prepared in the same manner using 0.50 ml of the 0.00200*F* ferric chloride solution. The solution of the complex was prepared by diluting 0.50 ml of the 0.00200*F* 2:2′-dipyridine solution and 0.50 ml of the 0.00200*F* ferric chloride solution to 25 ml with glacial acetic acid in a glass-stoppered volumetric flask. All solution transfers were made with measuring pipettes.

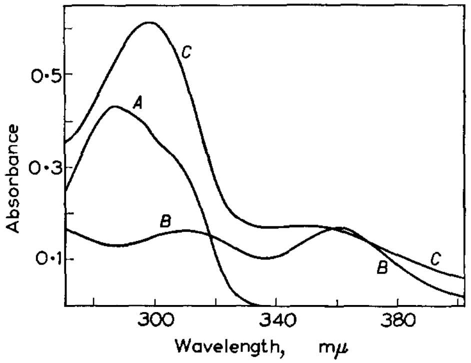

FIG. 1. A—0.50 ml of 0.00200*F* 2:2′-dipyridine (*a*) diluted to 25 ml, B—0.50 ml of 0.00200*F* ferric chloride (*b*) diluted to 25 ml, C—0.50 ml of (*a*) and 0.50 ml of (*b*) diluted to 25 ml.

These solutions were then examined spectrophotometrically on the Cary Recording Spectrophotometer, Model 14 M, using 1-cm silica cells. The 270–400 mμ region of the spectrum was scanned employing glacial acetic acid in the reference cell. The spectrum of each of these solutions is shown in Fig. 1.

The wavelength of 340 mμ was selected as the most suitable for use in the spectrophotometric identification of the mole ratio of ligand to iron in solutions of the complex.

Two more solutions of the complex in glacial acetic acid were prepared using the procedure described above. The amount of 2:2′-dipyridine solution used, however, was 2.00 ml for one of the solutions and 3.00 ml for the other. The absorbance of each of these solutions of the complex at 340 mμ was exactly the same and of such magnitude as to discount a ligand to iron mole ratio of 3 to 1 for the complex in solution.

The mole ratio method described by Yoe and Jones[5] was used for the quantitative identification of the iron^{III} complex of 2:2′-dipyridine in glacial acetic acid. The procedure used in this mole ratio study was as follows: to each of a series of 25-ml glass-stoppered volumetric flasks containing 2.00 ml of the standard ferric chloride solution was added a known volume of the 0.00200*F* 2:2′-dipyridine solution. Dilution to volume was then made with glacial acetic acid. The volume of the 2:2′-dipyridine solution added to each flask was varied so that the mole ratio of 2:2′-dipyridine to iron ranged from 5.0 to 0.75. All volume measurements were made with measuring pipettes.

The solutions of the complex thus prepared were examined spectrophotometrically on the Cary Recording Spectrophotometer, Model 14 M, using 1-cm silica cells.

For those solutions in which the mole ratio of ligand to iron was 2 to 1 or greater, glacial acetic acid was used in the reference cell. For solutions in which the ratio was less than 2 to 1, the reference cell contained solutions of ferric chloride in order to compensate for absorbance due to uncomplexed iron. Calculations of the amount of uncomplexed iron were made assuming a complex which had a ligand to iron mole ratio of 2 to 1.

The absorbance values of these solutions at 340 mμ were plotted against the ligand to iron mole ratio. An excellent mole ratio plot was obtained which indicated, however, a ligand to iron mole ratio of 1.75 to 1.

These same solutions were re-examined using different ferric chloride blank solutions (where necessary). The amounts of ferric chloride used in preparing the different blank solutions were calculated assuming a ligand to iron mole ratio of 3 to 2 (1.67 to 1).

The spectrophotometric data obtained from these measurements are given in Table I These data were used to construct the mole ratio plot shown in Fig 2. The mole ratio plot gives a value of 1.60 for the ligand to iron mole ratio, indicating a ligand to iron mole ratio of 3 to 2 for the complex in solution

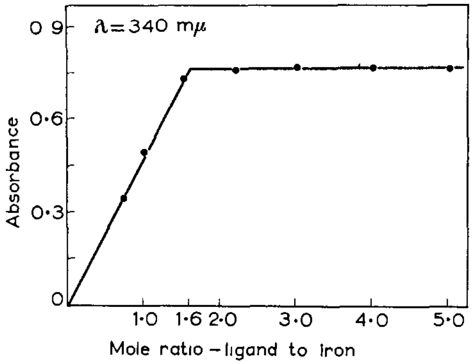

Fig 2. Mole ratio plot

An orange-yellow crystalline salt was isolated from a solution containing 2.2′-dipyridine and ferric chloride using the following procedure a stoichiometric amount of ferric chloride was added to 25 ml of hot glacial acetic acid containing 0 630 g of dissolved 2:2′-dipyridine The resultant orange-coloured solution was cooled and the orange-yellow salt which precipitated was collected by filtration and washed with glacial acetic acid The salt was then dried at 85° for four hours

This salt was soluble in water and in 95 % ethanol, yielding brown-coloured solutions Aqueous solutions of the salt gave a white precipitate with silver nitrate. A quantitative determination of iron in this salt was carried out spectrophotometrically using 2.2′-dipyridine. Duplicate analyses gave 17.7 % and 17 8 % iron These results suggested the formula of the salt to be Fe(dipy)Cl$_3$ or possibly Fe$_2$(dipy)$_2$Cl$_6$—in which compounds the iron content is 17 5 %

Table I Mole-ratio study of the iron^{III} complex of 2·2′-dipyridine in glacial acetic acid

ml of 2:2′-dipyridine solution	Mole-ratio, ligand to iron	Absorbance at 340 mμ
10 0	5 00	0 769
8 0	4 00	0 770
6 0	3 00	0 772
4 0	2 00	0 764
3 0	1 50	0 738
2 0	1 00	0.497
1 5	0 75	0 346

DETERMINATION OF SPECTROPHOTOMETRIC DATA

Solutions of the iron^{III} complex of 2:2′-dipyridine and its 4 4′-disubstituted derivatives were prepared for spectrophotometric examination using the following procedure: 0 50 ml of the standard ferric chloride solution and 1.67 ml of the 0 00100*F* dipyridine solution were transferred to a 50-ml glass-stoppered volumetric flask using measuring pipettes The contents of the flask were diluted to volume with glacial acetic acid and examined spectrophotometrically. The 250–350 mμ region of the spectrum was scanned using glacial acetic acid in the reference cell.

The absorption spectra of glacial acetic acid solutions of the 2·2′-dipyridines were also obtained in the same region of the spectrum The solutions of the 2·2′-dipyridines were prepared by diluting 1 00 ml of the 0 00100*F* solutions of the dipyridines to 25 ml in a glass-stoppered volumetric flask. Spectrophotometric examination of these solutions was carried out using the same instrument and procedure as described above

The ultraviolet absorption spectra of the 2 2′-dipyridines and their iron^{III} complexes are shown in Figs 3 to 10 The spectrophotometric constants of the ligands and complexes are summarised in Table II All calculations of the molar absorptivities of the complexes were based on the amount of iron added

TABLE II SPECTROPHOTOMETRIC DATA FOR THE 2 2′-DIPYRIDINES AND THEIR IRON^{III} COMPLEXES IN GLACIAL ACETIC ACID

Substitution derivative of 2:2′-dipyridine	Substitution derivative		Iron^{III} complex	
	λ_{max}	Molar absorptivity	λ_{max}	Molar absorptivity
1 unsubstituted	288 mμ	11,100	297 mμ	25,200
2 4,4′-diethyl-	295 mμ	13,100	295 mμ	26,800
3. 4,4′-dibromo-	283 mμ	12,700	294 mμ	24,500
4 4,4′-dichloro-	282 mμ	12,800	292 mμ	23,000
5. 4,4′-diethoxy-	283 mμ	12,400	285 mμ	24,800
6. 4,4′-diphenoxy-	280 mμ	12,500	286 mμ	26,300
7 4,4′-dicarbethoxy-	301 mμ	11,600	308 mμ	20,900
8 4,4′-diphenyl-	295 mμ	19,800	305 mμ	38,400

DISCUSSION

The iron^{III} complexes of the 4:4′-disubstituted 2:2′-dipyridines like the iron^{III} complex of 2:2′-dipyridine have one strong absorption maximum in the 250–350 mμ region of the spectrum. In this respect the spectra of the complexes resemble the spectra of the free ligands

The spectra of 2:2′-dipyridine and the 4:4′-diethyl, -diphenoxy, and -diphenyl derivatives in glacial acetic acid are quite similar to the spectra of their iron^{III} complexes in this same solvent over the spectral range of 250–350 mμ. On the other hand, the absorption spectra for glacial acetic acid solutions of the dibromo, dichloro, diethoxy, and dicarbethoxy derivatives are somewhat different from the spectra of their iron^{III} complexes in this same solvent over the spectral range of 250–350 mμ. For all the dipyridines studied, however, the iron^{III} complex has a longer wavelength of maximum absorption than the corresponding ligand

Only three of the derivatives studied yielded an iron^{III} complex which had a molar absorptivity greater than the molar absorptivity of the 2·2′-dipyridine-iron^{III} complex This might be considered unusual in view of the fact that the molar absorptivities of all the derivatives were greater than the molar absorptivity of the unsubstituted ligand. As expected the iron^{III} complex of the diphenyl derivative has the largest molar absorptivity.

The ligand to metal mole-ratio of 1 60 to 1 (3 to 2) for the iron^{III} complex of 2:2′-dipyridine in glacial acetic acid differentiates it from the iron^{III} complex of 1:10-phenanthroline, which has a ligand to metal mole ratio of 1 to 1 in glacial acetic acid.[3] It is perhaps of interest that the mole ratio value of 1.60 obtained here for the

ABSORPTION SPECTRA OF THE DIPYRIDINES AND THEIR FERRIC COMPLEXES IN GLACIAL ACETIC ACID

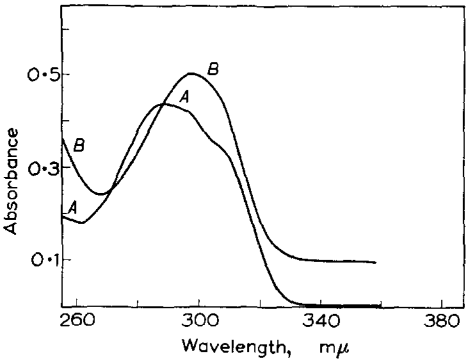

FIG 3 A—2 2′-dipyridine, B—2.2′dipyridine-iron$^{\text{III}}$ complex.

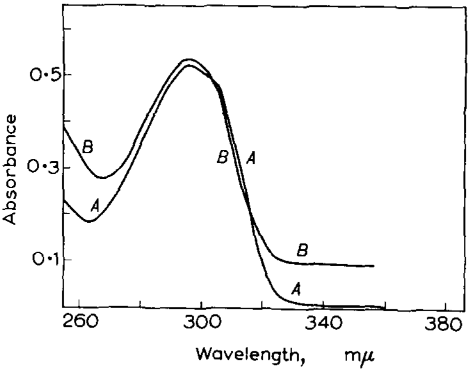

FIG. 4 A—4 4′-diethyl-2 2′-dipyridine, B—4 4′-diethyl-2 2′-dipyridine-iron$^{\text{III}}$ complex

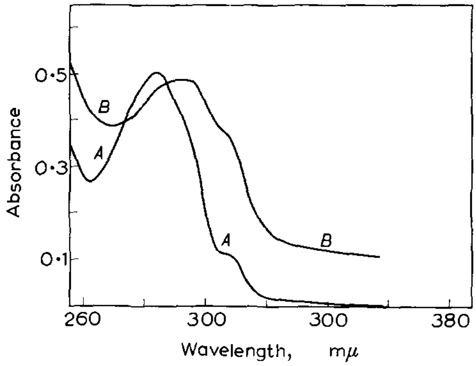

FIG 5 A—4 4′-dibromo 2 2′ dipyridine, B—4 4′-dibromo-2 2′-dipyridine-iron$^{\text{III}}$ complex

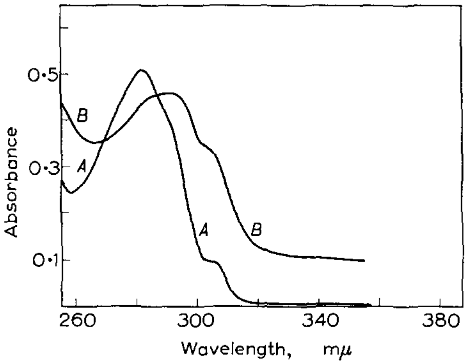

FIG 6. A—4 4′-dichloro-2 2′-dipyridine, B—4 4′-dichloro-2 2′-dipyridine-iron$^{\text{III}}$ complex

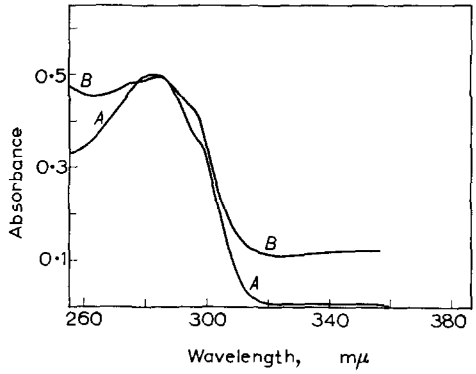

FIG 7 A—4 4′-diethoxy-2 2′-dipyridine, B—4 4′-diethoxy-2 2′-dipyridine-iron$^{\text{III}}$ complex

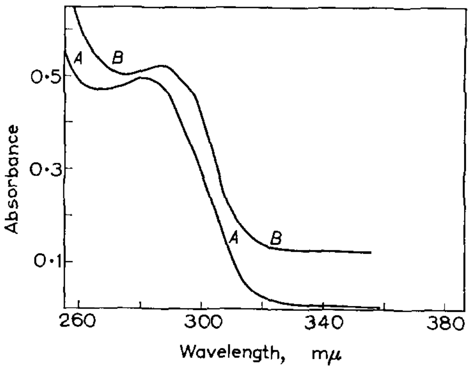

FIG. 8 A—4 4′-diphenoxy-2 2′-dipyridine; B—4 4′-diphenoxy-2 2′-dipyridine-iron$^{\text{III}}$ complex

iron^{III} complex of 2:2′-dipyridine in glacial acetic acid is almost identical to the mole ratio value of 1.63 reported by Manning and Harvey for the iron^{III} complex of 1:10-phenanthroline in aqueous solution.

The almost instantaneous fading of the yellow-green complex of the diamino derivative could possibly be a result of the reduction of the iron^{III} by the chelation reagent.

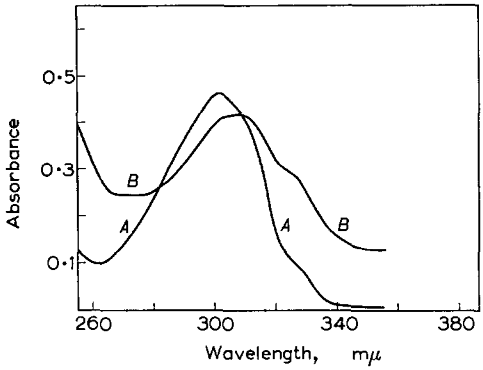

FIG 9. A—4 4′-dicarbethoxy-2 2′-dipyridine, B—4 4′-dicarbethoxy-2 2′-dipyridine-iron^{III} complex.

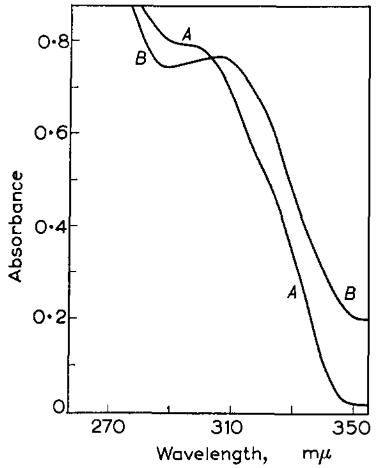

FIG 10. A—4.4′-diphenyl-2 2′-dipyridine B—4,4′diphenyl-2,2′-dipyridine-iron^{III} complex.

Zusammenfassung—2 2′-Dipyridin bildet mit Eisen-III in Eisessig einen stabilen gelb-grunen Komplex worin es ein Ligand-zu-Eisen mol-Verhaltnis von 1,60 : 1 (3 :2) gibt Die 4 4′-disubstituierten Derivate bilden auch einen gelb-grunen Komplex Losungen dieser Komplexe werden durch ein starkes Absorptionsmaximum im 250–350 mμ Spektrumsgebiet charakterisiert Die spektrofotometrischen Konstanten der Eisen-III Komplexe werden an diesem Maximum ausgearbeitet Der Eisen-III-Komplex des Diphenyl-Derivats hat die grosste Molabsorptivitat von allen studierten 2·2′-Dipyridinen

Résumé—La 2 2′-dipyridine donne avec le fer-III en milieu acide acétique glacial un complexe jaune-vert stable dont le rapport moléculaire du ligand à fer est 1,60 : 1 (3 2) Les dérivés 4·4′-disubstitués forment également un complexe jaune-vert. Les solutions de ces complexes sont caractérisées par un maximum d'absorption prononcé dans la région du spectre 250 à 350 mμ. On a évalué, à ce maximum, les constantes spectrophotométriques des complexes du fer-III De toutes les 2:2′-dipyridines qu'on a étudiées c'est le complexe fer-III du dérivé du diphényle qui a la plus grande absorptivité molaire

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STUDIEN ÜBER DIE POTENTIOMETRISCHE GOLDBESTIMMUNG DURCH ASCORBINSÄURE

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(*Received* 13 *February* 1958)

Zusammenfassung—Es wurde die ascorbinometrische Gold-III-Bestimmung mit potentiometrischer Endpunktsindication ausgearbeitet und die Versuchsumstände ausführlich untersucht. Ascorbinsäure reduziert Gold-III zu metallischem Gold. Die Bestimmung führt man zwischen den pH-Werten 1,6–3 bei nicht höherer als 0,1*N* Chloridkonzentration bei 50° aus. Den Endpunkt gibt ein deutlicher Potentialsprung bekannt. Die Genauigkeit beträgt in 0,01*N* Mass ±1%. Die Anwesenheit von Hg-II, Cu-II, Fe-III stört nicht. Pt-IV verursacht einen Masslösungsüberverbrauch. Der Einfluss der Temperatur, der Wasserstoff-, Chlorid- und Salzsäurekonzentration wurde ebenfalls untersucht und aus den Versuchsergebnissen theoretische Folgerungen bezugs des Reaktionsverlaufs gezogen.

Die ersten massanalytischen Goldbestimmungsverfahren waren auf Rücktitration gegründet. Man benützte hierzu Eisen-II-lösungen, deren Überschuss man permanganometrisch,[16,14] Wasserstoffperoxyd- und Hydroxylaminlösungen[29] die man jodometrisch rücktitriert. Zur Reduktion des Gold-III-s wurde auch Kaliumjodid benützt, das freigesetzte Jod titrierte man mit Thiosulfat.[26] Diese Verfahren, besonders die jodometrischen liessen jedoch viel zu wünschen übrig, besonders deshalb, weil das entstehende Gold-I-jodid eine Disproportionierung erleidet, demzufolge man höhere Werte erhielt als man sollte.[29] Die Titration des Jods durch arsenige Säure[15] bzw. durch schwefelige Säure[17] soll zu besseren Ergebnissen führen. Die Reduktion des Goldes durch arsenige Säure mit jodometrischer Rücktitration lieferte ziemlich genaue Resultate.[29]

Spätere Verfasser bearbeiteten direkte Methoden durch reduzierende Masslösungen. Man benützte dazu in saurer Lösung Titan-III-chlorid,[19,21,36] Eisen-II-sulfat,[23] Chrom-II-chlorid,[35] Zinn-II-chlorid,[20] Kupfer-I-chlorid[22] und Hydrochinon,[28,30] in alkalischer Lösung Vanadinsulfat,[13] alle mit potentiometrischer Endpunktsindication. In diese Reihe gehört auch die Kaliumjodidmasslösung.[31] Bei ihrer Anwendung wird im Laufe der Titration neben gleichzeitiger Gold-I-jodidausscheidung Jod freigesetzt. Im Äquivalenzpunkt tritt ein deutlicher Potentialsprung ein. Da jedoch Chlorid stört, sind die Anwendungsmöglichkeiten des Verfahrens sehr beschränkt. Aus der Reihe der erwähnten Masslösungen eignet sich zur Bestimmung die Eisen-II-sulfatlösung am besten. Titan-III-chlorid und Chrom-II-chlorid erleiden infolge des Ausscheidens von kolloidalem Gold eine katalytische Zersetzung, wodurch ein Masslösungsüberverbrauch eintritt. Ein Nachteil der meisten dieser Masslösungen besteht darin, dass die Titrationen mit denselben eine inerte Gasatmosphäre erfordern. Man entwarf auch Verfahren mit visualer Endpunktsindikation. So kann man z.B. in Anwesenheit von Katalysatoren das Gold-III-mit arseniger Säure bis zu metallischem Gold reduzieren. Der Lösung setzt man Kaliumjodid zu, das freigesetzte Jod verschwindet im Endpunkte.[27] Ein anderes Verfahren titriert die gelbe Gold-III-lösung neben Magnesium- oder Natriumchlorid mit schwefeliger Säure bis Farblosigkeit.[17] Ähnlich verfährt ein Mikroverfahren, jedoch in Anwesenheit von Bromiden und bei 95°.[33] Die Anwendung von *o*-Dianisidin empfahl man zur Titration mit Hydrochinon als Redoxindikator,[18] der Endpunkt is jedoch wegen der Abscheidung des Goldkolloids schlecht wahrnehmbar. Alle diese Verfahren haben den Nachteil, dass sie entweder verwickelt sind oder von vielen Metallen gestört werden und meistens eine potentiometrische Endpunktsindikation erfordern.

Wir versuchten deshalb die Ascorbinsäure,[7,6] die zu vielen Metallbestimmungen als Masslösung erfolgvoll benützt wurde auch zur Goldbestimmung heranzuziehen. Die reduzierende Wirkung der Ascorbinsäure wurde schon von Brintzinger[2] zur Herstellung von Goldkolloiden ausgenützt Stathis[32] entwarf ein Verfahren, bei welchem das durch Ascorbinsäure reduzierte Goldmetall gravimetrisch oder der Ascorbinsäure überschuss jodometrisch bestimmt wird. Die Ascorbinsäure bewahrte sich schon bei Silber- und Quecksilberbestimmungen als gute, direkt anwendbare reduktometrische Masslösung[10,11] Die Silberbestimmung kann man mit ±0,01%iger Genauigkeit neben potentiometrischer Indication oder Variaminblau ausführen. Im letzteren Falle puffert man die Lösung mit Natriumacetat. Die Bestimmung kann noch in 0,001*N* Mass auch ausgeführt werden. Ähnlich dazu ist auch die Quecksilberbestimmung. In chloridfreier Lösung reduziert Ascorbinsäure Quecksilber-II zu metallischem Quecksilber. Die Bestimmung kann bis 0,01*N* Mass erfolgen.

Bei Abschluss unserer Versuche enthielten wir aus Dokumentation[4] Nachricht darüber, dass Pchenitsyn und Mitarbeiter ebenfalls ein ascorbinometrisches Verfahren zur Gold-[24] und Iridium-bestimmung[25] veröffentlichten. Näheres darüber gelang uns jedoch nicht zu erfahren

Bereitung der Lösungen

Die 0,1*N* Gold-III-chloridstammlösung wurde durch Auflösen von Reingold in Königwasser und darauffolgende Eindampfung bereitet. Vor Verdunnung wurde soviel Salzsäure zugesetzt, dass die Wasserstoffionenkonzentration der Lösung zwischen 0,5*N* und 0,1*N* sich bewegte Die Faktorbestimmung erfolgte nach Reduktion durch Eisen-II-sulfat und durch Ascorbinsäure, gravimetrisch. 0,01 und 0,001*N* Lösungen wurden aus der Lösung durch Verdunnung hergestellt

Zur Bereitung einer 0,1*N* Ascorbinsäuremasslösung löste man 8,90 g Ascorbinsäure in Wasser, welches in Glaseinrichtung destilliert wurde Zur Stabilisation setzte man 100 mg ÄDTA zu und ergänzte auf 1 Liter[8] Die Titerbestimmung erfolgte auf Kaliumjodat-Kaliumjodid gegen Variaminblau als Indicator.[9] 0,01 und 0,002*N* Lösungen wurden durch Verdunnung bereitet Der Faktor der Lösungen wurde täglich zweimal, vor und nach den Versuchen bestimmt Wir fanden, dass eine täglich einmalige Titerbestimmung bei 0,01*N* Lösungen genügend war, falls diese in einer Flasche mit Glasstopfen lichtgeschützt aufbewahrt wurde. Tabelle I zeigt die Wirkungswertänderung einer 0,01*N* Ascorbinsäurelösung während 3 Wochen.

UNTERSUCHUNG DER BESTIMMUNGSUMSTÄNDE

Zwischen Ascorbinsäure und Gold-III-chlorid verläuft theoretisch folgende Reaktion:

$$2\,AuCl_3 + 3\,C_6H_8O_6 \rightleftharpoons 2\,Au + 3\,C_6H_6O_6 + 6\,HCl$$

Das Redoxnormalpotential des Au-III-Au Systems beträgt +1,39 Volt, das des Systems Ascorbinsäure-Dehydroascorbinsäure +0,165 Volt [pH = 4] Theoretisch ist also die Ascorbinsäure zur Reduktion von Gold-III geeignet.

TABELLE I. TITERÄNDERUNG EINER STABILISIERTEN 0,01N ASCORBINSÄURELÖSUNG

Tag	Tageszeit	Faktor	%
0	morgens	1,0252	
	nachmittags	1,0231	0,2
1	morgens	1,0204	0,27
	nachmittags	1,0176	0,28
2	morgens	1,0135	0,40
5	morgens	1,000	1,3
6	morgens	0,9940	0,6
7	morgens	0,9868	0,7
8	morgens	0,9804	0,65
9	morgens	0,9770	0,35
10	morgens	0,9738	0,32
11	morgens	0,9705	0,35
12	morgens	0,9674	0,32
13	morgens	0,9639	0,33
14	morgens	0,9609	0,30
15	morgens	0,9577	0,32
16	morgens	0,9543	0,34
17	morgens	0,9510	0,33
19	morgens	0,9446	0,65
20	morgens	0,9384	0,62
21	morgens	0,9326	0,60

Einfluss der Temperatur

Um zu klären, ob die Reduktion von Gold-III mit Ascorbinsäure stöchiometrisch verlauft, verdünnte man eine bekannte Menge der Gold-III-chloridlösung mit Wasser auf 100 ml [pH = 1,6 — 1,9] und titrierte sie zwischen einer gesättigten Kalomelbezugselektrode und einer Platinindikatorelektrode, die infolge des darauf im Laufe weniger Titrationen abgeschiedenen Goldes eigentlich als Goldelektrode betrachtet werden kann, mit Ascorbinsäuremasslösung bei Zimmertemperatur. Das Anfangspotential der Lösung betrug 760–780 mV, das im Laufe der Titration langsam über 900 mV wuchs, wobei die gelbe Lösung sich allmählich entfärbte. In diesem Gebiet änderten sich die Potentialwerte kaum Nach 3/4 Teil des theoretischen Masslösungsverbrauches, gleichzeitig mit der Erscheinung des kolloidalen Goldes, sank das Potential langsam und erreichte allmählich den ursprünglichen Wert In der Nähe des Äquivalenzpunktes erfolgte dann eine Potentialabnahme von 300–400 mV [Abb. 1. Kurve 1).

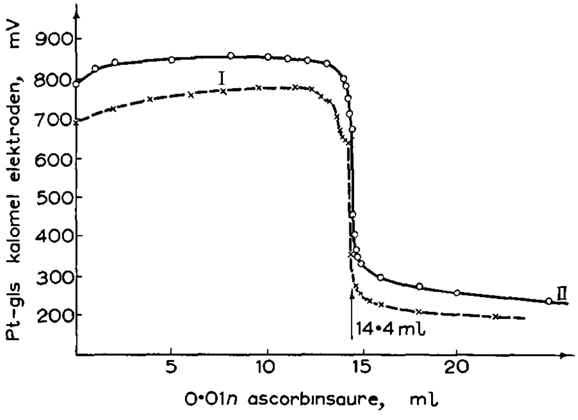

ABB. 1 14,14 ml 0,01N Au-III-lösung + 85 ml Wasser, titriert. I. bei 20°, II. bei 50°.

Bei Zimmertemperatur verlief die Reaktion langsam, man muss ziemlich viel warten, bis sich die Potentialwerte einstellten In warmer Losung ging die Reaktion viel schneller vor sich, bei 80° waren jedoch die Ergebnisse viel niedriger als die Sollwerte Der Gedanke lag nahe ob dieser Fehler eventuell nicht der reduzierenden Wirkung der gebildeten Dehydroascorbinsaure zu verschreiben sei Dies zu klaren unternahmen wir folgende Versuche: 15 ml 0,01*N* Gold-III-losung wurden mit Wasser auf 100 ml verdunnt, dazu 15 ml 0,01*N* Dehydroascorbinsaurelosung gesetzt und die Losung wahrend 30 Minuten bei 50, 60, 70 und 100° gehalten, und dann bei 50° mit 0,01*N* Ascorbinsaurelosung titriert. Die Ergebnisse zeigten, dass bei 50° keine Reduktionstattfand, [Abb 2, Kurve 1.] uber 70° jedoch die Dehydroascorbinsaure schon eine betrachtliche Menge der Gold-III-Ionen [ungefahr 50%] reduzierte [Kurve 2], bei 100° schon wahrend des Kochens das kolloidale Gold erschien. Die ascorbinometrische Goldtitration darf man folglich nicht uber 60° durchfuhren. Es empfiehlt sich die Titration bei 50–55° vorzunehmen und die im Laufe der Titration abgekuhlte Losung beim ersten Erscheinen des Kolloidgolds neuerlich zu erwarmen Die weiteren Versuche wurden stets derart unternommen.

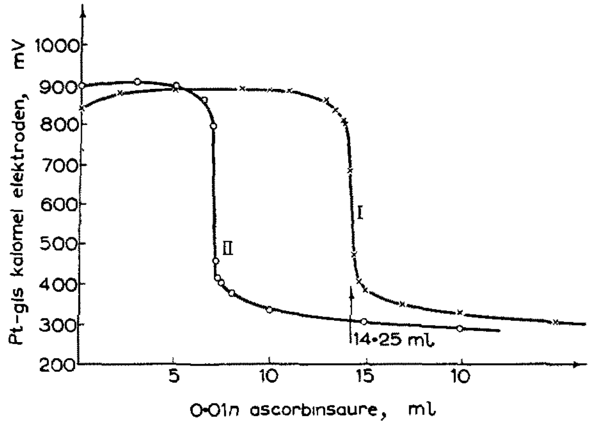

ABB 2 14,14 ml 0,01*N* Au-III-losung + 15 ml 0,01*N* Dehydroascorbinsäurelosung + 70 ml Wasser, titriert. I. vorangehend während 30 Minuten bei 50°, II. vorangehend während 30 Minuten bei 70° gehalten.

Einfluss des pH

Zu je 15 ml der 0,01*N* Gold-III-losung setzte man soviel 2*N* Salzsaure, dass 100 ml Anfangsvolumen der zu titrierenden Losung auf Saure 2*N*, 1*N*, 0,5*N*, 0,1*N* und 0,01*N* wurde, mit Kaliumdihydrogensphosphat und Dinatriumhydrogenphosphat Puffergemische stellte man das pH weiterer Losungen auf die Werte 3,4, 4,6 und 6 ein Die so bereiteten Losungen titrierte man dann mit 0,01*N* Ascorbinsaurelosung potentiometrisch Die in Abb 3 graphisch dargestellten Ergebnisse zeigen, dass in 2*N* und 1*N* salzsauren Losungen die Reaktionsgeschwindigkeit der Reduktion des Gold-III-s zu metallischem Gold vernachlassigt werden kann. [Kurve 1, 2] Die geringe Potentialzunahme und die Entfarbung der Losung deutet dahin, dass die Au^{3+}–Au^+ Reduktion schnell vor sich geht die Au^+–Au Reduktion dagegen nicht zustande kommt Dies bezeugt das Unterbleiben der Erscheinung des kolloidalen Goldes, weiterhin, dass auch noch bei 100%iger Übertitration keine nennenswerte Potentialanderung eintritt. In 0,5*N* saurer Losung tritt eine auswertbare Potentialanderung auch nur erst bei einer 20%igen Übertitration ein In 0,1*N* saurer Losung besteht noch immer ein 3–5% iger positiver Fehler. Im pH-Gebiet 1,5–3 stimmt das Ergebnis schon innerhalb 1% mit dem Sollwert. Über pH 3 gestaltet sich der Fehler schon negativ und uber pH 4,6 kann man die Titration praktisch nicht mehr ausfuhren.

Die Versuchsdaten zeigen, dass nicht nur im Ablauf der potentiometrischen Kurven sich eine betrachtliche Abweichung gestaltet, sondern auch schon bei den anfanglichen Potentialwerten. Diese erreichen im weiten nicht die theoretischen Potentialwerte des Systems Au^{3+}–Au. Diese Erscheinung ist aber verstandlich In der Losung ist Chlorid anwesend, folglich bestimmen hier die damit entstehenden Komplexionen das Potential Das Tetrachloroaureat-III-dissociiert in salzsaurer Losung folgendermassen.

$$AuCl_4^- \rightleftharpoons Au^{3+} + 4\,Cl^- \qquad p_K = 20$$

Infolge des niedrigen Wertes der Dissociationskonstante ist die wahrliche Gold-III-ionenkonzentration in chloridhaltiger Losung niedriger als es der Einwaage entsprache, demzufolge der Elektrodenpotentialwert der Losung der Nernstschen Gleichung gemass sich ebenfalls wesentlich niedriger gestaltet. Die Dissociation der Komplexsaure wird durch die Wasserstoffionenkonzentration der Losung, die des Komplexions durch die Chloridkonzentration beeinflusst.

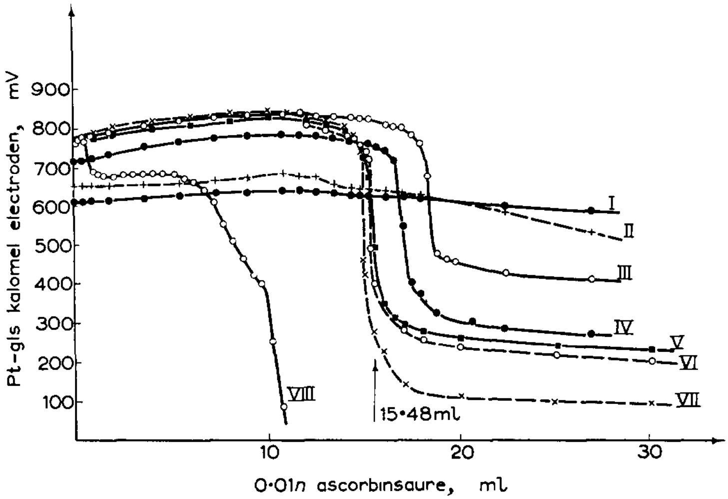

Abb. 3. 15,52 ml 0,01*N* Au-III-losung + verschiedene Mengen Säure- bzw. Pufferlosungen auf 100 ml ergänzt und bei 50° titriert in folgenden medien. I. 2*N* Salzsäure, II. 1*N* Salzsäure, III. 2*N* Schwefelsäure, IV 0,5*N* Salzsäure, V. 0,1*N* Salzsäure [pH = 1,4], VI 0,01*N* Salzsäure [pH = 2,3], VII. Essigsäure-Natrium-acetat Puffer [pH = 3,6], VIII. Phosphatpuffer [pH = 6]

Die Reduktion des Gold-III-s durch Ascorbinsaure verlauft folglich in Übereinstimmung mit unseren Erfahrungen gemass den verschiedenen Media veranderlich. Die Reduktion des Gold-III-s erfolgt also in zwei Stufen durch eine Gold-I-Verbindung zu metallischem Gold Im folgenden wurde also die auf den Elektrodenpotentialwert der Systeme Au^{3+}–Au bzw. Au^{+}–Au ausgeubte Einwirkung der Wasserstoffionen-, der Chloridionen- und der Salzsaurekonzentration abgesondert zahlenmassig untersucht.

15,52 ml 0,01*N* Gold-III-Losung wurden mit 85 ml Wasser versetzt und das Potential zwischen einer vergoldeten Platinelektrode und einer gesattigten Kalomelelektrode bestimmt, dann zu einer Versuchsserie 8*N* Schwefelsaure [Abb. 4, Kurve 1], zu einer anderen 6*N* Kaliumchloridlosung [Kurve 2] und zu einer dritten 6*N* Salzsaure [Kurve 3] in verschiedenen Mengen zugefugt Wie aus

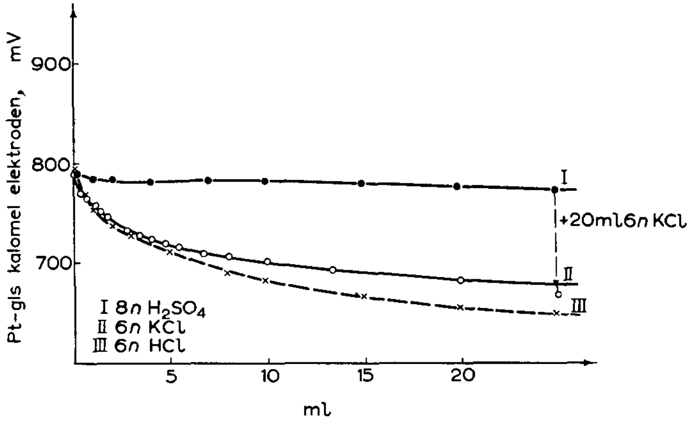

Abb. 4. 15,52 ml 0,01*N* Au-III-losung + 85 ml Wasser versetzt mit, I. 8*N* Schwefelsäure, II 6*N* Kaliumchloridlosung, III. 6*N* Salzsäure.

Abb. 4 ersichtlich beeinflusst die Zunahme der Wasserstoffionenkonzentration die Redoxpotentialwerte nicht, die Zunahme der Chlorid- und Salzsaurekonzentration erniedrigt sie dagegen betrachtlich. Die in salzsaurer Losung gefundenen Potentialwerte stimmen ubrigens gut mit den Literaturdaten[1,5] uberein. Die Versuche begrunden gut die Redoxpotentialwerte der in Abb. 3 dargestellten Titrationskurven und innerhalb dieser auch den Befund, dass in 2*N* Salzsaure der anfangliche Potentialwert 610 mV, in 2*N* Schwefelsaure jedoch 780 mV betrug

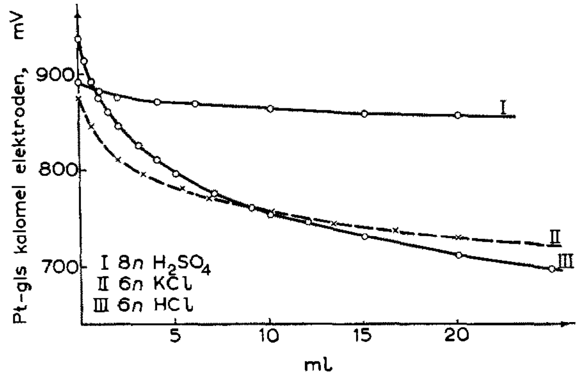

Abb. 5. 15,52 ml 0,01*N* Au-III-losung + 10,34 ml 0,01*N* Ascorbinsäurelosung + 75 ml Wasser versetzt mit I. 8*N* Schwefelsäure, II. 6*N* Kaliumchloridlosung, III. 6*N* Salzsaure.

In folgenden wurden zu 15,52 ml 0,01*N* Gold-III-losung 10,34 ml 0,01*N* Ascorbinsaurelosung gefugt, mit Wasser auf 100 ml erganzt und das Redoxpotential der so erzeugten Gold-I-losungen zwischen den gleichen Elektroden gemessen indem zu den Losungen in einer Probe 8*N* Schwefelsaure [Abb 5, Kurve 1.], in einer anderen Probe 6*N* Kaliumchloridlösung [Kurve 2.] und in einer dritten Losung 6*N* Salzsaure [Kurve 3.] gegeben wurde. Aus Abb 5 ist es ersichtlich, dass die Änderung der Wasserstoffionenkonzentration die Potentialwerte des Systems Au^+–Au in messbarem Masse beeintrachtigt, dass die Zunahme der Chloridkonzentration eine bedeutende Abnahme des Potentialwertes verursacht und dass ein Salzsaurezusatz die Werte wie erwartbar in noch betrachtlicherer Weise andert Die Messergebnisse bezeugen folglich, dass man auch in 2*N* Schwefelsaurelosung uber den Äquivalenzpunkt titrieren muss um eine ermittelbare Potentialanderung zu erhalten [Abb. 3, Kurve 3], da die Zunahme der Wasserstoffionenkonzentration die Au^+–Au Reduktion beeintrachtigt. Laut der gemessenen Redoxpotentialwerte musste jedoch theoretisch die ascorbinometrische Reduktion der Gold-III-ionen in stark saurer und sogar in chloridhaltiger Losung glatt ablaufen Der Grund, dass dies doch nicht in allen Fallen eintritt, ist wahrscheinlich in der Kinetik der Reduktion des Gold-I-chlorids zu suchen Laut Abb 3 verlief unter allen Umstanden die Reduktion des Gold-III-s zu Gold-I. Dies wird durch die Entfarbung der ursprunglich gelben Losung, weiterhin durch die Zunahme des Potentialwertes bezeugt. Die Reduktion des Gold-I-s verlauft dagegen nicht immer mit genugender Geschwindigkeit. Vergleicht man die Redoxnormalpotentialwerte der verschiedenen Goldchloridkomplexe,[3] so kommt man zur Folgerung, dass die entstehenden Gold-I-ionen eigentlich eine Disproportionierung gemass $3\,Au^+ \rightleftharpoons Au^{3+} + 2\,Au$ erleiden mussten

$$AuCl_4^- + 3\,e^- \rightleftharpoons Au + 4\,Cl^- \qquad E_0 = 0{,}99\ V$$

$$AuCl_4^- + 2\,e^- \rightleftharpoons AuCl_2^- + 2\,Cl^- \qquad E_0 = 0{,}95\ V$$

$$AuCl_2^- + e^- \rightleftharpoons Au + 2\,Cl^- \qquad E_0 = 1{,}13\ V$$

Gemass diesen Daten müsste man eigentlich am Anfang der Titration schon eine kolloidale Goldausscheidung beobachten. Da dies jedoch unterbleibt muss unter gegebenen Umstanden die Geschwindigkeit der Disproportionierung sehr gering sein. Sogar die ascorbinometrische Reduktion der im Laufe der Titration entstandenen Gold-I-ionen verlauft trotz des positiveren Normalpotentials langsamer als die der Gold-III-ionen Ein jeder weiterer Masslosungszusatz reduziert namlich immer Gold-III-ionen anstatt der gleichzeitig anwesenden Gold-I-ionen.

Die Zunahme der Chloridkonzentration und Abnahme des pH-wertes der Losung verlangsamt noch weiter die ursprunglich sowieso langame Reduktion der Gold-I-ionen zu Gold. Dies bezeugt, dass in 2N salzsaurem Medium die Losung sich entfarbt, jedoch auf Einwirkung einer weiteren Masslosungszugabe weder eine bedeutende Potentialanderung noch Ausscheidung von Goldkolloid zu beobachten ist. Wird aber letztere Losung fur 24 Stunden bei seitegestellt, so tritt Goldausscheidung ein Auch in 0,5N salzsauren Losungen kann man den Fehler ermindern, wenn man im theoretischen Aquivalenzpunkt die Losung fur 30–50 Minuten bei 55° halt All dies deutet auf einelang same Reaktionsgeschwindigkeit

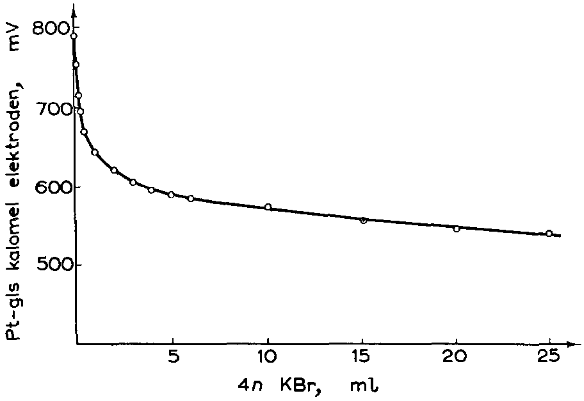

Abb. 6. 15,52 ml 0,01N Au-III-losung + 85 ml Wasser versetzt mit 4N Kaliumbromidlosung.

Ausser den bisher erwahnten Faktoren muss man noch in Betracht nehmen, dass der Redoxpotentialwert des Systems Ascorbinsaure-Dehydroascorbinsaure ebenfalls vom pH abhangig ist.[1] Zunehmende Saurekonzentration erniedrigt die Reduktionsfahigkeit. In stark saurer Losung nimmt also die Distanz der Redoxpotentialwerte der zwei Systeme betrachtlich ab, das ebenfalls den Ablauf der Reduktion beeinflusst

Als Ergebnis der vielen Versuche konnen wir feststellen, dass eine Gold-III-chloridlosung in 0,01 bzw. 0,001N Mass mit Ascorbinsauremasslosung neben potentiometrischer Endpunktsindication ausgezeichnet titriert werden kann, falls der pH-Wert der Losung sich zwischen 1,5–3 befindet und die Chloridkonzentration nicht das 1N Mass ubertrifft. Man soll bei 50–60° titrieren. Der Fehler betragt unter diesen Umstanden ungefahr 1 %

Einfluss verschiedener Anionen

Alle diejenigen Anionen storen, die geschilderte Goldbestimmung, die mit Gold-III-bzw. Gold-I-ionen den Chloriden ahnlich stabile oder noch stabilere Komplexverbindungen bilden So storen z B. Bromid, Cyanid und Rhodanid Aus der Reihe dieser Anionen bildet das Bromid die lockersten

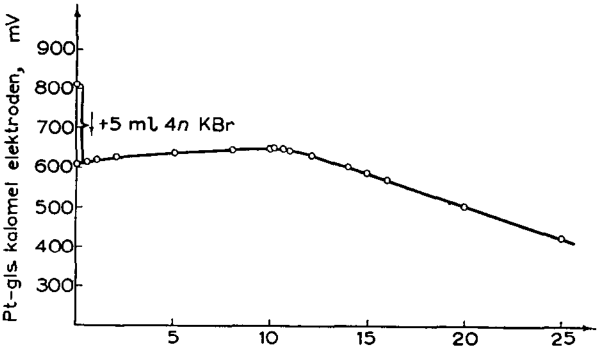

Abb. 7. 15,52 ml 0,01N Au-III-losung + 80 ml Wasser + 5 ml 4N Kaliumbromidlosung titriert mit 0,01N Ascorbinsäure bei 50°.

Komplexe, trotzdem sinkt der Redoxpotentialwert der Gold-III-lösung schon in Anwesenheit sehr geringer Mengen von Bromiden beträchtlich [Abb. 6.]. In Anwesenheit von Bromiden ändert sich das Redoxpotential der Lösung nicht in solchem Masse, dass man den Endpunkt der ascorbinometrischen Titration potentiometrisch wahrnehmen konnte [Abb 7.]. Aus der Entfärbung der Lösung und geringfügiger Zunahme der Potentialwerte kann man darauf folgern, dass die Tetrabromaureat-III-Ionen zu Bromaureat-I-Ionen reduziert werden, die weitere Reduktion, die infolge einer Disproportionierung verläuft, erfolgt jedoch nur sehr langsam Rhodanide und Cyanide stören ebenfalls im gleichen Sinne. Nitrate stören bis zu einer 150-fachen Menge nicht. In Anwesenheit von freien Halogenen kann man die Titration ausführen, zuerst reduziert in diesem Falle die Masslösung die Halogene. Den Endpunkt dieses Vorganges kündigt ein deutlicher Potentialsprung an Den dementsprechenden Masslösungsverbrauch muss man aus dem Gesamtverbrauch substrahieren

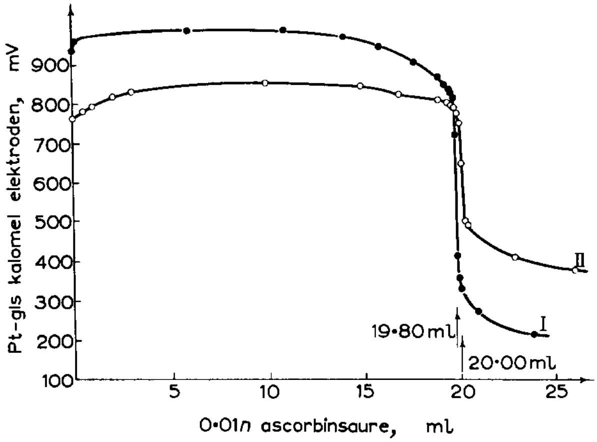

Abb. 8. I. 19,75 ml 0,01N Au-III-lösung + 80 ml Wasser II. 19,75 ml 0,01N Au-III-lösung + 80 ml Wasser + 1 g $HgCl_2$ titriert mit 0,01N Ascorbinsäure bei 50°.

Einfluss verschiedener Kationen

Alle diejenigen Kationen stören die ascorbinometrische Bestimmung des Goldes deren Redoxpotential in chloridhaltiger Lösung grösser oder gleich dem des Goldes ist. Die Anwesenheit von äquivalenten Mengen von Platin-IV-ionen verursacht einen 10%igen Masslösungüberverbrauch. Ohne Gold-III reagieren jedoch die Chloroplatinat-IV-ionen unter vorliegenden Umständen mit

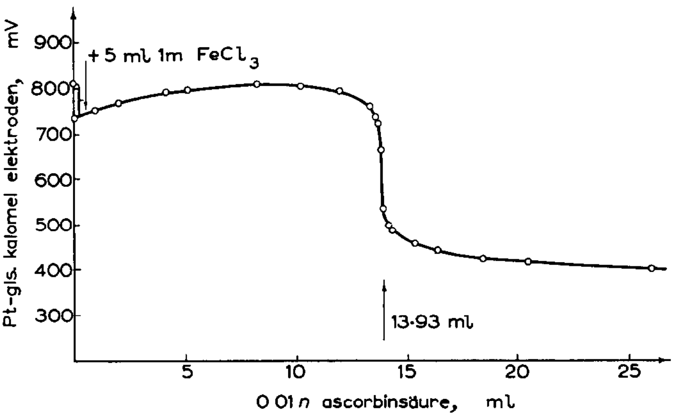

Abb. 9. 14,14 ml 0,01N Au-III-lösung + 5 ml 1M Fe-III-lösung + 1 ml konz. H_3PO_4 + 80 ml Wasser titriert mit 0,01N Ascorbinsäure bei 50°.

Ascorbinsaure nicht Quecksilber-II-ionen in 120-facher Menge [Abb. 8] und Kupfer-II-ionen in 50-facher Menge storen die Bestimmung nicht Bei einer 10-fachen Menge von Eisen-III kann man die Bestimmung in Anwesenheit von 1 ml Phosphorsaure [sp G 1,74] noch gut ausführen [Abb 9] Die Genauigkeit der Bestimmung betragt in Gegenwart dieser Ionen ±1–3%

Endpunktsindication ohne Salzbrucke

Zwecks Beseitigung der Kalomelelektrode fuhrten wir die Titrationen auch neben Platin- und Glaselektroden bzw Platin- und Silberchloridelektroden aus [Abb 10]. Bei der Anwendung eines Platin- Glaselektrodenpaars beeinflussten die im Laufe der Reaktion freiwerdenden Wasserstoffionen die Endpunktsindication nicht Auch das Platin-Silberchloridelektrodenpaar bewahrte sich zur Endpunktsbestimmung, es hat jedoch den Nachteil, dass nach 3–4 Titrationen eine neue Silberchloridelektrode zu bereiten ist

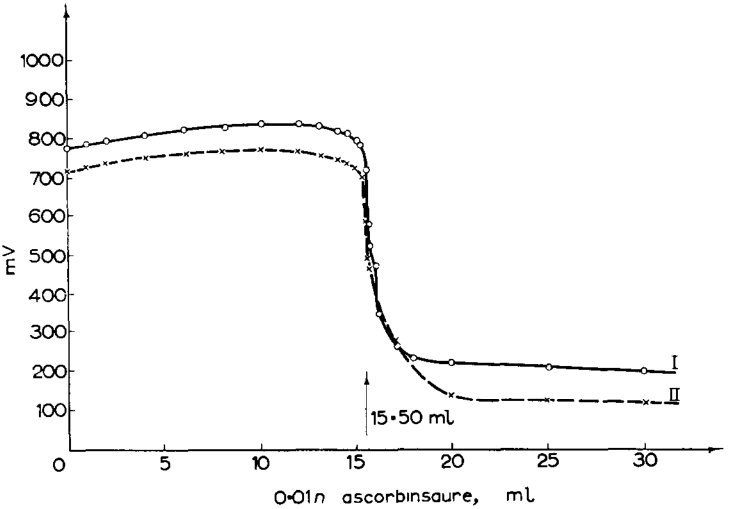

Abb. 10 15,52 ml 0,01N Au-III-losung + 80 ml Wasser titriert mit 0,01N Ascorbinsaure bei 50° I zwischen einem Platin- Glaselektrodenpaar, II. Platin–Ag–AgCl Elektrodenpaar

Über die ascorbinometrische Goldbestimmung mit Farbstoffindikatoren wird in einer folgenden Mitteilung berichtet.

Summary—A potentiometric method for the determination of gold^{III} using ascorbic acid is described Ascorbic acid reduces gold^{III} ions to metallic gold, and the titration is carried out at 50°, between pH 1 6–3, in a chloride medium with a maximum concentration of 0 1N. At the end-point a considerable potential jump occurs The accuracy of the method is about ±1% using 0 01N solutions. Mercuric, cupric or ferric ions do not interfere, but Pt^{IV} causes a positive error.

The influence of a number of factors such as temperature and pH on the accuracy are discussed.

Résumé—Les auteurs décrivent une méthode potentiométrique pour le dosage de l'or-III au moyen de l'acide ascorbique Les ions or-III sont réduits par l'acide ascorbique en or métallique, le titrage étant effectué à 50°, entre pH 1,6–3, dans une solution de chlorure ne dépassant pas 0,1N La fin de la réaction est marquée par un saut de potentiel considerable. Utilisant des solutions à 0,01N la précision de cette méthode est d'environ ±1% Les ions mercuriques, cupriques ou ferriques ne genent pas

L'influence de divers facteurs, tels que la température et le pH, est discutée.

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ANALYTICAL APPLICATIONS OF CACOTHELINE—I

COLORIMETRIC DETECTION AND DETERMINATION OF IRON^{II} AND IRON^{III}

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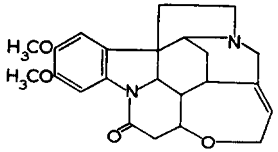
(*Received* 5 *February* 1958)

Summary—An account is given of the authors' investigations into the use of cacotheline as a reagent for the colorimetric detection and determination of iron^{II} and iron^{III}. Under well-defined conditions iron^{II} salts reduce cacotheline, in the presence of a complexing agent for iron^{III}, such as oxalate, yielding a product with an intense pink colour This colour reaction has been used for the detection of microgram quantities of iron^{II}. The stability of the colour is greatly increased by carrying out the reaction under vacuum in a Thunberg tube Employing matched Thunberg tubes the reaction has been used for the colorimetric determination of iron^{II}. The percentage transmissions have been measured in a Lumetron photoelectric colorimeter, Model 400 A against a reagent blank, using a yellow green filter (5300 Å). Iron^{III} salts have been reduced by exposure to light in the presence of oxalate before treatment with cacotheline

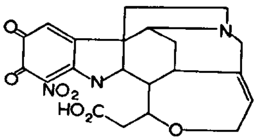
CACOTHELINE is a yellow crystalline substance, obtained by the action of hot 5*N* nitric acid on the alkaloid brucine. This substance appears to have been prepared by Gerhardt (1847), Strecker (1854), Moufang and Tafel[1] (1899) and later by Leuchs and Leuchs[2] (1910). It is sparingly soluble in water giving a yellow solution.

Cacotheline is variously described as (1) the nitrate of *bis*dimethyl mononitrobrucine hydrate (Moufang and Tafel[3] and Welcher[4]), (2) a nitroderivative of brucine of unknown constitution (Feigl[5]); (3) bruciquinone hydrate (Mellan[6]); (4) nitrate of *bis*-desmethyl-nitrobrucine hydrate (Manske and Holmes[7]); and (5) nitrate of nitrobruciquinone hydrate ($C_{21}H_{21}O_7N_3 \cdot HNO_3$) (B.D H). For a correct understanding of the structure of cacotheline, it is necessary to comprehend the structure of brucine, which is a dimethoxystrychnine. Brucine ($C_{23}H_{26}O_4N_2$) differs from strychnine ($C_{21}H_{22}O_2N_2$) by two methoxyl groups, which may be removed by heating brucine with concentrated hydrochloric acid in a sealed tube. The degradation reactions of brucine parallel those of strychnine and in many instances lead to the same degradation products. According to Leuchs, Seeger and Jaeger[8] brucine is oxidised by 5*N* nitric acid or chloric acid at 0–5° to a rose-coloured solution from which a red bruciquinone can be isolated, while hot nitric acid gives yellow cacotheline. Quinone formation indicates that the two methoxyl groups of brucine are either in the *ortho*- or *para*- position to each other. The methoxyl groups of brucine are finally and definitely assigned to the *ortho*- positions (C_4' and C_5') in view of the oxidation of brucine to N'-oxalyl-4:5-dimethoxy anthranilic acid (Spath and Bretschneider[9]). The researches of Robinson[10] and collaborators have established the basic structure of brucine as (I):



I

Brucine.



II

Cacotheline.

It has already been stated that treatment of brucine with dilute nitric acid at 0–5° yields red bruciquinone, which is a typical quinone, as it can be reduced by sulphurous acid to a hydroquinone, *bis*-apomethylbrucine. No other alterations occur in the brucine molecule during this transformation, because it can be shown that methylation with dimethyl sulphate converts *bis*-apomethylbrucine to a quaternary salt of brucine.

More vigorous treatment with warm nitric acid effects a simultaneous nitration of the quinone nucleus and a hydrolysis of the lactam ring resulting in the production of cacotheline which has therefore been assigned the formula (II).

Leuchs, Osterburg and Kaehrn[11] established the cleavage of the lactam grouping through ester formation. Cacotheline is reduced by suitable reducing agents to a compound with an intense pink colour; owing to the extreme sensitiveness of this reaction, it can be used for the detection of traces of reducing substances. Leuchs and Leuchs[12] noticed that in aqueous solution cacotheline is reduced by stannous chloride to give a characteristic pink colour. Leuchs and Kaehrn[13] and Winkler and Leuchs[14] have reported that cacotheline is similarly reduced by sulphide, sulphite, bisulphite and thiosulphate. Gutzeit[15] proposed the detection of Sn^{II} with cacotheline. According to him a solution of stannic chloride, reduced with metallic iron, can be used for the test, because ferrous salts by themselves have no action on cacotheline in the absence of fluoride or phosphate. Later, Feigl[16] suggested this reaction as a sensitive spot test for the detection of tin. Newell, Ficklen and Maxfield[17] carried out a detailed investigation on the sensitivity of this test and the interference of various ions. Beck[18] found that lower oxides of uranium, rhenium, molybdenum, tungsten, vanadium, niobium and titanium also reduce cacotheline to a pink coloured compound. In a later publication Beck[19] reported that the bivalent salt of europium also reduces cacotheline to a pink-coloured compound and stated that the reaction is not answered by other rare earths. Rosenthaler[20] also stated that cacotheline is reduced to a pink-coloured compound by titanium^{III}, uranium^{III}, rhenium^{III} and the lower oxides of molybdenum, tungsten and niobium. Rosenthaler also found that ascorbic acid reduces cacotheline in hydrochloric acid solution. Feigl[20a] has employed cacotheline as a reagent for the spot-test detection of vanadium^{III}. Feigl and West[21] have developed a test for selenium based on the catalytic effect of this element on the reduction of cacotheline with alkali sulphides

REDUCTION OF CACOTHELINE BY IRON^{II} IN THE PRESENCE OF COMPLEXING AGENTS

A dilute solution of ferrous sulphate or ferrous chloride does not reduce cacotheline to the pink coloured compound. But it is well known that the reducing capacity of iron^{II} is markedly increased in the presence of substances which can form complexes with iron^{III}. From the equation

$$Fe^{2+} \leftrightarrows Fe^{3+} + e^-$$

it can be seen that the reaction proceeds more and more favourably in the forward direction, if the tervalent ferric ions formed are removed from the reaction sphere by complexing with a suitable substance Thus the potential of the ferric–ferrous system will be markedly lowered in the presence of an agent which will reduce the concentration of the ferric ion by complex formation. The oxidising power of the ferric ion will, consequently, be diminished and the reducing power of ferrous ion increased in the presence of substances which can effectively complex ferric iron. Since the stability of a metal complex may be altered by the hydrogen ion concentration of the solution it will often be found that the influence of a complexing agent on the potential of a redox system may be markedly affected by a change in pH. Michaelis and Friedheim[22] made a study of the influence of pH on the variation of the Fe^{3+}/Fe^{2+} potential in the presence of oxalate, malonate, acetate, salicylate, and pyrophosphate. Belcher[23] *et al.* have studied the effect of the strong complex-forming agent EDTA on the Fe^{3+}/Fe^{2+} potential at different hydrogen ion concentrations.

TABLE 1. 5.0 ML OF WALPOLE BUFFER (pH 3.61) + 0.15 ML OF CACOTHELINE (0.25%) + 0.5 ML OF 0.01*M* Fe^{II} SOLUTION + *X* ML OF SODIUM OXALATE (0.1*M*) + WATER TO MAKE UP TO 10 ML

Volume of oxalate, (*ml*)	Colour observed	Stability (*min*)
0.5	pink	15
1.0	pink	20
2.0	pink	60
3.0	pink	60
4.0	pink	60
5.0	pink	60

Gopala Rao, Narayana Rao, Somidevamma and Lalitha[24] have studied the reduction of cacotheline by iron^{II}, in the presence of various complexing agents under varying conditions of pH. Iron^{II}, by itself, cannot reduce cacotheline. But in the presence of a suitable complexing agent, it is capable of reducing cacotheline. Oxalate, citrate, malate, tartrate, lactate, and EDTA have been studied, in addition to the inorganic complexing agents phosphate, metaphosphate and pyrophosphate. In each case a detailed study of the influence of pH on the reaction has been made.

From such studies, it was observed that the pH value at which a strong pink colour is obtained varies from substance to substance. Evidently the pH of the best colour formation corresponds to the best reduction of the cacotheline by the ferrous salt present. The most favourable reduction of the cacotheline will correspond to the lowest potential, which will in its turn correspond to the best possible complexing of the Fe^{3+} ions with the complexing agent under study. Michaelis and Freidheim[22] have indeed shown that the effect of a complexing agent on the redox potential of the Fe^{3+}/Fe^{2+} system depends upon the pH of the solution.

EXPERIMENTAL

With oxalate as the complexing agent and using a sodium acetate–hydrochloric acid buffer, it was found by us that the pH range 3–3.95 is the best for the reduction of cacotheline by iron^{II}. In order to obtain a fairly stable colour, the oxalate must be used in large excess, in about 40 times the concentration of the ferrous iron present. This is evident by the results in Table I.

Even after one hour, the last four solutions retain the colour, although less intense than at the start.

We have also observed that the concentration of cacotheline that has to be used bears a certain relation to the amount of iron^{II} present in the test solution. When the concentration of iron^{II} is low, a relatively high concentration of cacotheline not only masks the pink colour of the reaction-product but also decreases the stability of the pink colour. The right concentration to be employed can be ascertained from Table II. It is also seen that one cannot use a concentration of cacotheline lower than 0.025%.

From the results in Table II, it is also observed that the limit of identification of iron^{II}, by a test tube reaction, is 14 μg of iron in a volume of 7 5 ml

INTERFERENCE OF IRON^{III} IN THE DETECTION OF IRON^{II}

Our studies have shown that ferric alum corresponding to an amount of 250 μg of iron^{III} does not interfere in the detection of as little as 14 μg of iron^{II}, although the stability of the pink colour is somewhat decreased in the presence of iron^{III} Amounts of iron^{III} higher than 250 μg reduce the intensity of the pink colour produced, so that at about 1000 μg of iron^{III} the pink colour produced is imperceptible We believe that the effect of iron^{III} is partly due to the oxidation of the pink-coloured product by the iron^{III} (mass action effect) and partly due to a masking of the light pink-colour by the yellow colour of the iron^{III}.

TABLE II 5 0 ML OF WALPOLE BUFFER (pH 3 61) + 0 25 ML OF CACOTHELINE (X%) + 2 0 ML OF SODIUM OXALATE (0 1M) + 0 25 ML OF IRON-II SOLUTION

Concentration of cacotheline	Amount of iron^{II} (μg)	Colour	Stability (*min*)
0·05%	28·0	pink	13
	14 0	light pink	10
	5·6	very light pink	4
0 025%	28 0	pink	15
	14·0	pink	15
	5 6	light pink	10
	2·8	no colour	—
0 01%	14 0	very light pink	4
	5 6	no colour	—
	2 8	no colour	—

EFFECT OF OTHER IONS

It has been observed by us that copper^{II} decolorises the pink, even at as low a concentration as 1·0 mg per 7 5 ml. Mn^{II}, Ni^{II} and Cr^{III} do not interfere unless they are present at a fairly high concentration, where their own colours interfere in the observation of the pink Mo^{VI} and W^{VI} do not interfere. Chloride, bromide and iodide also do not interfere. Ti^{III}, Sn^{II}, U^{III}, U^{IV}, V^{III}, Re^{III}, Eu^{II} and sulphite, thiosulphate and sulphide interfere

COLORIMETRIC DETERMINATION OF IRON^{II}

From the results in the preceding section, it is evident that cacotheline gives a very sensitive colour reaction with iron^{II}, under conditions which can be well defined. We have therefore investigated the possibility of utilising this colour reaction for the colorimetric determination of iron^{II}. But since it has been noticed that the pink reduction-product of cacotheline is somewhat unstable, it is necessary, for quantitative purposes, to work under conditions where the colour is stable for relatively long time, compared with the time required for carrying out a sufficient number of colorimetric determinations Preliminary studies have led us to the conclusion that the oxygen of the atmosphere is mostly responsible for the fading of the colour. Experiments made in Thunberg tubes, under a fairly high degree of vacuum, have shown that the pink colour is stable for over five hours A diagrammatic sketch of the Thunberg tube employed by us is given in Fig. 1. It consists of a Pyrex glass tube, provided with a hollow-ground glass stopper which is bent in the shape of an inverted "U". The Thunberg tube is also provided with a side tube for connection to a vacuum pump A mixture of the required amounts of the buffer solution, cacotheline and sodium oxalate is placed in the main tube, while the iron^{II} solution is placed in the hollow of the stopper. At first the stopper is turned so that there is connection between the inside of the main tube and the side-arm which is connected to the pump Gentle suction is applied and maintained for about ten minutes

When it is certain that all the air has been removed from inside the tube, the stopper is turned so that the connection to the side-arm is cut off. The side-arm of the Thunberg tube is then disconnected from the pump. The Thunberg tube is now inverted and suitably tilted, so that the contents of the main tube are mixed thoroughly with the iron^{II} solution contained in the hollow of the stopper. The tube is now brought upright, and the colour formed is observed

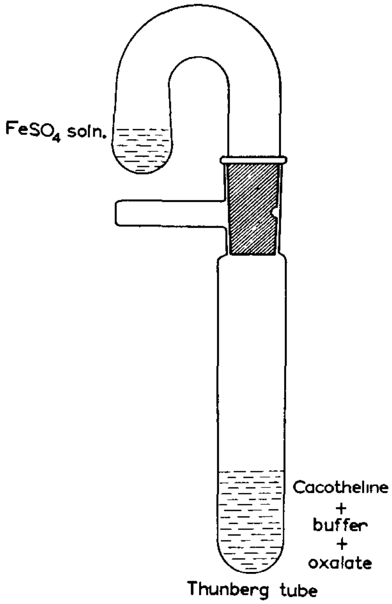


FIG. 1

For the colorimetric determination, optically matched Pyrex glass tubes (supplied by Messrs. James Jobling) have been employed; and the percentage transmissions have been measured in a Lumetron photoelectric colorimeter (Model 400A), using a yellow-green filter (5300 Å) The percentage transmission of the pink solution is measured against a reagent blank

TABLE III 10 ML BUFFER pH 3 95 + 0 5 ML CACOTHELINE (0 08%) + 2 ML SODIUM OXALATE (0·1*M*) + 0 5 ML OF FERROUS SULPHATE (89 6 μg OF Fe) + 2 0 ML WATER

Time of observation after mixing the reagents (*min*)	% Transmission	
	In air	In vacuum
0—1	61 0	57 0
3	64 0	57·0
5	68 0	57 0
10	72 0	57·0
15	78 0	57 0
20	85 0	57 0
30	—	57 0
40	—	57 0

QUANTITATIVE STUDY OF COLOUR STABILITY

In the following experiments the concentration of ferrous iron is just about half that required for complete reaction with the cacotheline taken. For comparison of relative stabilities of the pink colour in air and vacuum, parallel experiments have been made The results are given in Table III.

The results in Table III indicate that (i) the colour developed in the absence of air is more intense than that developed in air and (ii) that the pink colour rapidly falls in intensity in air Hence for a sensitive and accurate determination of Fe^{II}, the mixing of the reactants and the measurement of the colour developed should be done in the absence of air.

TABLE IV 10 ML BUFFER pH 3 95 + 0 5 ML CACOTHELINE (0 08%) + 2 ML SODIUM OXALATE, *X* ML Fe^{II} SOLUTION + WATER TO MAKE UP TO 15 ML

Amount of Fe-II, *μg*	% *T* (5300 Å)	Extinction	*E*/*C*
12	90 0	0 046	0 003283
20	84 0	0 076	0 003800
24	81 0	0 092	0 003800
32	76 0	0 120	0 003750
40	70 5	0 152	0 003800
48	66 0	0 181	0 003771
60	59 5	0 225	0 003750
80	49 0	0 305	0 003813
100	49 5	0 305	0 003050
132	49 5	0 305	0 002311

VALIDITY OF BEER'S LAW—VARIATION OF Fe^{II} CONCENTRATION

In these experiments, the concentration of Fe^{II} is varied, keeping a constant but adequate cacotheline concentration

The results, shown in Table IV, indicate that the colour developed obeys Beer's Law in the range of 20 *μg* to 80 *μg* of Fe^{II}, under the experimental conditions

TABLE V

Amount of iron taken (*μg*)	Amount of iron found (*μg*)
20 0	19 94
25 0	24 78
25 0	24 80
28 0	28 05
30 0	29 96
35 0	35 30
35 0	34 90
36 0	35 86
37 0	36 54
40 0	39 70
40 0	39 70
45 0	45 00
45 0	45 00
60 0	60 26
70 0	70 15
80 0	80 50

COLORIMETRIC DETERMINATION OF FERROUS IRON WITH CACOTHELINE AS REAGENT

A large number of colorimetric determinations of Fe^{II} have been carried out by the method presented above. A selection of the results given in Table V shows that Fe^{II} can be estimated accurately by this method within ±1% in the range prescribed (20 *μg* to 80 *μg* of Fe^{II}).

DETERMINATION OF IRON^{III}

About 1 to 5 ml of the given solution is taken in a Thunberg tube and 10 ml of the buffer (pH 3·61) containing excess of sodium oxalate is added. 0·5 ml of 0·08% cacotheline is taken in the hollow of the stopper. After the stopper is replaced in position, the tube is evacuated and exposed to the light from a 125-watt high pressure mercury lamp for thirty minutes, or to sunlight for 5 to 15 minutes depending on the intensity of the sun. During exposure to light, iron^{III} is reduced to the iron^{II} state quantitatively, as shown by Gopala Rao and Madhusudhana Rao.[25] If now the cacotheline solution in the hollow stopper is allowed to mix thoroughly with the iron^{II} solution in the main tube, a pink colour is produced because of the reduction of cacotheline. The transmission percentage of this solution is measured as already described in the previous section. The results of some typical experiments are given in Table VI.

Table VI. 10 ml Walpole buffer pH 3·61 + 2 ml of sodium oxalate (0·1*N*) + iron^{III} solution + 0·5 ml cacotheline (0·08%)—made up to 15 ml

Iron^{III} taken (μg)	Iron^{III} found (μg)
16·0	16·2
19·2	19·1
26·0	26·1
32·0	32·1
40·0	39·9
48·0	48·4
64·0	64·4
77·0	76·1

Zusammenfassung—Es wird ein Bericht von den Untersuchungen über den Gebrauch Cacothelins als Reagens für den kolorimetrischen Nachweis und die Bestimmung von Eisen-II und -III angegeben.

Unter genau bestimmten Bedingungen in der Anwesenheit einer Komplexreagens für Eisen, z.B. Oxalsalz, Ferrosalze reduzieren Cacothelin und lieferen ein Produkt mit einer intensiven rosa Farbe.

Diese Farbenreaktionen wurde für den Nachweis von Mikrogrammmengen von Eisen-II benutzt. Die Stabilität der Farbe nimmt sehr zu, wenn die Reaktion unter Vakuum in einem Thumberg-Rohr gemacht wird. Durch den Gebrauch von verglichenen Thumberg-Röhren wird die Reaktion für die kolorimetrische Bestimmung von Eisen-II angewandt.

Die prozentigen Durchlassungen werden unter Gebrauch von einem gelb-grünen Durchlass in einem Lumetron-photometrischen Kolorimeter gegen Leer-Reagens gemessen.

Ferrisalze werden durch Belichtung in der Anwesenheit von Oxalsalz vor Behandlung mit Cacothelin reduziert.

Résumé—Les auteurs ont étudié la possibilité d'utiliser la cacothéline comme réactif pour l'identification et le dosage colorimétrique du fer-II et du fer-III. Dans les conditions opératoires bien définies la cacothéline est réduite par les sels ferreux en présence d'un agent qui complexe le fer-III, tel que l'oxalate, donnant un produit rose intense. Cette réaction colorée a permis de déceler des quantités de fer-II à l'échelle du microgramme. La coloration devient beaucoup plus stable si la réaction s'effectue à vide dans une tube de Thumberg. Utilisant des tubes de Thumberg identiques la réaction a permis d'effectuer le dosage colorimétrique du fer-II. Les transmissions en % ont été mesurées dans un colorimétre photoélectrique de Lumetron, modèle 400 A, vis à vis d'un essai à blanc utilisant un filtre jaune-vert (5300 Å). Exposés à la lumière en présence de l'oxalate les sels ferriques ont été réduits avant leur traitement à la cacothéline.

Acknowledgement—One of us, V. Narayana Rao, D.Sc., desires to thank the Government of India for the award of a Research Scholarship, which has enabled him to participate in this investigation.

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SOME DEVELOPMENTS IN RECORDING POLAROGRAPHY

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(*Received* 2 *December* 1957)

Summary—The polarograph has developed in step with the progress of the recorder To-day numerous polarographs exist with pen-writing recorders, such as the photo-pen type, the ammeter type with d c. amplification, and the potentiometer type with automatic balance. The recording polarograph with compensating bridge is now widely used in Japan, and continues to displace the conventional instrument

THE polarograph is an instrument which measures or records the fluctuating direct current flowing between a depolarized dropping-mercury electrode and a mercury-pool electrode, when direct current voltage is applied between them, and is increased gradually by means of a potentiometer. The instrument permits measurement of the fluctuating and minute current with an accuracy approaching that for the measurement of a constant current.

Normally polarography is carried out using a dropping-mercury cathode, at which reduction occurs At relatively minute concentration of reducible substance and large concentration of conducting ions, *i.e.*, non-differentiating supporting electrolyte, the reduction rate of the reducible substance is controlled only by its diffusion rate from the body of the solution into the interface. The fact that the diffusion rate is proportional to the concentration of reducible substance in the body of the solution allows the field of polarography to extend to the qualitive and quantitative determination of reducible substance.

The first polarograph designed by Heyrovsky and Shigata recorded a current–voltage curve (polarogram) on a photographic plate This type of polarograph was employed during the period from 1925 to about 1940, and contributed greatly to the development of the theory and application of polarography to chemical analysis and other fields.

THE ROLE OF THE RECORDER IN POLAROGRAPHIC DEVELOPMENT

The polarograph has developed further step by step with progress in the development of recorders It is therefore, obvious that the recorder plays a most important or essential role. In 1934 recording polarographs appeared in the U.S.A.,[1] and were followed by numerous polarographs fitted with pen recorders.

Recording Polarographs may at present be divided into the following types:—

(1) Photo-pen type
(2) Ammeter type with direct current amplification
(3) Potentiometer type with automatic balance

(1) The photo-pen type polarograph, typified in the research of Lykken *et al.*,[2]

is one which traces the light beam from a mirror galvanometer on a chart by means of a so-called "photo-pen". The RCA photo-pen used in Lykken's instrument is movable in either direction by the action of a reversible motor so that the light beam from the mirror of the galvanometer always focuses between the two cathodes of a phototube ("double cathode phototube") mounted directly on the pen carriage.

The pen-writing recorder of the photoelectric scanning type used in Lange's Polarometer[3] also belongs to this group. It traces the light beam from the galvanometer by means of a CdS-photoelectric cell, the light beam falling on one half of the cell only. It is particularly valuable because of the very simple amplification due to the high sensitivity of the photoelectric cell.

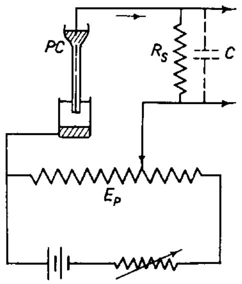

FIG. 1. Ammeter-type polarograph

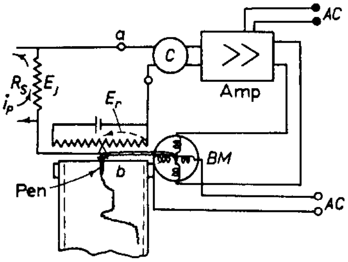

FIG 2 Automatic balancing potentiometer type polarograph BM = two-phase balancing motor, C = a.c. converter.

Polarographs of this type can be used in recording the current flow either on photographic paper or on a paper chart.

(2) In the ammeter type with direct current amplification, as shown in Fig. 1, the standard resistor R_S (in some cases, with its parallel condenser C) takes the place of the galvanometer in the Heyrovsky-Shigata Polarograph. When the polarographic current, I_p, flows through R_S, there is a voltage-drop, $R_S I_p$, which is then amplified and indicated on the recording ammeter or voltmeter. The movement of the recording paper is synchronized with the revolution of the potentiometer drum. There are two methods of amplification, (*a*) the direct method of d.c. amplification, and (*b*) a.c. amplification after conversion of d.c. to a.c. For example, the Cambridge polarograph and Radiometer belong to the latter type.

In these polarographs, the pen traces the arc of a circle, so that a chart with circular abscissa must be used. It is obvious that in such a polarograph there is some inconvenience in measuring the half-wave potential. It is necessary to contrive some means of converting it to the normal co-ordinate system either by a mechanism making the pen draw in a straight line or by using a cylindrical chart such as is employed in Radiometer.

(3) Two kinds of circuit are employed in the potentiometer type with automatic electronic balance. One of them is illustrated in Fig 2, in which $R_S I_p = E_j$ is connected as input and the voltage difference, $E_j - E_r$, where E_r is the indicating voltage in the recorder, is amplified after conversion to a.c ; it is then put in conjunction with one phase of a two-phase a.c. balancing motor, BM, providing the motive force to drive BM and move the slider (b) of the recorder in the direction which equalizes E_r and E_j.

For this purpose, the a.c. balancing motor, BM, should rotate counter-clockwise at $E_j > E_r$, and clockwise at $E_j < E_r$, stopping when $E_j = E_r$. When in balance, the following relationship exists for the polarographic current being measured:—

$$I_p = E_r/R_s \qquad (1)$$

In the above methods, as shown in Fig. 1 and Fig. 2, the d.c. voltage impressed on the polarographic cell, PC, is smaller by E_j than the potentiometer voltage E_p. R_s must therefore be as small as possible in order to make E_j relatively small.

For example, the recording potentiometer of the Sargent XXI Polarograph (Brown Electronic Co., full scale 2·5 mV) uses 2·5 KΩ as R_s, resulting in a sensitivity of 1 μA per 280 mm.

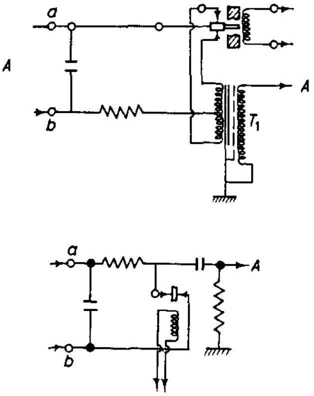

FIG. 3. Converter circuit using a vibrator.

The conversion of d.c. voltage to a.c. voltage can conveniently be carried out by means of a "chopper" or vibrator and also in some cases, by a conversion galvanometer, vibrating condenser-type converter or conversion reactor.

As the current flow in the polarograph is very minute, the polarographic recorder should have a high current sensitivity, and this depends on the indicating voltage E_r of the maximum scale in the recorder and the maximum external resistor R_s, as given in Equation (1).

Figs. 3(A) and 3(B) illustrate a specially suitable circuit employing a vibrator as converter Circuit (A) uses the same principle as the recording pyrometer, but in order to enhance the current sensitivity sufficiently, the input transformer T_1 is modified to a high-impedance type.

Circuit (B) has been used in conventional pH-meters with the glass electrode, and is one of high-impedance type, but in this circuit the effect of noise due to the chopper is too great in comparison with circuit (A) when the voltage sensitivity is increased, although the current sensitivity is always very high.

RECORDING POLAROGRAPHS WITH A COMPENSATING BRIDGE

The principle of the recording polarograph with compensating bridge is shown in Fig 4. This polarograph is an example of the potentiometer type with balancing vacuum tubes The converter (C) replaces the galvanometer of the conventional polarograph and the standard resistance (R_s), the sliding resistance in the recorder

(R_r), the polarographic cell (PC), and the resistance (R_p) of the potentiometer for applying the d.c. voltage form a Kohlrausch's Bridge.

In this circuit the voltage drop R_sI_p due to the current flow of the polarographic current is compensated by the indicating voltage E_r, which is adjustable by the balancing motor BM. When properly balanced, the voltage between (a) and (b) becomes zero, with the result that the potentiometric voltage E_p equals the voltage applied to the polarographic cell.

It is of importance that R_p and R_r should be chosen with lower resistances than R_s, since a current that is large compared with the polarographic current I_p must flow through the sliding resistance of the polarographic potentiometer and that of the recording potentiometer.

The errors in both potentiometers become large when the current is measured under low sensitivity, but there is no problem of errors, when a minute current is to be measured.

The voltage sensitivity of the recording potentiometer need not be so high as that in other polarographs, so that a recorder of any kind, 40 mV, 50 mV or 200 mV, may be used if the standard resistance R_s is increased as the voltage sensitivity of the recording potentiometer decreases.

In Fig. 1, the standard resistance R_s corresponds to the internal resistance, but in Fig. 4, that resistance becomes zero in a static sense since there is no voltage drop between (a) and (b). On the contrary, in a dynamic sense some voltage difference occurs due to lag in the balancing motor. Therefore some apparent internal resistance must occur. This is represented by the ratio of E(a)–(b) to I_p.

In the dropping mercury electrode, the internal resistance is positive and small in comparison with R_s while the current is increasing, but when the mercury drop falls and little current flows, the indicating voltage E_r lags behind, so that the sign of E(a)–(b) and I_p become reversed and the internal resistance apparently has a negative value. This seems to have some effect on the measurement of the maximum wave. Therefore even in the polarograph with compensating bridge, the indicating voltage of the recorder has to be kept as small as possible.

The rate of application of d c. voltage to the polarographic cell is one of the most important factors. It is very essential for accurate measurement to control either the application rate of the voltage, or the speed of the recording chart, whichever seems preferable.

DAMPING CIRCUITS IN THE RECORDING POLAROGRAPH

The electrolytic current increases to a maximum during the growth of the mercury drop and then suddenly decreases at the moment that the drop falls. Such an instantaneously changing current can be traced in 1/1000-sec by means of an electromagnetic oscillograph. The electrolytic current at a certain moment can be measured by the Brown oscillograph, although this requires about 1/10 sec for scanning.

In the conventional polarograph which records the current on a photographic plate by using the galvanometer, the average of the fluctuating current equals the average current approximately.[7] Pen-recording polarographs, apart from the photopen type, include a damping circuit for measurement of the average current, although they may be used to measure the maximum current

In the recording polarograph with automatic balance, the characteristics of the

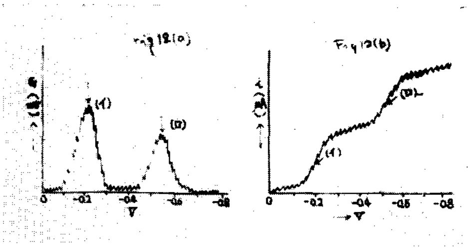

FIG. 4. Compensating bridge circuit.

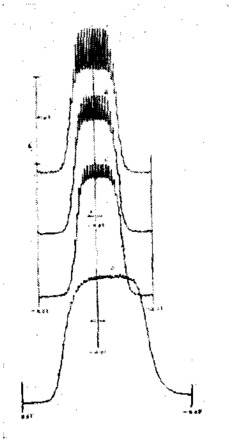

FIG. 8. Half-wave potential shift. (A) no damping, (B) $a = 2$, (C) $a = 1/1{\cdot}5$, (D) $a = 1/4$, due to damping.

balancing motor are of special importance, and the condenser C for damping must be put in parallel with the standard resistance R_s.[8]

Some damping circuits are illustrated in Fig. 5 (A)–(D). Among them, (A) and (B) are damping circuits for the galvanometer, where R_a is an Ayrton shunt and r_d a damping resistance. The circuit (B) proposed by Leveque[9] as a damping circuit is a differential circuit. The circuits (C) and (D) are damping circuits for pen-recorders. In the circuit (C) an electrolytic condenser of relatively large capacity is put in parallel with the standard resistance R_s and the ends are connected as the input of a d.c. amplifier or converter. This connection is shown dotted in Figs. 1 and 4. Since the damping of the condenser C is influenced by change in the resistance of the standard resistance R_s, the capacity of the condenser C must be changed in a series of steps (usually 5 to 12 steps).

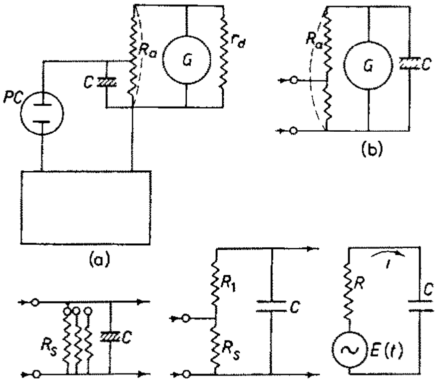

FIG. 5. Damping circuit.

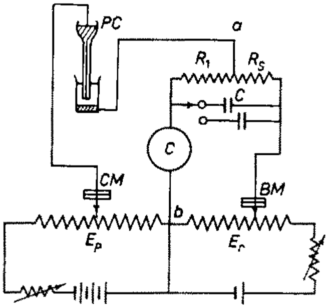

FIG. 6. Combination of the definite time-constant circuit and the compensating bridge circuit.

The circuit (D) is a circuit with a definite time constant, *i.e.*, it holds $R\,(= R_s + R_1)$ constant, thus keeping constant the value of RC, where C is the capacity of the condenser, although the value of R_s is changed by a switch in accordance with the current sensitivity in the course of the measurement. In practice sufficient damping is provided by changing three kinds of condenser and three steps of the time constant. In this circuit, though the value of R_s changes, the damping conditions do not vary, so that we can choose the optimum condition of damping in accordance with the dropping interval of the mercury.

The layout of circuit (D) is almost the same as that of Fig. 2, and that with a compensating bridge is illustrated in Fig 6. In the latter the compensation of the voltage between a and b changes to a greater or less degree according to the value of R_s and R_1. The circuit shown in Fig 6 allows a relatively high value of R.

For example, if we prefer $R = 50$ KΩ in the 50-mV recording potentiometer, it is sufficient for damping to take $C = 10 - 100\ \mu$F, so that a proper condenser may be used instead of a large-capacity electrolytic condenser.

Considering the equivalent circuit (E) of Fig 5 in order to analyse the circuit of (C) or (D) in Fig 5, the current, i, of the closed circuit satisfies the following formulae.

$$Ri + \frac{1}{C}\int i\,dt = E(t) \tag{2}$$

As the polarographic current satisfies approximately the Ilkovic equation, $E(t)$ becomes $e_0 t^{1/6}$, where e_0 is the constant. In other words, $E(t)$ is the periodic function of the mercury dropping interval (T). Equation (2) may be solved by means of the differential analyser, but is also solved by means of Heaviside's operational calculus, the following relation being derived.

$$\left(R + \frac{1}{Cp}\right) i = E(t) \cdot 1 \tag{3}$$

where p is the Heaviside operator and 1 the unit function. When the current reaches a constant value after frequent periodical introduction of $E(t)$, the terminal voltage between the ends of the condenser (C) becomes the following:

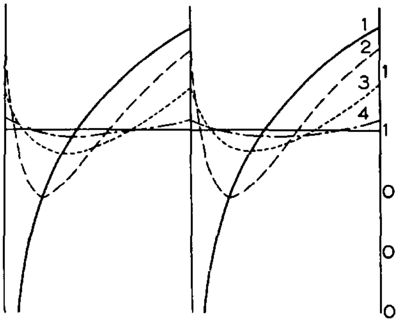

FIG 7. Damping and wave form (1) no damping ($R = 50$ KΩ, $C = 0$), (2) $a = 2$, ($R = 50$ KΩ, $C = 10\,\mu$F), (3) $a = 1/1{\cdot}5$, ($R = 50$ KΩ, $C = 30\,\mu$F), (4) $a = 1/6$, ($R = 50$ KΩ, $C = 120\,\mu$F).

$$Et = ae_0 e^{-at}\left(\int_o^t e^{a\xi}\xi^{1/6}\, d\xi + \frac{e^{-at}}{1 - \beta^{-at}}\int_o^t e^{a\xi}\xi^{1/6}\, d\xi\right) \tag{4}$$

where $a = 1/RC(\Omega^{-1}F^{-1})$
t = period (sec) of growth of the dropping mercury
T = dropping interval (sec)
ξ = integration variable.

Fig. 7 gives the wave forms at different values (2, 1/1·5, and 1/6) of a, when $T =$ 3 sec, where the ordinate is the current (the average integration current) and the abscissa is the dropping time This wave form, as indicated in equation (4), changes in accordance with the value of aT, the curve (1) shows the current without damping, while the curves (2)–(4) may be drawn on the chart of the recorder when the current is damped and the recorder can follow properly.

The average current between the maximum and minimum of the amplitude shows the following deviation from the average integration current.

$$+1{\cdot}2\,\% \text{ at } a = 2, \quad +1{\cdot}4\,\% \text{ at } a = 1/1{\cdot}5, \quad \text{and} \quad +0{\cdot}4\,\% \text{ at } a = 1/6$$

Fig. 7 shows that the average fluctuation is 23·0%, 10·4%, or 2·8% of the integration current respectively in each case of a.

If employing the no-damping circuit, the current-fluctuation changes according to the ability of the balancing motor to follow, and the average current between maximum and minimum shows a positive or negative error compared with the average integration current. In the damped circuit, the current fluctuation becomes small compared with the change of the current, resulting in measurement of the constant average current.

For the time necessary to reach the diffusion current from the zero current on sudden introduction of the definite voltage, the following results are obtained; at $a = 2$, after one drop, at 1/1·5 after three drops, and at 1/6 at 15 drops. Therefore it is found that, as seen in Fig. 8, the shift of the half-wave potential becomes greater as the damping of the current becomes greater.

Zusammenfassung—Der Polarograph wurde stufenartig dem Fortschritt des Registrierapparats entsprechend entwickelt Heutzutage, liegen zahlreiche Polarographen mit federschreibenden Registrierapparaten wie der Photofedertypus, der Amperemeter-Typus mit Gleichstrom-Vergrosserung, und der potentiometrische Typus mit automatischem Gleichgewicht vor. Der rekordierende Polarograph mit kompensierender Brucke wird jetzt weitgehend in Japan benutzt und nimmt im allgemeinen den Platz des normalen Instruments ein.

Résumé—Le développement du polarographe suit de près celui des techniques nouvelles d'enregistrement. Il existe actuellement de nombreux polarographes qui comportent des dispositifs divers d'enregistrement automatique, tels que le photo-style, le type ammètre avec amplificateur à courant continu, le type potentiomètre comportant un dispositif de compensation automatique. Le polarographe à enregistrement automatique avec pont compensateur, aujourd'hui très rèpandu au Japon, continue à remplacer l'instrument classique.

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Talanta, 1958, Vol 1, pp 184–188 Pergamon Press Ltd., London

SHORT COMMUNICATIONS

Titrimetric determination of mercuric chloride

(*Received* 17 *January* 1958)

The standard method of determining mercuric nitrate by titration with thiocyanate cannot be applied directly to the determination of mercuric chloride. It is necessary to convert the mercuric chloride to the oxide, which is then filtered off, washed and dissolved in nitric acid.[1] On the other hand, the direct determination of mercuric chloride using potassium iodide is not usually included in modern textbooks of inorganic analysis, since the titration involves a substantial correction for the appearance of the turbidity of mercuric iodide before the equivalence-point, due to dissociation of the HgI_4^{2-} ions formed. The direct titration of mercuric chloride with potassium cyanide has been discussed.[2] It is stated that the titration is successful only with solutions more concentrated than 0·5N.

The use of potassium cyanide for the direct titrimetric determination of mercuric chloride, with particular reference to the pH changes involved, leading to the choice of suitable indicators, is described below.

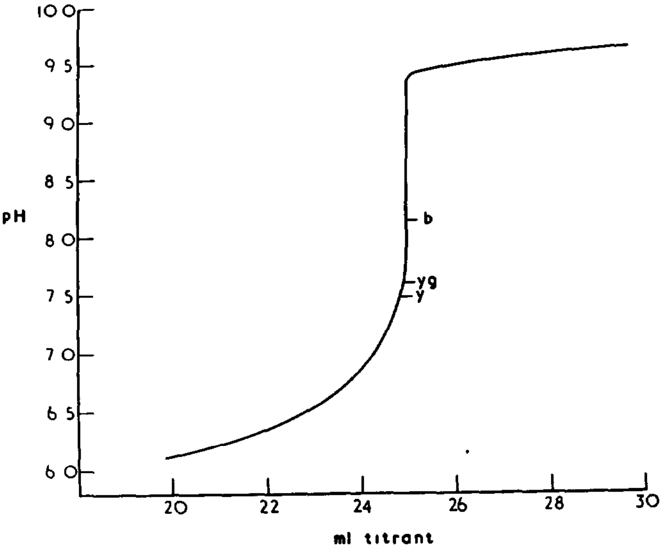

FIG. 1

EXPERIMENTAL

The variation in the pH of 0·1N mercuric chloride on addition of 0·1N potassium cyanide solution was followed by means of a Cambridge pH meter, and is shown in Fig 1. A sharp change in pH occurs over the range 7·6–9·4 on addition of a small amount of titrant in the region of the theoretical end-point. At the equivalence-point the solution contains dissociated potassium chloride and very slightly dissociated mercuric cyanide, so that the pH is close to 7 The addition of a small excess of potassium cyanide solution gives rise to alkaline conditions

A number of commonly used indicators giving a colour change in the pH range 7·6–9·4 were then tried out for the titration of 0·1N solutions of mercuric chloride with 0·1N potassium cyanide Of those investigated, cresol red, thymol blue and phenolphthalein appeared to be the most useful Cresol red showed a moderately sharp change from pink to a dark tone, but the gradual change from yellow to pink before the end-point made detection difficult Both thymol blue and phenolphthalein gave more satisfactory end-point indications Thymol blue, used with 0 1*N* solutions, gave a sharp change from yellow–green (y–g) to dark blue (b) at the end-point on addition of a 0 03-ml drop of titrant About 0 10 ml before this the solution changed from yellow (y) to yellow–green, giving a warning of the approaching end-point The positions of these colour changes on the titration curve were determined and are shown in Fig 1

RESULTS

Several "unknown" solutions, approximately 0 1*N*, prepared by weighing dry "AnalaR" mercuric chloride, were determined, using potassium cyanide which had been standardized against silver nitrate Thymol blue was used as indicator The concentration of the "unknown" solutions was determined with an accuracy of +0 35%, *i e* +0 09 ml in 25 ml. More accurate results were given by 0 1*N* potassium cyanide solutions than by 0 05*N* solutions In the latter, indication of the end-point is delayed, leading to error

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A rapid micro method for the determination of phosphorus in organic compounds

(*Received* 26 *April* 1958)

Several papers have been published during the last few years describing the method of decomposing organic compounds by burning them in a closed flask filled with oxygen The technique seems to have been used first in 1892 by Hempel[1] who determined sulphur gravimetrically as barium sulphate after the combustion; it was later extended to the determination of halogens [2] In more recent times, the method was re-examined by Mikl and Pech[3] and was adapted to the microscale by Schoniger [4] It is surprising that this simple way of decomposing organic compounds had been overlooked for so long, for it seems possible to apply it to the determination of most of the acidic elements likely to be found in organic compounds To date, the halogens[4,5,6], and sulphur[5,7,8] have been determined on both the micro and semimicro scale by various workers. In our experience, the best general method for completing the sulphur determination is based on direct titration with barium perchlorate [5,7] The present communication describes the extension of the oxygen flask technique to the determination of phosphorus Since the start of our work, Fleischer *et al* [9] have reported a similar decomposition method for phosphorus-containing compounds but they complete the determination colorimetrically or by precipitation as magnesium ammonium phosphate

Methods for the determination of the phosphate ion

The most widely applied method for completing the micro determination of phosphorus in organic compounds is by precipitation as ammonium phosphomolybdate This procedure is subject to many sources of error but no better one has been available Jorgensen's salt is satisfactory as those investigated, cresol red, thymol blue and phenolphthalein appeared to be the most useful. Cresol red showed a moderately sharp change from pink to a dark tone, but the gradual change from yellow to pink before the end-point made detection difficult. Both thymol blue and phenolphthalein gave more satisfactory end-point indications. Thymol blue, used with 0.1*N* solutions, gave a sharp change from yellow–green (y–g) to dark blue (b) at the end-point on addition of a 0.03-ml drop of titrant. About 0.10 ml before this the solution changed from yellow (y) to yellow–green, giving a warning of the approaching end-point. The positions of these colour changes on the titration curve were determined and are shown in Fig. 1.

RESULTS

Several "unknown" solutions, approximately 0.1*N*, prepared by weighing dry "AnalaR" mercuric chloride, were determined, using potassium cyanide which had been standardized against silver nitrate. Thymol blue was used as indicator. The concentration of the "unknown" solutions was determined with an accuracy of +0.35%, *i.e.* +0.09 ml in 25 ml. More accurate results were given by 0.1*N* potassium cyanide solutions than by 0.05*N* solutions. In the latter, indication of the end-point is delayed, leading to error.

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A rapid micro method for the determination of phosphorus in organic compounds

(*Received* 26 *April* 1958)

Several papers have been published during the last few years describing the method of decomposing organic compounds by burning them in a closed flask filled with oxygen. The technique seems to have been used first in 1892 by Hempel[1] who determined sulphur gravimetrically as barium sulphate after the combustion; it was later extended to the determination of halogens.[2] In more recent times, the method was re-examined by Mikl and Pech[3] and was adapted to the microscale by Schoniger.[4] It is surprising that this simple way of decomposing organic compounds had been overlooked for so long, for it seems possible to apply it to the determination of most of the acidic elements likely to be found in organic compounds. To date, the halogens[4,5,6,] and sulphur[5,7,8] have been determined on both the micro and semimicro scale by various workers. In our experience, the best general method for completing the sulphur determination is based on direct titration with barium perchlorate.[5,7] The present communication describes the extension of the oxygen flask technique to the determination of phosphorus. Since the start of our work, Fleischer *et al.*[9] have reported a similar decomposition method for phosphorus-containing compounds but they complete the determination colorimetrically or by precipitation as magnesium ammonium phosphate.

Methods for the determination of the phosphate ion

The most widely applied method for completing the micro determination of phosphorus in organic compounds is by precipitation as ammonium phosphomolybdate. This procedure is subject to many sources of error but no better one has been available. Jorgensen's salt is satisfactory as precipitant on the semimicro scale and has advantages over ammonium molybdate, but the solubility of its phosphate precludes its use on the micro scale. Fleischer *et al* [9] precipitated phosphorus as magnesium ammonium phosphate and titrated the precipitate with EDTA, but the method is unattractive Previously, an extensive examination[10] of this method (and of the determination of arsenic after precipitation as magnesium ammonium arsenate) had been made in these laboratories in order to have a general titration procedure based on EDTA It was concluded that the method is too tedious on either the micro or semimicro scale, owing to the well-known difficulties associated with this precipitate.

Several organic bases have been suggested to replace the ammonium ion in the phosphomolybdate precipitate The most promising method, that of Wilson, uses quinoline,[11] when the precipitate is evaluated titrimetrically, the theoretical factor is applicable. The use of quinoline phosphomolybdate in organic analysis was suggested by Belcher and Godbert,[12] but so far it has only been applied[13] after decomposition of the organic material in a peroxide bomb and the determination was completed by the original method of Wilson Fernlund *et al* [14] applied a modified Wilson method to the determination of phosphorus in steels and later recommended[15] a single reagent solution and a rapid precipitation and filtration technique. We have examined this method on pure solutions with entirely satisfactory results and have successfully employed it for the analysis of organic compounds after burning the sample in the oxygen flask.

Application to organic compounds

The main problem in achieving an accurate method for organic compounds lay in finding a suitable absorption solution. To avoid later neutralisation complications, the first tests were made absorbing in 0 2*N* hydrochloric acid containing potassium chlorate; reasonable results were obtained for triphenylphosphate, but triphenylphosphine gave rather low recoveries Obviously, the phosphorus was not completely converted to phosphate by the combustion unless it was originally present in the phosphate form, and an oxidising absorption solution was necessary Nitric acid[9] or hydrogen peroxide solutions were ineffective but a solution of sodium hypobromite proved satisfactory for all the compounds encountered except quinine hypophosphite; this was an isolated case which would require special treatment (see later) When an aqueous solution of bromine was used, nearly all the bromine was removed from the solution by the rapid flow of oxygen required to sweep the flask before the combustion, hence the alkaline solution was preferred

In preliminary tests, we found very high recoveries which were caused by the attack of phosphorus pentoxide on the walls of the flask The silica thus formed naturally interfered with the usual quinoline phosphomolybdate procedure; this could be avoided by the addition of a small amount of citric acid [11] It was important not to add too much citric acid, otherwise a slight attack on the phosphomolybdate precipitate occurred

The method has been used to analyse a wide variety of different compounds. Typical results are shown in Table I. The average deviation from the theoretical on a consecutive series of twenty analyses using different batches of reagent was 0 16% with a maximum error of 0 31% The other acidic elements likely to be found in organic compounds do not interfere

Application to fluorine-containing compounds

When compounds containing fluorine were burnt, the attack on the flask wall was increased and high results were obtained. The addition of boric acid to the alkaline absorption solution would not complex the fluoride ion and appeared to interfere with complete absorption of phosphorus pentoxide. However, satisfactory results were obtained when boric acid was added after the flask had been opened and the amount of citric acid added was increased slightly Boric acid itself does not interfere with the precipitation.[11] A uniform addition of citric and boric acids gave good results for a range of compounds containing widely different percentages of fluorine The accuracy of this procedure was as good as that obtained with unfluorinated materials. Typical results are given in Table II.

The method is very suitable for routine use, for the precipitation and titration are carried out in the combustion flask. One determination can be completed in 30 minutes and four can be done in one hour The accuracy of the method is similar to that of the much longer standard procedures. The only compound encountered which failed to yield its phosphorus quantitatively as phosphate was

TABLE I

Compound	Amount taken (mg)	% P found	% P (theor.)
Triphenylphosphate (4 results)	3·5–5·5	9·47 ± 0·17	9·52
Triphenylphosphine (3 results)	4·5–7	11·83 ± 0·14	11·82
β-Aminoethyldiphenylphosphate-picrolonate	4·449	5·83	5·55
β-Ethylaminoethyldiphenylphosphate picrolonate	5·092	5·37	5·29
Piperazine-*bis*(diphenylphosphate)	3·965	10·44	10·6
Diphenylphosphorodicyanodimidate	7·008	9·82	9·80
N,N′-*bis*(Diphenoxylphosphinyl)-ethylenediamine	4·370	11·55	11·81
5-Chloro-4-hydroxy-3-methoxy-benzylisothiouronium phosphate	6·531	8·70	8·99

quinine hypophosphite. Possibly some phosphorus remains as hypophosphite, which is notoriously difficult to oxidise, for better recoveries were obtained when longer standing times in contact with the hypobromite absorption solution were used; but the results were sometimes low even after 60 minutes standing time. Complete oxidation might occur if the oxidation were allowed to proceed overnight, but this would detract from the main advantage of the method, which is its speed of operation.

The main disadvantage of the procedure lies in the preparation of the single reagent solution. We have found that some batches of sodium molybdate and molybdic trioxide yield a heavy precipitate of molybdic acid after standing overnight. In our opinion, the effort involved in obtaining a satisfactory batch of molybdic trioxide is well worth-while, for the procedure with the single reagent solution is much simpler and faster than when the quinoline and molybdate solutions are added separately. The single reagent solution is stable for 7–10 days after mixing. Its two parts are stable for at least one month when stored separately; appropriate amounts are then mixed, left overnight and filtered before use.

Some preliminary experiments indicate that a similar quinoline molybdate procedure may be suitable for the determination of arsenic.[17] The iodimetric method was tried first, but somewhat variable results were obtained. It is well-known that conditions for the successful operation of this method are critical;[12] the results with quinoline molybdate are more promising and further work with this reagent is proceeding.

EXPERIMENTAL

Apparatus

A 250-ml flask is equipped with a ground-glass stopper through which is fitted a strong platinum wire (6–8 cm long). A piece of strong platinum gauze (2 × 1·5 cm) is attached to the wire so that it hangs 4–5 cm above the base of the flask and can be squeezed together to clasp the sample

TABLE II

Compound	Amount taken (mg)	% P found	% P present	% F present
$C_3F_7CH_2OPO(NHC_6H_5)_2$	4·576	7·00	7·20	30·9
$(C_3F_7CH_2O)_2PONHC_6H_5$	5·575	5·82	5·77	49·1
$CF_3C_6H_4P(C_2H_5)_2\ CuI$	4·059	7·12	7·29	13·42
$CF_3C_6H_4P(C_2H_5)_2\ HgBr_2$	6·856	5·47	5·20	9·57
$(CF_3C_6H_4P(C_2H_5)_2)_2AgI$	5·059	8·66	8·81	16·21

Quinoline molybdate solution

Dissolve 150 g of AnalaR molybdenum trioxide and 30 g of AnalaR sodium hydroxide in 500 ml of distilled water by heating for 30 minutes. Filter and add 460 ml of concentrated hydrochloric acid and 1–2 drops of 100-vol hydrogen peroxide to clear the greenish-blue colour Dissolve 28 ml of distilled quinoline in 600 ml of 1 1 hydrochloric acid Pour together, boil briefly, leave overnight and filter into a polythene bottle.

Procedure

Weigh 3–6 mg of the sample on to a piece of filter paper (2 5 × 2 5 cm) with a 3-cm length of paper projecting as a fuse.[5] Fold the paper and fix it between the platinum gauze so that part of the paper and all the fuse lies outside the gauze

Place 5 ml of *ca* 0 5*N* sodium hydroxide and 4 ml of saturated aqueous bromine solution in the 250-ml flask and fill the flask with oxygen Light the paper fuse, quickly insert the stopper and invert the flask, holding both flask and stopper firmly. After the combustion has finished (5–10 seconds), shake the flask for 10 minutes, or for 2–3 minutes after the cloud of phosphoruspent oxide has disappeared Open the flask, rinse down the stopper and gauze with about 5 ml of water, and heat to boiling. If fluoride is present, add 200–300 mg of boric acid Then add 2 5 ml of *ca.* 1*N* hydrochloric acid to neutralise the solution, pouring the acid through the gauze which is then rinsed with a little water The volume of the final solution should not be greater than 20 ml. Boil gently to remove most of the bromine and add 70–90 mg of citric acid. If the compound contains fluorine, add 2 ml of a freshly prepared 10% citric acid solution instead of the solid citric acid. Precipitate by adding 5 ml of quinoline molybdate solution from a fairly fast-flowing pipette while swirling the hot solution Again boil briefly and then leave to cool for a few minutes. The time of standing is unimportant

Filter through a paper pulp pad (1–1 5 cm thick) supported on a Witt plate[16] and wash the flask thrice with 5-ml portions of water (washing with hydrochloric acid is unnecessary in the presence of citric acid[11]) Then wash the precipitate and filter until the washings are neutral to litmus paper Transfer the pad and precipitate quantitatively to the original flask, add an excess of standard 0 1*N* sodium hydroxide, close the flask and shake well. Rinse down the stopper and flask walls and back-titrate with standard 0 05*N* hydrochloric acid using phenolphthalein indicator.

1 ml of 0 1*N* NaOH corresponds to 0 119 mg of phosphorus

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BOOK REVIEWS

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Those interested in the practical applications of complexometric titrations will be more concerned with the second part of the book In this, an introductory paragraph lists the more important solutions, reagents, buffers and the like, giving precise procedures for their preparation, storage, etc The descriptions of the detailed procedures for titration of a wide variety of cations and anions are very clear Most of the individual descriptions are followed by additional comments which direct the reader's attention to matters which may be important for the application of that particular method

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NOTICES

Second Conference on Analytical Chemistry in Nuclear Reactor Technology

(*Gatlinburg, Tennessee, September* 29, 30 *and October* 1, 1958)

THE Oak Ridge National Laboratory has announced that the Second Conference in a series of unclassified meetings on the role of Analytical Chemistry in Nuclear Reactor Technology will be held in the Civic Auditorium at Gatlinburg, Tennessee, on September 29, 30 and October 1, 1958 This meeting is a continuation of the first conference which was also held at Gatlinburg in November 1957. A brief news account of the discussions which took place at that meeting was reported in the December 1957 issue of *Analytical Chemistry.*

At the first conference the subject matter of the papers dealt specifically with a review of recent developments in the analytical chemistry of important reactor materials. At the forthcoming conference, it is intended to continue these discussions, but only with respect to those facets of analytical chemistry which relate specifically to analyses which are required before the start-up of nuclear reactors and during reactor operations. Analytical chemistry as it pertains to post-operational activities is believed to be a matter of sufficiently broad interest and scope to warrant the holding of separate, future conferences on this aspect alone

Two 3-hour sessions of technical presentations will be held each day during the three-day conference The last hour of each session, except that on Tuesday morning, will be devoted to panel discussions of the respective subject matter of those sessions The panel discussion on Tuesday will be held during the last hour of the afternoon session and will be concerned with the subject matter of the entire day

It is intended that the programme will be contributory and any worker in the field who feels that he has some worthwhile contribution to offer is encouraged and invited to participate in the programme Papers of any length which may require up to 30 minutes for presentation will be considered. Abstracts of approximately 200 words are asked for by July 1. Publication of the proceedings is intended and copies of all manuscripts received before October 1 will be included in the publication.

The tentative programme is as follows:

MONDAY, SEPTEMBER 29

Registration

Morning Session

Particle-size analyses of reactor fuels intended for use in slurry-type reactors

Afternoon

Open

Evening Session

Applications of instrumentation in the analytical chemistry of nuclear reactor technology

TUESDAY, SEPTEMBER 30

Pre-operational Methods of Analyses

Morning and Afternoon Sessions

Devoted to a discussion of analytical chemistry, including research, development and operational problems, on reactor materials and components in their broadest aspects These reactor components and materials include such items as fuels, moderators, coolants, reflectors and structural materials for all types of reactors.

Evening

Dinner and an informal get-together

WEDNESDAY, OCTOBER 1

Analytical Chemistry During The Operational Stage of Reactors

Morning Session

Radiochemical methods of analysis

Afternoon Session

Remote control analyses

The distinction between radiochemical methods of analysis and remote control analyses is intended to mean that those methods of analysis which must be performed by the manipulation of automated devices, particularly in hot cells, fall in the latter category, whereas other papers on the analysis of radioactive materials will be included in the first session as ordinary radiochemical methods of analysis.

For further information concerning the details of this meeting and for the submission of contributions and abstracts of papers, please write to C. D Susano, Oak Ridge National Laboratory, P.O. Box Y, Oak Ridge, Tennessee, U.S A.

For reservations and other accommodation, please contact Mr Tom Woods, Manager, Mountain View Hotel, Gatlinburg, Tennessee, U S A.

International Symposium in Microchemistry, 1958

(Organised by the Midlands Sections and the Microchemistry Group of the Society for Analytical Chemistry. Under the patronage of the International Union of Pure and Applied Chemistry)

THE provisional programme of the International Symposium in Microchemistry, which is to be held in Birmingham University from 20th August to 27th August inclusive, refers to four plenary lectures, by Professor Dr Ing Fritz Feigl (Brazil), Professor Dr. H Leib (Austria), Professor A A Benedetti-Pichler (U S.A) and Dr. R. Belcher (U.K) Demonstrations and discussion periods have been arranged, and the programme includes the following papers

Analytical Problems in the Electrical Industry The Application of Micro Techniques—R C Chirnside

Solvent Extraction Methods in the Determination of Trace Metals—F. Hecht

Rapid Methods of Micro-titration of Halogens and Sulphur in Organic Compounds—R Levy

Determination of Sulphur and Halogens—W. J Kirsten

The Micro-determination of Nitrogen by a Simple Modification of the Pregl-Dumas Method, and some Observations on Methane as a Source of Error—A F. Colson

Radio-isotopes in Microbiochemical Research—F P. Winteringham

Determination of Trace Elements in Semi-conductors—J A James

The Determination of Minute Amounts of Fission Product Activity in Waters and Biological Materials F J Bryant, G S Spicer and R G D Osmond

Micro-identification of Organic Compounds, with particular attention to Biological Systems—N D. Cheronis

Recent Developments in the use of the Ring Oven—H Weisz

Practical Applications of Chemical Microscopy—Philip W West

Current Trends in Infra-red Structural Analysis—L J Bellamy and R L Williams

Atomic Absorption Spectroscopy—A C Menzies

Flame Photometry using Micro Samples and Micro Concentrations—F Burriel-Martí

Separation of Fission Products by Ion-exchange on Micro Columns—I G. Swainbank and E. A. C. Crouch

Polarography in Microchemistry—G Semerano

Application of the Overtone Region in Chemical Analysis—H A Willis
Quantitative Analysis in the Infra-red—A. R. Philpots and W F. Maddams
Some Theoretical Considerations of the Separation of Copper–Cadmium–Bismuth with Butanol–Hydrochloric Acid—M Lederer and J A Coch-Frugeni
The Chromatography of the Larger Molecules—S. G. Tudor Jones
Polarographic Micro-analysis in Reaction Kinetics—P. Zuman
Polarographic Micro-analysis by an Oscillograph Method—Kalvoda
Functional Group Determination on the Micro Scale—T. S Ma
Specific and Selective Analytical Reagents—F. J. Welcher
Microbiological assay of Antibiotics, Vitamins and Amino Acids—D. C. M. Adamson and J. S. Simpson
The Use of Micro-organisms for Determining Trace Metals in Biological Materials—D J. D. Nicholas
The Microbiological Assay of Protein Quality—G. D. Rosen
Survey of Methods useful in Functional Group Determination of Organic Substances—S. Veibel
Organic Functional Group Analysis, Particularly Referred to the Alkoxyl Determination—W. I. Stephen
A Short Survey of all Applications of the Thermo-balance—C Duval
Microchemical Balance Accuracy—G F. Hodsman
Errors in Weighing not Inherent in the Balance—M. Corner
Some Observations on Organic Analysis—J. Haslam
Some Problems in Industrial Inorganic Micro-analysis—C. Whalley
Microdetermination of Hydrogen by a Galvanic Method—P. Hersch
Microdetermination of Physical Constants—M. Sobotka
Micro-heterometric Analysis and the Micro-heterometric Study of Chemical Reactions—M. Bobtelsky
The Determination of Nitrate by Dead-stop Titrimetry—A. F Williams
The Titrimetric Finish of Chromatographic Spots—A. Lacourt
Compulsory Microanalytical Teaching—C. J. van Nieuwenbuerg
Standardization of Apparatus and Methods—A Steyermark
New Chelating Agents and Metal Indicators—G. Schwarzenbach
The Present State of Chelatometry in Czechoslovakia—R Přibil
New Reagents in Complexometric Analysis—T. S. West
The Problem of Selectivity of Complexometric Titrations—H. Flaschka
The Teaching of Organic Microchemistry—M. K Zacherl

The Symposium Secretary is Mr. W. T. Elwell, F R I C , I C I (Metals Division) Ltd., P.O Box No. 216, Research Department, Kynoch Works, Witton, Birmingham 6, England.

Talanta, 1958, Vol 1, pp 195-196, Pergamon Press Ltd, London

BOOKS RECEIVED

Qualitative Inorganic Analysis G Charlot, translated by R C Murray. Methuen, London, 1954 pp. xi + 354. 42s

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—I

THE STATUS OF CHLORAMINE-T AS A TITRIMETRIC REAGENT

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(*Received* 3 *March* 1958)

Summary—The behaviour of Chloramine-T as a titrimetric reagent is fully discussed. Methods of standardising solutions of the reagent have been critically examined.

MANY papers have appeared on the applications of chloramine-T in titrimetry since Noll[1] first advocated its use, but this literature is marred by vagueness, discordance and uncertainty, which are reflected in the standard textbooks, even in the latest reference text.[2] Aside from the lack of good visual indicators, only one of which has been checked potentiometrically,[3] and the inadequate investigation of conditions with those which have been proposed, dissatisfaction with published accounts of the reagent arises in several ways:

(*a*) the purity of the reagent is usually either unspecified or assumed to be 100%;
(*b*) ambiguity arises because of sparse and often vague experimental detail, and the range of conditions investigated is often narrow, giving rise to apparent contradiction between accounts;
(*c*) the absolute accuracy of the determination of many substances is uncertain, because methods of standardisation or purification are not given, and the specification of the reagents and their treatment in solution preparation is omitted;
(*d*) the hydrolysis of chloramine-T is often incompletely described, so that chloramine-T and hypochlorite solutions are regarded as completely similar in properties.

These matters will be illustrated where appropriate, but point (*d*) may be further discussed. The tacit assumption follows from this that chloramine-T may be substituted directly for hypochlorite; or for bromate in the presence of bromide, iodate in the presence of iodine monochloride, or iodine in the presence of iodide. Though these substitutions are often possible, and the indicators used with the original reagent may be applicable to chloramine-T, this is by no means invariably the case. For example, chloramine-T cannot be substituted for bromate in the determination of hydrazine, hydroxylamine, antimony^{III} or thallium^{I}.

It is commonly stated[2] that chloramine-T hydrolyses in water to *p*-toluene sulphonamide and sodium hypochlorite (1) (the *p*-toluenesulphonyl—part of the molecule $CH_3C_6H_4SO_2$—is designated by the symbol R—),

$$RNClNa + H_2O \rightleftharpoons RNH_2 + NaOCl \qquad (1)$$

Obviously the latter will then ionise and, except in alkaline solution, the hypochlorite

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* Present address: S.E.R.L., Baldock, Herts.

ion will hydrolyse to hypochlorous acid, which is then taken to be the reacting species, giving rise to the assumptions noted above.

The present work, and that of Soper,[4] Dietzel and Taufel[5] and Morris *et al.*[6] indicate that quite different equilibria are set up in the hydrolysis. Chloramine-T is the sodium salt of the acid *p*-toluenesulphon-N-chloramide, which is a fairly strong acid, since the salt is very little hydrolysed in solution; the pH of a 0·05*M* solution is 7·7, giving an apparent value for the ionisation constant of $2{\cdot}38 \times 10^{-3}$. Though the acid has not been isolated, there is ample evidence[4,6,7] for its existence in solution. The salt is a strong electrolyte which first dissociates:

$$\mathrm{RNClNa} \rightleftharpoons \mathrm{RNCl^-} + \mathrm{Na^+} \tag{2}$$

The anion then takes up hydrogen ion to form the free acid:

$$\mathrm{RNCl^-} + \mathrm{H^+} \rightleftharpoons \mathrm{RNHCl} \tag{3}$$

which disproportions to give *p*-toluenesulphonamide and sparingly soluble dichloramine-T:

$$2\mathrm{RNHCl} \rightleftharpoons \mathrm{RNCl_2} + \mathrm{RNH_2} \tag{4}$$

The equilibrium constant[6] for the disproportioning is $6{\cdot}1 \times 10^{-2}$. The dichloramine-T and the free acid hydrolyse:

$$\mathrm{RNCl_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{RNHCl} + \mathrm{HOCl} \tag{5}$$

$$\mathrm{RNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{RNH_2} + \mathrm{HOCl} \tag{6}$$

The hydrolysis constants for these two reactions[4,6] are 8×10^{-7} and $4{\cdot}88 \times 10^{-8}$; hydrolysis is therefore slight. Finally the hypochlorous acid ionises, K_a being $3{\cdot}3 \times 10^{-8}$.

The disproportioning (4) is not itself hydrogen ion-dependent, but formation of the dichloramine-T (the white precipitate formed on acidifying chloramine-T solution) depends on the prior formation of the free acid (3) which is hydrogen ion-dependent, and significant amounts of the dichloramine-T are formed in moderately or strongly acid solution. First-approximation calculations based upon a decinormal (0·05*M*) solution of chloramine-T indicate the order of the concentrations of the various species present at various pH values (Table I), and show that in strong acid medium the free acid and dichloramine predominate, but as the pH rises the anion of the acid assumes importance, reaching predominance in weak acid or neutral solution. Even in weakly alkaline medium the acid anion predominates over hypochlorite; hypochlorous acid maintains a constant concentration throughout the range.

Though hypochlorous acid, or even hypochlorite ion, may be the reactive species in chloramine-T oxidations, it is reasonable to suppose that the species present in greater concentration should react directly, and that such reactions should differ in certain circumstances from those of hypochlorous acid or hypochlorites. Certain dissimilarities have been recorded in the past,[8-10] and others will be reported in due course. Thus chloramine-T even in strong acid medium has feeble oxidising powers in the absence of added halides, and fails to react in the presence of chloride at pH values greater than 1, but will react in the presence of bromides up to pH 5 and in

TABLE I. CONCENTRATIONS OF VARIOUS SPECIES PRESENT IN A 0·05M CHLORAMINE-T SOLUTION OVER A RANGE OF pH VALUES

pH	$[RNCl^-]$	$[RNHCl]$	$[RNCl_2] = [RNH_2]$	$[HOCl]$	$[OCl^-]$
0	$9{\cdot}6 \times 10^{-5}$	$4{\cdot}01 \times 10^{-2}$	$9{\cdot}9 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-14}$
1	$9{\cdot}6 \times 10^{-4}$	$4{\cdot}01 \times 10^{-2}$	$9{\cdot}9 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-13}$
2	$7{\cdot}8 \times 10^{-3}$	$3{\cdot}24 \times 10^{-2}$	$7{\cdot}98 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-12}$
3	$2{\cdot}83 \times 10^{-2}$	$1{\cdot}18 \times 10^{-2}$	$2{\cdot}92 \times 10^{-3}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-11}$
4	$3{\cdot}84 \times 10^{-2}$	$1{\cdot}60 \times 10^{-3}$	$3{\cdot}95 \times 10^{-4}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-10}$
5	4×10^{-2}	$1{\cdot}67 \times 10^{-4}$	$4{\cdot}1 \times 10^{-5}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-9}$
6	4×10^{-2}	$1{\cdot}67 \times 10^{-5}$	$4{\cdot}1 \times 10^{-6}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-8}$
7	4×10^{-2}	$1{\cdot}67 \times 10^{-6}$	$4{\cdot}1 \times 10^{-7}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-7}$
8	4×10^{-2}	$1{\cdot}67 \times 10^{-7}$	$4{\cdot}1 \times 10^{-8}$	$3{\cdot}95 \times 10^{-7}$	$1{\cdot}3 \times 10^{-6}$

the presence of iodides up to pH 9. It would thus appear to be virtually restricted to oxidation of halides, except perhaps in strong acid solution.

No matter how the reduction of chloramine-T is formulated, two electrons and two hydrogen ions are consumed per initial molecule of reagent, so that its equivalent is always the same, and the final products after completion of the reaction (other than the decompositive oxidation of the reagent molecule by itself to form acidic compounds[5]) are *p*-toluenesulphonamide and chloride ion. Nevertheless, formulation through the more probable reacting species safeguards against misconstruction. In strong acid solution the free acid and dichloramine predominate and may react directly:

$$RNHCl + H^+ + 2e^- = RNH_2 + Cl^- \tag{7}$$

$$RNCl_2 + 2H^+ + 4e^- = RNH_2 + 2Cl^- \tag{8}$$

It is notable that chloramine-T in the presence of chloride fails as an oxidant when the free anion $RNCl^-$ begins to predominate; the reactions of this ion may be limited to oxidation of bromide or iodide to free halogen:

$$RNCl^- + 2H^+ + 2e^- = RNH_2 + Cl^- \tag{9}$$

The occasional behaviour of chloramine-T at variance with the reactions of hypochlorites, and the general uncertainty as to conditions and quantitativeness of its reactions led to a detailed examination of the reagent with a view to resolving the uncertainties and ambiguities, searching for new indicators, developing its applications, and establishing with certainty its status as a standard titrimetric oxidant.

At first sight, chloramine-T offers many attractive features. It is cheaply and readily available in reasonable purity as a by-product of saccharine manufacture. It may be purified by simple crystallisation, and is neither hygroscopic nor efflorescent, so being susceptible of direct weighing in the preparation of solutions. It has a high equivalent weight. Hypochlorites, hypochlorous acid and monochloramine (NH_2Cl) effect many useful oxidations, but are difficult to prepare and purify, and cannot be obtained as pure solids. Chloramine-T (or its homologue chloramine-B) appear to offer a very convenient substitute in a solid weighable form for these reagents, and for the more expensive iodine, iodate and bromate. Against this, the presence of three molecules of water of hydration in the solid render it suspect as a primary standard. To establish its status firmly it is necessary to ascertain whether it can be prepared in a purity closely approaching 100%, or, if not, whether a reproducible purity can be attained in a simple fashion; and, in the latter case, whether solutions can readily be standardised with a high degree of accuracy. The stability on storage of the solid and solution must also conform to the requirements of a standard reagent. Once these points are settled, attention can be turned to the applications.

TABLE II.—PURIFICATION OF COMMERCIAL CHLORAMINE-T BY RECRYSTALLISATION FROM WATER

	% Purity of solid chloramine-T trihydrate. Assay precision ±0·03%
Original sample	98·50
Original sample stored 10 weeks in open dish	98·48
After first recrystallisation	99·14
After second recrystallisation	99·55
After third recrystallisation	99·54
After fourth recrystallisation	99·55

PURIFICATION OF CHLORAMINE-T

Recrystallisation from water is generally adopted,[1,4,6,11–16] and the crystals are dried either in air or in a vacuum desiccator. Many authors assume the commercial pure grade to be 100% pure; of those quoted, some assume that the product of crystallisation is pure, others[12,16] claim it to be, but others make no such claim. Determination of total chloride, as by Morris,[6] may give a figure in agreement with theory, but since the principal impurities are sodium chloride and *p*-toluenesulphonamide, this can be misleading.

Large scale successive crystallisations from conductivity water increased the purity to 99·5%, but further recrystallisations gave no further improvement (Table II). Repetition of the recrystallisation of the sample of 99·5% purity from (*a*) 0·01*M* sodium hydroxide, (*b*) 0·01*M* sodium hypochlorite, freshly prepared at 0° and free from chlorate, (*c*) a combination of (*a*) and (*b*), (*d*) 0·1*M* sodium chloride, and (*e*) a combination of (*c*) and (*d*), gave no significant improvement.

An anhydrous compound is more acceptable as a standard, so attempts were made to dehydrate the trihydrate. Heating in an air oven above 40°, or on a water or steam bath, produced a sintered yellow substance, believed to be dichloramine-T, which decomposed on further heating. At higher temperatures this decomposition is violent, becoming explosive at 120°. Dehydration over sulphuric acid indicated some stability of a dihydrate, but further dehydration led to the gradual formation of the yellow substance. Complete removal of water could not be effected over sulphuric acid. Rehydration in a hygrostat of the fine powder produced by dehydration was unprofitable, as the material continued to absorb water in excess of $3H_2O$.

Samples of a high and reproducible purity can therefore be prepared by recrystallisation, but the maximum attainable purity is inadequate for a primary standard. Though the 0·5% deficiency may perhaps be largely moisture, there is no simple method of removing this without decomposing the trihydrate. The hopes, based on earlier optimistic reports of the purity of the reagent, that chloramine-T might be a useful addition to the range of primary standards are not fulfilled.

TABLE III. STABILITY OF SOLID CHLORAMINE-T
STORED IN BROWN GLASS SCREW CAP BOTTLE EXPOSED TO DAYLIGHT

Time of exposure, months	% Purity of sample (precision ±0·03%)
0	99·18
10	99·06
19	98·86

STABILITY OF CHLORAMINE-T

Chloramine-T in all its forms has been shown to be unstable to heat, and unstable on storage in any but the trihydrate form, which is neither effloresecent nor hygroscopic. There are conflicting reports[5,8,17,18,19] on the stability of chloramine-T in the solid state. The most significant work is that of Dietzel and Taufel,[5] who report a decline in assay of 1·4% in 12 months on storage in brown glass, and 5% in clear glass.

Storage in a brown glass screw cap bottle on an open shelf in these laboratories caused a decline in strength of only 0·02% per month, as indicated in Table III. Stored in clear glass, the contents close to the glass wall on the sides facing the windows darkened to a pale creamy yellow colour, and samples from this region showed a decline in strength of 5–7% in 12 months, though samples from the interior of the bottle were little affected. Protected from sunlight by storage in brown glass, therefore, chloramine-T in the solid state is of admirable stability.

Stability in solution has been examined,[1,3,5,11,14,18–24] and, while there is some agreement that solutions exposed to sunlight are unstable,[3,11,25] and that solutions protected from daylight hold their titre well enough for four weeks, there is considerable disagreement over longer term stability.[1,3,5,11,20,21,22,24] For example, Komarowski *et al.*[21] report a loss of titre of 1·3% in 4½ months, while Poethke and Wolf[20] claim a loss of less than 0·1% in the same period.

To settle this point, five two-litre batches of 0·05*M* chloramine-T solution were prepared, standardised, and stored in winchester bottles fitted with polythene screw caps. Four of the bottles were of brown glass, and one of clear glass. Three of the brown glass bottles (solutions I, II and III) were stored in a cupboard and the contents analysed at intervals. Solution IV in brown glass and solution V in clear glass were stored side by side on an open laboratory shelf, and similarly analysed at intervals. The results given in Table IV show that storage in darkness or daylight makes no difference so long as the solution is stored in brown glass. Only after 5 months is any change perceptible, in agreement with Poethke and Wolf, while the loss in one year is only 0·5%. Exposure to daylight, however, causes an immediate and continuous drop in titre; 0·4% in the first week, and nearly 20% in one year. Solutions stored in brown glass remained perfectly clear, and there was no detectable change

TABLE IV.–THE STABILITY OF CHLORAMINE-T IN AQUEOUS SOLUTION

(*a*) SOLUTIONS STORED IN BROWN GLASS WINCHESTERS IN THE DARK

Length of storage, months	Factor of 0·05*M* Chloramine-T solution		
	Solution I	Solution II	Solution III
0	0·989	1·007	1·011
9	0·986	1·004	1·005

(*b*) SOLUTION IV STORED IN BROWN GLASS, SOLUTION V IN CLEAR GLASS, EXPOSED TO DAYLIGHT ON LABORATORY SHELF

Length of storage	Factor of 0·05*M* Chloramine-T solution	
	Solution IV	Solution V
0 weeks	1·005	1·005
1 week	1·005	1·001
2 weeks	1·005	0·997
3 weeks	1·005	0·992
4 weeks	1·005	0·989
6 weeks	1·005	0·985
3 months	1·005	0·970
5 months	1·004	0·947
7 months	1·002	0·904
9 months	1·001	0·859
12 months	1·000	0·811

in pH from the initial value of 7·7. In clear glass, the solution soon became cloudy. This precipitate was not the same as the dichloramine-T thrown down in acid solution, and the pH fell to 5·6 over 12 months, giving support to the contention of Dietzel and Taufel[5] that the photochemical, self-oxidation decomposition products are acidic in nature.

Though chloramine-T is unstable in direct daylight, brown glass vessels afford sufficient protection to permit of storage of the reagent both in the solid state and in solution, and the stability over periods of three months or more is sufficient to meet the requirements of a standard reagent.

STANDARDISATION OF CHLORAMINE-T SOLUTION

The principal methods advocated for the standardisation are:

(a) titration against standard arsenic^{III} solution in bicarbonate buffer in the presence of a small amount of iodide, with starch as indicator,[1,3,12,13,21,25–29]

and

(b) titration with thiosulphate of the iodine liberated on addition of potassium iodide to an acidified chloramine-T solution, again with starch as indicator.[1,13,17,21,23,27,28,30,31]

Descriptions of these methods are somewhat vague,[2] conditions are ill-defined, and details of the influence of the nature or concentration of the buffer or acid, or the amount of iodide used are lacking. No simple method is available for standardisation against arsenic^{III} in acid solution.

1. *Standardisation through arsenic*^{III}

A very thorough investigation of the chloramine-T-arsenic^{III} reaction, from which optimum conditions for the present methods were selected, has been made and will be reported later; only the special investigation relevent to standardisation will briefly be recounted here. Direct standardisation is possible if arsenious oxide of a suitable grade is available, or, since the highest precision and accuracy are attainable with the bromate-arsenic^{III} reaction,[32] and the iodate–arsenic^{III} reaction is accepted as being of a similar calibre,[33] chloramine-T may be standardised against bromate or iodate through arsenious oxide.

(a) *In acid solution.* Though arsenic^{III} has been titrated in acid media of uncertain concentration at unspecified temperatures,[3,20,25] no recommendations for a standardisation appear to have been made, probably because of the dearth of suitable indicators. Since rosaniline hydrochloride, a sensitive specific reagent for free bromine,[34] has proved eminently satisfactory in bromate titrimetry,[32,34] having an excellent and very sharp, though irreversible, colour change from pale yellow to bright purple and a negligible indicator error, it was thought that this reagent would prove useful in chloramine-T titrations in acid solution in the presence of bromide. Such is the case,[7,35] and a precise standardisation procedure on this basis is proposed. Replicate titrations on 50-ml aliquots of 0·05M arsenic^{III} solution by this method gave factors for a 0·05M chloramine-T solution of 1·053, 1·053, 1·053.

The effect of acid concentration. This was examined by holding the bromide concentration constant at 0·1M and varying the end-point hydrochloric acid concentration from 0·1 to 3·0M in small steps. The results replicated perfectly in complete agreement with the standardisation up to 2·5M and the end-points between 0·5M and 2·5M were sharp and pleasing. At 3·0M the colour change became sluggish and 0·15% late, while in 0·1M the acid concentration is insufficient to convert the magenta colour of the free rosaniline base into the yellow ionic form of the hydrochloride, though the end-point is still easily seen.

Effect of bromide concentration. The bromide concentration controls the bromine/bromide potential, and hence the effective oxidation potential of the system. In 2M hydrochloric acid, increasing the potential by reduction of the bromide concentration to 0·01M does not affect the sharpness or accuracy of the titration. Potentiometrically, the position of the end-point is unaltered by the same change, but the magnitude of the potential jump is increased from 200 to 260 mV in agreement with theory.

End-point concentrations of 0·01 to 0·1M bromide and 0·5 to 2·5M hydrochloric acid yield equally precise and accurate results using rosaniline hydrochloride as indicator. The preference for 2M hydrochloric acid and 0·1M bromide is based upon general felicity of titration and quality and character of end-point.

(b) *In "neutral" solution.* As will be shown in a later paper, the reaction between chloramine-T and arsenic^{III} is dependent on the generation of free halogen as an intermediate oxidant. In solutions of pH greater than 4, this intermediate is specifically iodine, and the reaction is essentially that between iodine and arsenic^{III}. Iodine oxidises arsenic^{III} quantitatively in neutral solution, but the potential of the As^{V}/As^{III} system increases with increasing hydrogen ion concentration, while iodine/iodide is unaffected, and there comes a point, about pH 4 when the reaction is no longer quantitative. Care must therefore be taken to ensure that the pH of the solution remains high enough to ensure quantitative reaction. The chloramine-T reaction producing the iodine consumes hydrogen ion; nevertheless, starting in neutral unbuffered solution, as is often suggested,[2] it will produce sufficient arsenic acid to run the pH below the quantitative limit, even discounting the net increase in hydrogen ions of reaction which may occur. A buffer medium is therefore essential. The permissible variation of pH does not seem to have been investigated.

The amount of iodide to be used is variously described as a little, a crystal, a small crystal, a pinch, etc., of potassium iodide, or a few drops of unspecified strength of solution. Only very seldom is any actual amount specified.[2] Preliminary irritating experience of these directions showed that if too little were used the appearance of the blue starch colour was subject to an induction period of anything from a few seconds to 24 hours, or did not occur at all; and too much iodide gave sluggish or premature end-points. It appeared that sufficient should be used to cause a blue colour to be formed momentarily during titration, when presumably an imperceptible amount of the starch complex remained to catalyse the reaction and remove the induction period.

A method is therefore proposed in which conditions are fully specified. Replicate titrations of 50-ml aliquots of a 0·05M arsenic^{III} solution by this method gave factors for a 0·05M chloramine-T solution of 1·053, 1·053, 1·053, in complete agreement with the method in acid solution using rosaniline as indicator.

Influence of conditions. Titrations at lower pH values than that of the bicarbonate buffer (or in higher iodide concentrations than those recommended) are disturbed by the slowness, or even incompleteness with which iodine, formed by local excess of titrant and complexed with starch, reacts with the arsenic^{III}, so tending to give low titration figures. The iodine/iodide potential is controllable by the iodide concentration, and by reducing the latter the iodine must be generated at a higher potential and should therefore react more quickly with the arsenic^{III}. By the same token, reducing the iodide concentration should extend to a lower pH the range over which the reaction is quantitative. At the upper end of the pH range, hypoiodite may be formed which will not react with starch or arsenic^{III}, giving rise to high titration figures, but by increasing the iodide concentration, this hydrolysis should be inhibited, thus extending the quantitative range to higher pH values. Investigation revealed evidence for the truth of these arguments.

Variation of iodide and buffer concentration in bicarbonate buffer. Titrations in iodide concentrations of 0·0005M to 0·05M, and in buffer concentrations of 0·2 to 0·4M gave uniformly accurate results (Table V), but in 0·0005M the colour change was very sluggish.

Variation of iodide concentration in various buffers. Results in Table VI of titrations in various buffers of pH 2·4 to 9·9 show that, as predicted, appropriate control of iodide concentration allows extension of the range over which quantitative reaction occurs, but there is no advantage to be gained in using buffers other than bicarbonate, particularly when the iodide concentration range is most convenient in this medium.

Quantitativeness of the reaction. Although the results by the two very different methods are in entire agreement, there is still a possibility that both reactions are incomplete to the same small extent. This lingers from the claims in the literature about the purity of chloramine-T, in contrast to the maximum assay of 99·5% by the rosaniline method. The reaction may become quantitative only with excess reductant, and, since this is the condition under which many analytical determinations finish, it is important to have a decision on this point. Since the bromate–arsenic^{III} reaction in acid solution is known to be quantitative,[32] addition of an aliquot of chloramine-T to an excess of arsenic^{III}, followed by titration of the excess by bromate should show whether consumption of arsenic^{III} by chloramine-T is greater than in the direct titration. Such titrations gave exactly the same value for the factor of the chloramine-T solution as methods (*a*) and (*b*) above (Table VII). A fourth confirmation was given by potentiometric titration in the same media as in the recommended methods, and further by yet a different method, titration in 2*M* hydrochloric acid free from other halides. The curves gave no indication of any side reactions or other interference, and showed that the reactions proceed smoothly with intermediate halogen production. The perfect agreement between a diversity of methods under very different conditions supports the conclusions that the reaction is quantitative, and that the indicator errors, compared with potentiometric results, are negligible. This contention will be further examined in a later paper.

TABLE V.—VARIATION OF IODIDE AND BUFFER CONCENTRATIONS: TITRATIONS OF 25 ML OF 0·05*M* ARSENIC SOLUTION (FACTOR 1·001) IN BICARBONATE BUFFER CONTAINING POTASSIUM IODIDE WITH 0·05*M* CHLORAMINE-T SOLUTION USING STARCH AS INDICATOR

Concentration of bicarbonate, *M*	Concentration of iodide, *M*	End-point,* *ml*	Factor of chloramine-T solution
0·4	0·05	24·93	1·004
0·4	0·005	24·93	1·004
0·4	0·0005	24·93	1·004
0·2	0·05	24·93	1·004
0·2	0·005	24·93	1·004
0·2	0·0005	24·93	1·004

* Titration in acid solution with rosaniline as indicator gave a factor of 1·004, and hence a calculated end-point of 24·93 ml.

2. *Standardisation through thiosulphate*

Though not itself a primary standard, thiosulphate can be accurately referred to the primary standard potassium iodate,[2] and offers an alternative path for relating chloramine-T to this standard, provided the chloramine-T–iodide reaction can be shown to be quantitative. This is a less advantageous method than those above, but is of particular value in standardising chloramine-T solutions which are to be used for liberating iodine in excess for a reaction where the excess is to be backtitrated with thiosulphate.

The iodine–thiosulphate reaction is not hydrogen ion-dependent, but the pH

TABLE VI.—VARIATION OF IODIDE CONCENTRATION IN VARIOUS BUFFER MEDIA

Conditions	Iodide concentration, *M*	End-point, *ml*	Factor of chloramine-T solution
(*a*)	0·00033	25·08	1·0235
	0·00016	25·11	1·025
	0·000033	25·12	1·0255
(*b*)	0·005	25·11	1·025
	0·0005	25·11	1·025
	0·00005	25·11	1·025
(*c*)	0·0225	25·11	1·025
	0·0045	25·12	1·0255
	0·000225	25·13	1·026
(*d*)	0·1	25·12	1·0255
	0·05	25·13	1·026
	0·005	no starch-iodine blue colour produced	—

(*a*) 50 ml of 0·2*M* potassium hydrogen phthalate and 10 ml of 0·5*M* hydrochloric acid added as buffer. Volume of titrated solution at the end-point 150 ml. Measured pH at the end-point 2·4.

(*b*) 25 ml of 0·6*M* sodium acetate, 1·4*M* acetic acid added as buffer. Volume of titrated solution at the end-point 100 ml. Measured pH at the end-point 4·1.

(*c*) 50 ml of saturated aqueous solution of borax added as buffer. Volume of titrated solution at the end-point 110 ml. Measured pH at the end-point 8·5.

(*d*) 1·59 g of anhydrous sodium carbonate added as buffer. Volume of titrated solution at the end-point 110 ml. Measured pH at the end-point 9·9.

must be kept low to keep the reaction fast and to prevent the formation of hypoiodite. If the pH is allowed to rise, hypoiodite, and indeed iodine itself, will oxidise thiosulphate to sulphate, and, since this consumes eight equivalents of oxidant instead of one, the volume of thiosulphate used will be low. The oxidation of iodide by chloramine-T consumes 2 moles of hydrogen ion per mole of oxidant, and if only just sufficient acid is present for this reaction, the pH may run undesirably high and cause low results. The amount of acid used is therefore of importance.

Furthermore, hypochlorites (and chlorine or bromine) oxidise thiosulphate to sulphate. Tests showed that chloramine-T does the same, but the reaction is not quantitative and other reactions also occur, so that oxidation to sulphate is not analytically useful. Nevertheless, if less iodide than the amount equivalent to the chloramine-T is initially added, and the solution titrated with thiosulphate, some of the latter may be oxidised to sulphate, and, as before, the end-point will be early. The iodide concentration is therefore also important.

Neither of these points, nor the effect of the nature of the acid used appear to have been systematically investigated before, and apparently conflicting recommendations have been made.

TABLE VII.—QUANTITATIVENESS OF THE CHLORAMINE-T–ARSENIC^{III} REACTION

(*a*) 20 ML OF 0·05M CHLORAMINE-T ADDED TO 50 ML 0·05M ARSENIC^{III} (FACTOR 1·005) IN 2M HYDROCHLORIC ACID AND 0·1M POTASSIUM BROMIDE, AND EXCESS ARSENIC^{III} TITRATED WITH 0·01667M POTASSIUM BROMATE (FACTOR 1·014) USING ROSANILINE HYDROCHLORIDE AS INDICATOR

Volume of bromate required, *ml*	Factor of chloramine-T solution*
28·76	1·053
28·77	1·0525
28·76	1·053

(*b*) POTENTIOMETRIC TITRATION OF 50 ML OF 0·05M ARSENIC^{III} SOLUTION (FACTOR 1·005) WITH 0·05M CHLORAMINE-T

Medium	End-point, *ml*	Factor of chloramine-T solution*
2M hydrochloric acid	47·70	1·0535
2M hydrochloric acid, 0·1M potassium bromide	47·72	1·053
0·5M sodium bicarbonate, 0·005M potassium iodide	47·72	1·053

* Arsenic^{III} and chloramine-T solutions as in Table V.

Influence of the nature and amount of the acid used

With the iodide maintained constant at 3 equivalents, various amounts of several acids were used with the results shown in Table VIII. As expected, if barely, or less than, the right quantity of acid required for the chloramine-T reaction is present, there is a marked increase in the pH of the solution and the end-points are early. In solutions containing more than 5 ml of 10N hydrochloric or sulphuric acid (20 equivalents) the end-points are not so sharp, though 10 ml of 10N acetic acid (40 equivalents) did not affect the quality of the end-point. Otherwise, with two or more equivalents of acid present, the reaction is quantitative.

Variation of iodide concentration was studied while maintaining the amount of acid initially added at 4 equivalents (10 ml of 1N). The results in Table IX show that with hydrochloric or sulphuric acid, the reaction is quantitative when one or more equivalents of iodide are used, but if less than one equivalent is added, the expected early end-points result. In the case of acetic acid, however, three equivalents of iodide are necessary for satisfactory titration. With two equivalents the reaction became slow, and with one equivalent there was no permanent end-point.

Table VIII.—Effect of variation of acid concentration in standardisation of chloramine-T against potassium iodate through sodium thiosulphate: titration of 25 ml of 0·05M chloramine-T solution (factor 1·004)* in acid solution containing 3 equivalents of iodide (15 ml of 0·5M potassium iodide) with 0·1M sodium thiosulphate (factor 1·008)† using starch as indicator

Volume added		Acid					
		Hydrochloric		Sulphuric		Acetic	
ml	*N*	End-point, *ml*	pH at end-point	End-point, *ml*	pH at end-point	End-point, *ml*	pH at end-point
10	0·1	21·7	10·4				
25	0·1	24·70	6·70	24·66	6·70	24·77	6·74
5	1	24·90	1·66	24·90	1·82	24·90	4·33
10	1	24·90	1·14	24·90	1·30	24·90	4·05
25	1	24·90		24·90		24·90	3·63
5	10	24·90		24·90		24·90	3·34
10	10	24·91		24·91		24·90	3·02
20	10	25·90					

* Obtained by standardisation against arsenic^{III} in 2M hydrochloric acid and 0·1M bromide using rosaniline as indicator, giving a calculated equivalence point of 24·91 in above titrations.

† Obtained by standardisation against potassium iodate, see text.

Table IX.—Effect of variation of acid concentration. Titration of 25 ml of 0·05M chloramine-T solution (factor 1·004)* in acid media (10 ml of 1N acid) containing potassium iodide with 0·1M thiosulphate (factor 1·008)† using starch as indicator

Volume 0·5M potassium iodide added, *ml*	Ratio of number of equivalents of iodide to chloramine-T used	End-points, *ml*		
		Hydrochloric acid	Sulphuric acid	Acetic acid
30	6	24·90	24·90	24·90
15	3	24·90	24·90	24·90
10	2	24·90	24·90	24·90
5	1	24·90	24·90	(24·82)
4	0·8	22·50	23·47	(24·58)
3	0·6	19·29	19·96	
2	0·4	15·38	17·19	
1	0·2	11·56	13·89	

* Obtained by standardisation against arsenic^{III} in 2M hydrochloric acid and 0·1M bromide using rosaniline as indicator, giving a calculated equivalence point of 24·91 in above titrations.

† Obtained by standardisation against potassium iodate, see text.

Chloramine-T and thiosulphate solutions as in Table VIII.

Potentiometric titrations with thiosulphate of the iodine liberated by chloramine-T on treatment with 4·6 equivalents of iodide and 4 equivalents of hydrochloric, sulphuric or acetic acid fully confirmed the quantitativeness of the overall reaction, and failed to reveal any side reactions or interference. Replication was perfect and in complete agreement with the arsenic figures.

The reactions involved in this method of standardisation are of a quality a little less than the highest required in the most refined work, and this method is not therefore recommended unless it ties in with the application in view. Nevertheless, with appropriate care, the results are no less accurate than those of the arsenic methods, and subject to the minimal requirements of acid and iodide, this method is suitable for the standardisation of chloramine-T solutions.

EXPERIMENTAL

Apparatus

Specially adjusted analytical balances of sensitivities 0·05 and 0·01 mg were used where appropriate, together with standard weights. Volumetric glassware was calibrated and used at 20°. All corrections were made. For potentiometric titrations, an open 400-ml beaker served as titration vessel, the solution was magnetically stirred, indicator electrodes of either 1 inch of 22-swg. bright platinum wire, or 1 cm^2 of 26-swg. bright platinum foil backed with glass, sealed into glass probes, were employed, in conjunction with a saturated calomel cell connected to the titration solution by means of a flushable saturated potassium chloride bridge plugged with filter paper; the potential across the cell was measured on either a mains-driven Marconi TF717A pH meter or a battery-driven Doran-type M4981 pH meter.

Reagents

Chloramine-T: usually May and Baker reagent grade; occasionally a recrystallised material. 0·05*M* aqueous solutions prepared in 2- or 10-litre batches.

Arsenious oxide: AnalaR dried at 120°, or, for exact work, sublimed in pure oxygen under reduced pressure. 0·05*M* solutions prepared by direct weighing, dissolving in pure sodium hydroxide solution and acidfying with pure hydrochloric acid to pH 1·2.

Potassium bromate and iodate: AnalaR grade recrystallised 5 times from conductivity water and dried to constant weight at 160°. 0·01667*M* solutions prepared by direct weighing.

Sodium thiosulphate: 0·1*M* solutions prepared from AnalaR pentahydrate in 0·01% sodium carbonate solution; standardised against potassium iodate immediately before use.

Potassium iodide: free from other halides and sulphate, but contained 0·35% potassium carbonate after drying.

Starch indicator: fresh 1% solution prepared daily.

Rosaniline hydrochloride: 0·1 g rosaniline base dissolved in water containing 1·0 ml of 2*M* hydrochloric acid, boiled, decanted and diluted to 100 ml.

Other reagents: of analaR grade. All reagents tested for active and inactive impurities by the appropriate methods.[2,36] Dust- and grease-free conductivity water was used throughout.

Purification of chloramine-T

750 g of chloramine-T were added to 1 litre of boiling conductivity water, filtered through a sintered-glass funnel fitted with a hot sleeve, and allowed to crystallise; the product was collected on sintered-glass, and washed with conductivity water. Filtration and washing were difficult because the crystals are soft, and felt together. A sample of the product was reserved and the remainder was recrystallised. This was repeated several times. The moist samples would not drain well at the pump, and drying was difficult. Microscopic examination of the crystals failed to reveal any vacuole inclusions of mother liquor. Desiccation over calcium chloride or sulphuric acid removes water of crystallisation, and heating, even at low temperature leads to formation and decomposition of dichloramine-T. Finally the samples were air-dried for 10 weeks in large basins protected from light and dust. Since chloramine-T has been reported to be efflorescent, a sample of the original product

was stored alongside the drying samples. This did fall to a fine powder, but analysis showed that there was no loss of water (Table II).

Assay of the dried samples and of other solid samples in this work was carried out by accurate preparation of 2 litres of 0·05*M* solution and titration against standard arsenic^{III} solution by the rosaniline hydrochloride method described below.

TABLE X.—STANDARDISATION OF CHLORAMINE-T SOLUTIONS: A COMPARISON OF METHODS

Method	Factor of 0·05*M* chloramine-T solution			
Against oxygen-sublimed As_2O_3				
in 2*M* HCl, 0·1*M* KBr, rosaniline	1·0022	1·0021	1·0021	1·0021
ditto, potentiometric	1·0021	1·0020	1·0021	1·0021
in 0·5*M* $NaHCO_3$, 0·005*M* KI, starch	1·0021	1·0022	1·0021	1·0022
ditto, potentiometric	1·0022	1·0021	1·0021	1·0021
in 2*M* HCl, potentiometric	1·0022	1·0020	1·0021	1·0021
excess As^{III}, back titrated with bromate as in Table VII	1·0021	1·0022	1·0021	1·0021
Against ultimate standard $KBrO_3$ through pure As_2O_3				
2*M* HCl, 0·1*M* KBr, rosaniline	1·0021	1·0023	1·0021	1·0021
0·5*M* $NaHCO_3$, 0·005*M* KI, starch	1·0021	1·0021	1·0020	1·0021
Against ultimate standard KIO_3 through $Na_2S_2O_3$, using 4 equivalents of acid and 3 equivalents of iodide				
H_2SO_4, starch	1·0021	1·0023	1·0021	1·0020
HCl, starch	1·0021	1·0019	1·0021	1·0022
HOAc, starch	1·0021	1·0022	1·0018	1·0021

Standardisation of chloramine-T

In the recommended methods below, the quantities actually used (Table X) are given in parentheses.

Method 1(*a*). *Against arsenic*^{III} *in acid solution using rosaniline hydrochloride as indicator.* Pipette an aliquot (50 ml) of standard 0·05*M* arsenic^{III} solution into a titration bottle (250–300 ml bottle with a well-ground glass stopper), add sufficient hydrochloric acid (40 ml of 10*M*) and potassium bromide (20 ml of 1·0*M*) to give concentrations of 2*M* and 0·1*M* respectively in the expected end-point volume (200 ml) and dilute appropriately (90 ml — volume of washings). Titrate with 0·05*M* chloranime-T to within 0·1 ml of the end-point. Add 2 drops (0·1 ml) of 0·1 % aqueous rosaniline hydrochloride per 100 ml of solution, and complete the titration split-dropwise till the very pale yellow colour changes to bright purple. The purple colour develops over a period of 5–10 secs. On each addition of titrant, rinse down, stopper the bottle, immediately shake vigorously and allow to stand for 15 secs. Rinse down stopper and repeat. Any delay in shaking, or too large an increment of titrant, will allow premature bromination of the indicator, and reddening of the solution. Warning of the end-point is given by a purple tint in the foam.

For a clean, brilliant end-point, it is necessary to delay addition of the indicator till within 0·05 to 0·1 ml before the end-point. To locate this point, a preliminary titration may be done to the first faintly perceptible smell of free bromine, or with a reversible indicator such as quinoline yellow or *o*-dianisidine (*cf.* Part II) and 0·1 ml deducted from the result. However, premature bromination of the rosaniline does not prevent observation of the end-point, and this indicator will serve in the rough titration if its addition is delayed as long as possible, and the titration solution mixed vigorously, as quickly as possible, after each increment of titrant. As the red colour develops, further indicator is added, 4 drops at a time. At the end-point, the red colour will suddenly deepen to a much more intense purplish-red. To check the end-point, a further addition of indicator is made. If the tint does not change, or becomes more intense, the end-point has been reached, but if the colour reverts to orange-red, the titration is incomplete.

Method 1(*b*). *Against arsenic^{III} in neutral buffer, using starch as indicator.* Pipette an aliquot (50 ml) of standard 0·05*M* arsenic^{III} solution into a conical flask, add sufficient sodium bicarbonate (100 ml of 1·0*M* solution) and potassium iodide (10 ml of 0·1*M* solution) to give concentrations of about 0·5 and 0·005*M* respectively in the expected end-point volume (200 ml), and titrate with 0·05*M* chloramine-T solution, adding 1 ml of freshly prepared 1% starch solution about 0·5 ml before the end-point. Finish slowly to a permanent clear very pale blue colour.

Method 2. *Against potassium iodate through thiosulphate.* Pipette an aliquot (25 ml) of 0·05*M* chloramine-T into a titration bottle, add three equivalents (15 ml of 0·5*M*) potassium iodide, and four equivalents (10 ml of 1·0*M*) hydrochloric acid, and titrate with 0·1*M* thiosulphate, adding 2 ml of freshly prepared 1% starch solution as indicator 0·5 ml before the end-point.

Standardise the thiosulphate by substituting an aliquot of standard 0·01667*M* iodate for the chloramine-T in the above process.

A direct comparison of the various methods on a 5-litre batch of chloramine-T solution is given in Table X, and illustrates the excellence of the standardisation, particularly against, or through, arsenic^{III}.

Zusammenfassung—Das Verhalten von Chloramin-T als titrimetrisches Reagens wird eingehend erörtet. Die Methoden zür Einstellung der Reagenslösung werden kritisch untersucht.

Résumé—Discussion détaillée du comportement de la chloramine-T comme réactif titrimétrique. On examine de façon critique des méthodes pour standardiser des solutions de ce réactif.

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USE OF BRUCINE AS AN OXIDATION-REDUCTION INDICATOR IN CERIMETRY

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(*Received* 2 *February* 1958)

Summary—The use of brucine as an internal indicator in the cerimetric determination of iron^{II} and ferrocyanide has been investigated. A 0·1% solution of brucine in 3*N* sulphuric acid is quite stable. Ten drops of this solution give a good end-point; with a slight excess of ceric salt solution a pink colour appears. The brucine indicator has slight advantages over the diphenylamine class of indicators.

SEIKICHI MIYAGI[1] appears to have been the first to employ brucine as internal indicator in the determination of ferrous iron with potassium dichromate. He employed 20 drops of a 1% solution of brucine in concentrated sulphuric acid for each titration. At the end-point, with a slight excess of dichromate, the indicator is reported to change to a vivid scarlet. Miyagi has also employed brucine as an internal indicator in the titration of stannous salts with dichromate. Narayana Murty and Seshadri[2] have also recommended the use of brucine in the titration of iron^{II} with potassium dichromate. Alexejewa and Andronikowa[3] have preferred the use of brucine as an indicator in the titration of Fe^{II} with potassium dichromate in the presence of hydrochloric acid, stating that when diphenylamine is used as an internal indicator the end-point is indefinite. We have now investigated the use of brucine as an internal indicator in cerimetric titrations.

EXPERIMENTAL

Indicator solution: A study of the stability of the indicator in sulphuric acid has led the authors to conclude that the stability depends upon two factors: (1) the concentration of the sulphuric acid; (2) the concentration of brucine. It is observed that the stability of the indicator solution decreases as the concentration of sulphuric acid is increased above 3·0*N*. The indicator solution also deteriorates with increasing rapidity as the concentration of brucine increases beyond 0·1%. Storage in an amber-coloured bottle did not improve the stability of the indicator solution.

A 0·1% solution of brucine in 3·0*N* sulphuric acid is most suitable as a stock indicator solution. Ten drops of this solution are enough to give a good indication of the end-point in most redox titrations, although one can go up to thirty drops without any significant indicator correction being necessary. Such a solution assumes a pale orange colour, when kept for a period of two months and a red colour after six months. Even after this apparent deterioration, the solution can still be used as an indicator without any correction. A 0·1% solution of brucine in 2·0 to 3·0*N* acetic acid can also be used as a good indicator.

Indicator correction: The correction to be applied when brucine is used as an indicator in titrations with ceric sulphate has been determined. For this purpose an aliquot volume of an iron^{II} solution was titrated with a 0·01*N* ceric sulphate solution in the presence of excess of ferric sulphate employing a known volume of the stock brucine solution as internal indicator. The average deviation between such a titre value and the average value obtained in a potentiometric titration was taken as the indicator correction. This is negligible when 0·5 ml to 1·5 ml of a freshly prepared 0·1% solution of brucine is employed. When higher amounts are used, significant deviations are obtained from the potentiometric titre values, showing the need for a high indicator correction.

Titration of iron$^{\text{II}}$ with ceric sulphate using brucine as indicator in sulphuric acid medium

Brucine works as a good indicator in the titration of iron$^{\text{II}}$ with ceric sulphate in sulphuric acid medium. For the purpose 0·5 ml of 0·1% brucine solution has been employed. The end-point is indicated sharply by the appearance of a pink colour which is stable for about a minute. The titration of iron$^{\text{II}}$ can be successfully carried out in solutions of varying concentration of sulphuric acid, 0·5*N* to 8·0*N*. The concentration of ceric sulphate can also be varied from 0·01*N* to 0·1*N*. The brucine indicator has an advantage that it can be used even in the absence of phosphoric acid, unlike the diphenylamine class of indicators. Tungstic acid does not interfere in the titration, as it does in the case of diphenylamine and diphenylbenzidine. Nickel salts do not interfere in the titration up to 1 g in 100 ml of the solution; cobalt salts interfere above 0·1 gm per 100 ml, since the colour of the cobalt ion is somewhat similar to that of the oxidised indicator. Typical results obtained by the authors on the determination of iron, under varying conditions, are given in Table I.

TABLE I

0·1*N* ceric sulphate (Indicator correction negligible)			0·01*N* ceric sulphate (indicator correction—0·02 ml)		
Iron$^{\text{II}}$ taken (Potentiometric) *m-moles*	Iron$^{\text{II}}$ found, *m-moles* Overall acid concentration		Iron$^{\text{II}}$ taken, *m-moles*	Iron$^{\text{II}}$ found, *m-moles* Overall acid concentration	
	0·05*N* H_2SO_4 without H_3PO_4	1·0*N* HCl without H_3PO_4		0·5*N* H_2SO_4 without H_3PO_4	1·0*N* HCl without H_3PO_4
0·2212	0·2218	0·2220	0·01894	0·01890	0·01896
0·4424	0·4422	0·4422	0·03788	0·03780	0·03792
0·5531	0·5533	0·5540	0·05682	0·05670	0·05708
0·6636	0·6633	0·6646	0·06630	0·06632	0·06632
0·7235	0·7239	0·7245	0·07576	0·07561	0·07568

Titration of iron$^{\text{II}}$ in hydrochloric acid medium

In titrations of Fe$^{\text{II}}$ in the presence of hydrochloric acid, the authors have found that the colour change at the end-point is from yellow to orange. This is presumably due to the toning down of the red colour of the oxidised brucine by the yellow colour of the ferric iron in hydrochloric acid medium. However, it has been found that the addition of phosphoric acid helps the attainment of an almost pink colour at the end-point. Moreover, the end-point colour is less stable in hydrochloric acid medium than in sulphuric acid. In titrations of Fe$^{\text{II}}$ in 1·0*N* to 2·0*N* overall hydrochloric acid, the orange colour appears sharply enough at the stoichiometric end-point but fades in about twenty seconds. If the hydrochloric acid concentration exceeds 2*N*, the end-points are extremely fleeting. This difficulty increases with increasing hydrochloric acid concentration. Above a concentration of 4*N* hydrochloric acid, it is not possible to perceive any colour change at any stage of the titration. Even the addition of phosphoric acid (5 ml of syrupy phosphoric acid in 100 ml) does not improve matters. It is thus obvious that the titration of Fe$^{\text{II}}$ in hydrochloric acid medium can be carried out only so long as the acidity does not exceed an overall concentration of 2*N*.

Determination of ferrocyanide with ceric sulphate using brucine as indicator

During the titration of ferrocyanide with 0·01*N* ceric sulphate (using 0·5 ml of 0·1% brucine solution as indicator), the pink colour of the oxidised brucine is masked by the deep colour of the ferricyanide that is formed. The difficulty can, however, be overcome by diluting the titration mixture before carrying out the titration. After dilution to 200 ml, 5 to 10 ml of 0·05*N* solution of ferrocyanide can be titrated with a 0·05*N* solution of ceric sulphate using 1 ml of a 0·1% solution of the indicator. In these titrations, the sulphuric acid concentration should not exceed 4*N*, because at higher acidities the ferricyanide that is formed can itself oxidise the brucine indicator, giving premature end-points. The titration of ferrocyanide should be carried out in 0·5*N* to 1*N* sulphuric acid. Some typical results are presented in Table II.

TABLE II

No.	Ferrocyanide taken, *m-mols*	Ferrocyanide found, *m-mols*
1	0·0216	0·0217
2	0·0433	0·0434
3	0·0865	0·0862
4	0·1619	0·1624
5	0·2428	0·2421
6	0·3238	0·3247

Results 1, 2, and 3 are taken from the titrations with 0·01*N* ceric sulphate, after deducting 0·02 ml from the titre value. Results 4, 5, and 6 represent titrations with 0·1*N* ceric sulphate employing 1 ml of 0·1 % brucine solution as the indicator; no indicator correction has been applied in this case.

Acknowledgement—One of us (T. P. Sastri) desires to thank the Government of India for the award of a Research Scholarship, which enabled him to participate in this investigation.

Zusammenfassung—Der Gebrauch von Brucin als innerer Indikator in der cerimetrischen Bestimmung von Eisen-II und Eisen-II-cyanid untersucht.

Eine 0,1 % Lösung von Brucin in 3*N* Schwefelsäure ist sehr stabil. Zehn Tropfen dieser Lösung geben einen guten Endpunkt; bei geringem Überschuss von Ceri-Salzlösung entsteht eine rosa Farbe. Der Brucin-Indikator hat kleine Vorteile gegenüber den Indikatoren der Diphenylaminklasse.

Résumé—On a utilisé la brucine comme indicateur interne pour le dosage cérimétrique du fer^{II} et du ferrocyanure. Une solution de brucine à 0·1 % dans l'acide sulfurique 3*N* est stable. Dix gouttes de cette solution donnent une fin de réaction très nette. Une coloration rose apparaît si l'on ajoute de la solution cérique en léger excès. La brucine comme indicateur a de légers avantages sur les dérivés de la diphénylamine.

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Talanta, 1958, Vol. 1, pp. 216–218. Pergamon Press Ltd., London.

URONIC ACID DETERMINATION

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(*Received* 20 *March* 1958)

Summary—Modifications of the McCready, Swensen and Maclay apparatus for uronic acid determination are described which enable determinations to be made on 20-mg samples.

During structural studies of two complex acidic polysaccharides elaborated by *Aerobacter aerogenes* (N.C.T.C. strains 418 and 8172) the small amounts of material available rendered difficult the determination of their uronic acid content by existing methods. Colorimetric methods based, for example, on carbazole[1] and anthrone[2] have been used for the determination of the uronic acid content of micro amounts of polysaccharides. The possibility that response to these colorimetric tests may be influenced by the nature of the uronic acid and by its molecular environment[2] suggests that alternative methods would be of value in those cases where the nature of the uronic acid is not known, or where more than one type of uronic acid is present in the polysaccharide. Analysis for uronic acid based on decarboxylation appears to be independent of the nature of the uronic acid. Modifications were therefore introduced to the apparatus described by McCready, Swensen and Maclay[3] which enabled the uronic acid content of 20-mg samples to be determined instead of the 250 mg recommended by these workers. No alterations, except those involved in scaling down, were introduced to their experimental procedure which involved decarboxylation with 19% hydrochloric acid, absorbing the carbon dioxide in

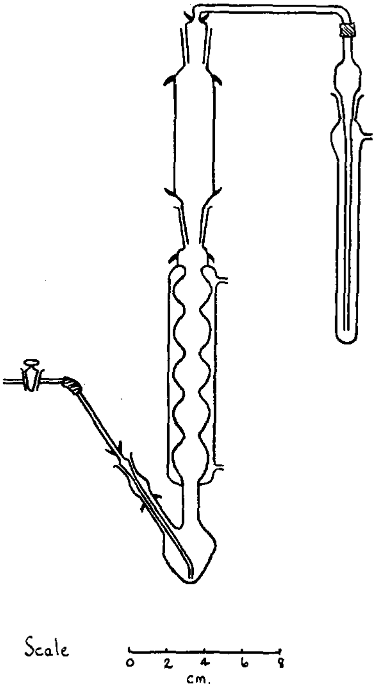

Fig. 1

standard 0·25N sodium hydroxide, and back titration with standard 0·1N hydrochloric acid. Nitrogen was used as the carrier gas in place of air. Control determinations on samples of crystalline glucurone gave reproducible results.

APPARATUS

The apparatus (Fig. 1) consisted of a pear-shaped flask with a sealed condenser and a Quickfit B7 neck carrying a narrow Quickfit tube reaching to the bottom of the flask. On top of the condenser, a trap was fitted containing closely packed granulated zinc held in position by silicon wool plugs. The top of the apparatus was connected by a tube to the absorption apparatus which consisted of an ordinary air-leak (B14/joint) fitted in a Quickfit tube with a side-arm. The entire apparatus was kept free of atmospheric carbon dioxide by ordinary calcium chloride tubes containing Ascarite retained by silicon wool plugs. The rate of flow of nitrogen was carefully controlled by a screw-clip and tap (see Fig. 1). All the Quickfit joints were lubricated with Silicone grease and held together by springs.

METHOD

The apparatus was cleaned with a warm chromic-sulphuric acid mixture, rinsed and dried before use.

The sample was weighed in a narrow tube (length 1 cm), placed in the dry reaction flask and 3 ml of 19% hydrochloric acid (51·3 ml of B.D.H. micro-analytical hydrochloric acid made to 100 ml with water) introduced by means of a pipette. A stream of carbon dioxide-free nitrogen was passed into the reaction flask to remove traces of carbon dioxide before connecting the absorption apparatus. The absorption apparatus was swept free of carbon dioxide and standard *ca.* 0·25N sodium hydroxide (5 ml) added to the absorption tube. The absorption apparatus was connected, the flow rate of nitrogen adjusted to *ca.* 1 bubble every 2–3 sec and the oil bath, previously heated to 145°, placed in position; the level of the oil was 0·25 cm below that of the liquid level in the reaction flask. Heating at 145° was continued for 2 hr. The bath was then removed and the flow rate of nitrogen increased to 2–3 bubbles per sec for about 10 min. The absorption apparatus was then disconnected and the contents carefully transferred and washed (5 × 5 ml) in a conical flask by fixing a rubber teat to the air leak.

A 10% solution of barium chloride dihydrate (2 ml) and two drops of phenolphthalein indicator were added to the titration flask and the excess alkali was titrated against standard *ca.* 0·1N hydrochloric acid. Control standardisations without the sample were also performed. The method was checked on samples of glucurone. All titrations were performed in an atmosphere of CO_2-free nitrogen.

RESULTS

TABLE I.—URONIC ACID DETERMINATIONS

Sample	Sample weight, *mg*	Volume of 0·106N HCl added	Titration difference, *ml*	% of uronic acid
Blank	—	12·5	0·0	—
Glucurone	22·90	10·05	2·45	99·6
,,	19·72	10·4	2·10	99·2
,,	20·74	10·25	2·25	100·8
,,	20·74	10·25	2·25	100·8
Polysaccharide	22·86	12·1	0·4	16·4
N.C.T.C. 418[a]	19·86	12·15	0·35	16·6
Blank	—	12·25[c]	0·0	—
N.C.T.C. 8172[b]	21·46	11·55[c]	0·70	28·7

[a] Contains[4] glucuronic acid and mannuronic acid.
[b] Contains[5] glucuronic acid.
[c] 0·10N Hydrochloric acid used in these titrations.

Zusammenfassung—Modifikationen des Apparates von McCready, Swensen und Maclay für die Bestimmung von Uronsäure werden beschrieben, die diese Bestimmungen auf 20 mg Proben ermöglichen.

Résumé—On décrit certaines modifications de l'appareil de M'Cready, Swensen et Maclay pour le dosage de l'acide uronique qui permettent d'effectuer des déterminations sur des échantillons de 20 mg.

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Talanta, 1958, Vol. 1, pp. 219–223. Pergamon Press Ltd., London.

SUBSTITUTIVE HALOGENATION OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION BY INTERHALOIDS—II

PREPARATION AND INVESTIGATION OF A STANDARD SOLUTION OF BROMINE MONOCHLORIDE

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(*Received* 14 *February* 1958)

Summary—A new method has been evolved for the preparation of a bromine chloride solution containing hydrochloric acid. In a hydrochloric acid solution bromate reacts quantitatively with bromide forming bromine chloride, provided that they are present in equivalent amounts. A 0·1*N* solution of bromine chloride containing hydrochloric acid showed less than 3–5% change of titre on storage for 3 months.

A new method has been evolved for the determination of the bromate content of the bromine chloride solution. The interaction of bromine chloride and cyanide yields chloride ions and cyanogen bromide, the latter after basic hydrolysis to bromide and cyanate ions, when acidified, hydrolysing to ammonium ions and carbon dioxide. Subsequently bromate can be measured by iodometry. A method has also been evolved for the determination of the content of elementary chlorine in bromine chloride solutions.

For purposes of bromination by excess bromine chloride, the use of a 0·1*N* solution of bromate which contains potassium bromide in an amount equivalent to bromate is suggested.

IN aqueous solution bromine monochloride shows an unequivocal action, behaving solely as a bromination agent.[1] The stability of an aqueous solution of iodine monochloride containing hydrochloric acid, and the fact that it acts exclusively as an iodinating agent, have been utilised for analytical purposes. Whilst an aqueous solution of iodine monochloride containing hydrochloric acid was first applied by Heisig[2] and Kubina[3] as an oxidizing agent, it was later used as an analytical standard solution by Gengrinovich, Fialkov and co-workers,[4] and by Cihalik and Vavrejnova.[5–7] The titre of the 0·1*N* solution of iodine chloride, about 0·4*N* with respect to hydrochloric acid, remained unchanged for 3–4 months. It was prepared by allowing appropriate quantities of potassium iodate and potassium iodide to react in a hydrochloric acid medium.

In addition to iodine monochloride (although very rarely) iodine monobromide dissolved in an organic solvent has been applied as a standard oxidising solution.[8] To the best of our knowledge, a standard solution of bromine monochloride of stoichiometric composition has not been used up to the present.

Schulek recently pointed out that bromine monochloride developed in a hydrochloric acid medium plays in certain bromometric measurements both a catalytic and a controlling role.

EXPERIMENTAL

Preparation of bromine monochloride solution

Having confirmed[1] that in aqueous solution, bromine monochloride reacts unequivocally with organic compounds, we set out to prepare a stable aqueous solution of bromine monochloride.

At first, the simple apparatus evolved by Schulek and Pungor[9-10] was used for the preparation. Analogous to the preparation of solutions of iodine monochloride, an attempt was made to prepare a solution of bromine monochloride by reacting stoichiometric quantities of potassium bromate and potassium bromide in the presence of hydrochloric acid, according to the equation

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl + 3H_2O \qquad (1)$$

Bromine monochloride containing hydrochloric acid prepared by this reaction was compared with a bromine monochloride solution of identical concentration, containing the same quantity of hydrochloric acid, produced by the Schulek apparatus. On establishing the ultraviolet absorption spectra of both solutions, the curves showed complete coincidence. At the same time, the ultraviolet absorption spectrum of bromine water of identical concentration and identical content of hydrochloric acid was established as well. It was found that it possesses a shape quite different from those of bromine monochloride solutions (Fig. 1). For establishing the ultraviolet absorption spectra, a Beckmann D.U. quartz spectrophotometer was applied, with 1 cm-quartz cuvettes. A hydrogen lamp served as light source.

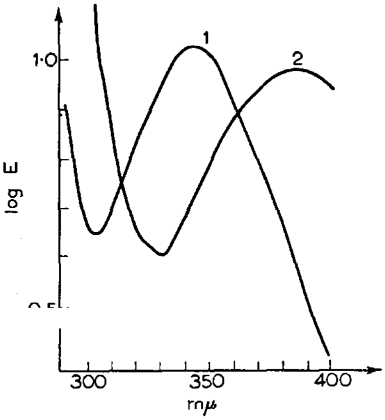

FIG. 1.—Ultraviolet absorption curves of a solution of bromine monochloride containing hydrochloric acid (1), and of a bromine solution containing hydrochloric acid (2), respectively.

In the course of experiments to be described elsewhere it was observed that the rate of the reaction between salicylic acid and bromine ranges much below that between salicylic acid and bromine monochloride. Therefore, bromination tests were carried out with bromine monochloride solutions prepared in the Schulek apparatus from bromate. On applying identical bromination periods, the consumption of bromine proved to be quite identical with both types of solution.

These experiments confirmed that, in a hydrochloric acid medium, potassium bromate and potassium bromide in stoichiometric proportions form bromine monochloride. The reaction proceeds in two steps. At first, elementary bromine is formed, being oxidised later by bromate to bromine monochloride. Although the reaction does not take place instantaneously, it is completed rather quickly in the presence of excess hydrochloric acid. (The preparation of 1000 ml of a 0·1*N* solution of bromine monochloride, which is at least 0·5*N* in hydrochloric acid, requires about 1–2 minutes.) On raising the concentration of hydrochloric acid, the rate of reaction increases (in the case of 1·5–2·0*N* hydrochloric acid only 10–20 seconds are necessary).

Preparation of the standard solution

On dissolving 2·7835 g of potassium bromate, (analytical grade) and 3·9670 g of potassium bromide, (analytical grade), in a 1000-ml measuring flask in 400–500 ml of water, 365 ml of 20% HCl is poured into the liquid, allowed to stand until it turns yellow, then made up to volume with distilled water.

The standard solution should be stored, with exclusion of sunlight, in a glass-stoppered flask completely filled.

Investigation of bromine monochloride solution

Determination of the content of bromate in the solution of bromine monochloride: On applying excess bromate to the preparation of the bromine monochloride solution, this excess reacted with hydrochloric acid to form elementary chlorine. In the course of the examination of bromine monochloride solution, this reaction was also subjected to a study. For this purpose, a method was evolved for the determination of bromate and elementary chlorine in the presence of excess bromine monochloride. No difficulties were encountered when determining the content of bromate in the solution of bromine monochloride. About 0·5 g of potassium cyanide was dissolved in the reaction mixture. On making the solution alkaline by addition of 20 ml of $2N$ sodium hydroxide, bromine monochloride reacted with the cyanide to form cyanogen bromide which hydrolysed in the alkaline medium to bromide and cyanate ions. On acidification, the latter extremely quickly hydrolysed to ammonium ions and carbon dioxide. Thus the oxidising power of bromine monochloride with respect to iodide ion was destroyed.[11] Subsequently on standing for 5 minutes, the bromate content of the solution was measured by iodometry.

This method proved to be suitable for the determination of the bromate content of bromine water, and of alkaline solutions of hypobromite or hypochlorite.[12]

By this method it has been proved that a bromine monochloride solution containing hydrochloric acid, (provided its concentration of hydrochloric acid is sufficiently high), does not contain any bromate some minutes after its preparation, even when a 5–10% excess bromate was originally added.

Determination of the content of elementary chlorine in a bromine monochloride solution: It proved to be more difficult to determine elementary chlorine in the presence of bromine monochloride. The method was based on differences in the behaviour of cyanogen bromide and cyanogen chloride.[13] About 0·2 g of potassium cyanide was added to the bromine monochloride solution containing hydrochloric acid. After some minutes, about 0·5 g of potassium iodide was dissolved in the reaction mixture and on allowing to stand for about 10 minutes, iodine liberated by the cyanogen bromide was measured. It is known that cyanogen chloride converts, when allowed to stand some minutes, into an electromeric form incapable of oxidising iodide.[9] Thus, the chlorine content of the solution of bromine monochloride was determined by subtracting the volume of standard thiosulphate consumed by iodine liberated in the reaction with cyanide from the volume of thiosulphate solution consumed by iodine directly liberated by the solution of bromine monochloride. This procedure afforded correct results in the cases when the solution of bromine monochloride actually contained free chlorine.

However, the method can only be applied under experimental conditions. According to our tests, results lower than actual values are obtained when a stoichiometric solution of bromine monochloride, containing no free chlorine at all, reacts with potassium cyanide. A similar experience is also mentioned by Molnár.[10] Accordingly, bromine monochloride reacts *quantitatively* with cyanide solely when elementary chlorine is present, the reaction affording cyanogen bromide.

This method proved suitable to establish that, on preparing a solution of bromine monochloride with the use of a known excess of bromate, the solution obtained contains a quantity of free chlorine precisely equivalent to the excess of bromate applied.

Reaction of bromine monochloride with bromide ions

The reaction between bromine monochloride and bromide ions was also subjected to an examination. It was found that bromine monochloride and bromide ions react, in an acid medium, to liberate elementary bromine.

Attempts to evolve an analytical method suitable for the determination of minute amounts of bromine in the presence of large quantities of bromine monochloride failed.

It follows that, on preparing bromine monochloride of stoichiometric composition in a hydrochloric acid solution, precisely equivalent quantities of carefully dried potassium bromate and potassium bromide of analytical grade should be weighed.

Determination of the titre of the standard solution of bromine monochloride

The titre of the standard solution of bromine monochloride has been determined in two ways: by iodometry, and by direct measurement of hydrazine sulphate.

(1) *Iodometric determination of the titre:* Ten ml of standard solution was added to 0·5 g of potassium iodide in about 30 ml of water, in a 100-ml Erlenmeyer flask. The liberated iodine was titrated by a standard solution of sodium thiosulphate.

(2) *Determination of the titre by hydrazine sulphate:* About 0·30 g of hydrazine sulphate (analytical grade) accurately weighed, was dissolved in water in a 100-ml measuring flask, made up to volume. Then 10-ml portions of this stock solution were transferred into a titration flask, diluted with distilled water to 30–50 ml, acidified with 2–10 ml of 20% hydrochloric or 10–20 ml of 2*N* sulphuric acid and, in the presence of one drop of a solution of *p*-ethoxychrysoïdine as indicator, titrated with a 0·1*N* standard solution of bromine monochloride.

1 ml of a 0·1*N* standard solution of bromine monochloride is equivalent to 3·253 mg of hydrazine sulphate.

Both methods yielded identical results.

Stability of the bromine monochloride solution

In further tests, the storage properties of bromine monochloride solutions prepared by the above methods, and containing various amounts of hydrochloric acid were examined. It was found that, during a storage for 3 months in a dark place, in a completely filled flask, the titre of a 0·1*N* solution of bromine monochloride (1·5–2·0*N* referred to hydrochloric acid) showed changes not exceeding 3–5% (Table I).

TABLE I

No.	Date of analysis	Concentration of HCl, *N*	Measured, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Titre	Change in titre, %
1	Feb. 29, 1956	1·5	4·850	4·85	1·000	
	April 6, 1956		4·850	4·77	1·017	
	June 7, 1956		4·850	4·65	1·049	+4·9%
2	July 2, 1956	2·0	10·03	9·78	1·025	
	Sep. 25, 1956		10·03	9·53	1·052	+2·5

According to our investigations, bromine monochloride is present in the form of a complex, in aqueous solution containing chlorides, and this fact is responsible for the relatively high stability of the solution. The physical chemistry of the chloride complex of bromine monochloride will be discussed elsewhere in detail.

In bromination processes with excess bromine monochloride, a 0·1*N* standard solution of potassium bromate containing potassium bromide in a quantity equivalent to the bromate according to equation (1), proved to be practical, due to its stable titre.

Preparation

2·7835 g of potassium bromate and 3·967 g of potassium bromide, (analytical grade) were dissolved in distilled water and diluted to 1000 ml.

The solution thus obtained showed, when stored properly, a stable titre. On acidification by hydrochloric acid it converted into a bromine monochloride solution (the solution should be 1·5–2·0*N* with respect to hydrochloric acid, after acidification).

The solution lends itself to analytical methods based upon bromination by excess bromine, particularly when bromine monochloride is to be used as a bromination agent.

Determinations with this solution are conducted analogously to the Koppeschaar method of bromination except, that the reaction mixture does not contain excess bromide.

The conditions of application of bromine monochloride as a bromination and standard oxidimetric solution will be discussed elsewhere in detail.[14–15]

In order to be able to prepare quickly a bromine monochloride solution containing hydrochloric acid, suitable for direct titration, it is practical to store a bromate solution containing bromide as follows.

2·7835 g of potassium bromate and 3·967 g of potassium bromide (analytical grade) are dissolved in water and diluted to 250 ml. The required 0·1*N* standard solution of bromine monochloride may be prepared at any time quickly by acidifying 25·00 ml portions of this stock solution with 36·5 ml of 20% hydrochloric acid and diluting with water to 100 ml.

The titre of the standard solution can be determined either by iodometry or against hydrazine sulphate.

Zusammenfassung—Es wird eine neue Methode für die Herstellung einer salzsäurehaltigen Bromchlorid-Lösung entwickelt.

In genügend stark salzsaurer Lösung reagiert das Bromat mit dem Bromid quantitativ unter Bildung von Brommonochlorid, vorausgesetzt, dass beide Bromat und Bromid in dem Molverhältnis 1 : 2 vorhanden sind.

Eine auf dieser Weise hergestellte 0,1*N* Bromchlorid-Lösung erwies sich nach 3 monatiger Aufbewahrung auf 3–5% als titerbeständig. Es wurden Methoden zur Bestimmung des eventuellen Bromatgehaltes, sowie des eventuellen Gehaltes an freiem Chlor der Bromchlorid-Lösungen ausgearbeitet. Die Reaktion zwischen Bromchlorid und Bromid-Ionen wurde eingehend untersucht.

Zur Bromierung durch überschüssige Bromchlorid-Lösung wird eine vollkommen titer-beständige neutrale 0,1*N* Bromat-Bromid-Lösung in Vorschlag gebracht deren Molverhältnis Bromat-Bromid genau 1 : 2 bemessen ist.

Résumé—Une nouvelle méthode a été élaborée pour préparer une solution de chlorure de brome contenant de l'acide chlorhydrique. En solution chlorhydrique, à condition qu'ils soient présents en quantités équivalentes, le bromate réagit quantitivement avec le bromure avec formation de chlorure de brome. La solution titrée 0·1*N* contenant de l'acide chlorhydrique s'est conservée pendant trois mois sans révéler des changements de titre excédant 3 à 5 pour cent.

On a mis au point une nouvelle méthode permettant de déterminer la teneur en bromate de cette solution. Le chlorure de brome a été traité au cyanure en milieu alcalin. La réaction du chlorure de brome et du cyanure donne le bromure de cyanogène lequelle s'hydrolyse en solution alcalin en ions bromure et cyanate. (Ceux-ci, acidifiés, s'hydrolysent trés rapidement en ions d'ammonium et CO_2, ce qui les rend inefficaces du point de vue iodométrique.) On peut par la suite mesurer le bromate par iodométrie. Une méthode pour déterminer la teneur de chlore élémentaire dans des solutions de chlorure de brome a été élaborée.

Pour opérer la bromuration au moyen du chlorure de brome en excès on propose l'utilisation d'une solution 0·1*N* de bromate, contenant en quantités équivalentes le bromure de potassium et le bromate.

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SUBSTITUTIVE HALOGENATION OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION BY INTERHALOIDS—III

DETERMINATION OF AROMATIC COMPOUNDS BY BROMINATION WITH BROMINE MONOCHLORIDE

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(*Received* 14 *February* 1958)

Summary—Bromination of certain phenols by bromine chloride was investigated, and the method was applied to quantitative measurements.

Bromine chloride was prepared in the bromination flask in a hydrochloric acid medium from equivalent amounts of bromate and bromide (1*M* : 2*M*).

It was found that whilst the application of bromine chloride does not increase the number of compounds capable of being brominated, it raises the rate of bromination appreciably.

THE quantitative bromometric determination of phenols, aromatic amines and their derivatives is based on substitution reactions with bromine, *i.e.*, on bromination, the *o*- and *p*-hydrogen atoms of the phenol ring are readily exchanged by bromine atoms. Bromination is carried out, according to the method of Koppeschaar,[1] in the presence of excess bromide, in a hydrochloric acid medium, by use of a standard bromate solution. Excess bromine is measured iodometrically.

Investigation of the reactions of bromine monochloride[2] proved that bromine chloride reacts unequivocally with organic aromatic compounds, acting solely as a brominating agent.

It was observed in the course of preparing bromine monochloride[3] that the interaction of bromate and bromide ions in a hydrochloric acid medium yields bromine monochloride, provided the bromate and bromide are applied in equivalent amounts, according to the reaction scheme

$$KBrO_3 + 2KBr + 6HCl \rightarrow 3BrCl + 3KCl + 3H_2O \qquad (1)$$

In the light of both of these facts, we were able to deal with the bromination of phenols by bromine monochloride and to apply this reaction in certain cases to the quantitative determination of phenols.

The present determinations were conducted in a way similar to the Koppeschaar method, except that the standard solution of bromate contained an equivalent amount of bromide, according to equation (1). Thus, on acidification with hydrochloric acid, instead of elementary bromine, bromine monochloride and its chloride complex were formed, and subsequently reacted with the substance to be determined.

EXPERIMENTAL

Preparation of the standard solution

2·7835 g of potassium bromate and 3·967 g of potassium bromide, analytical grade, were weighed accurately, dissolved in distilled water and diluted to 1000 ml.

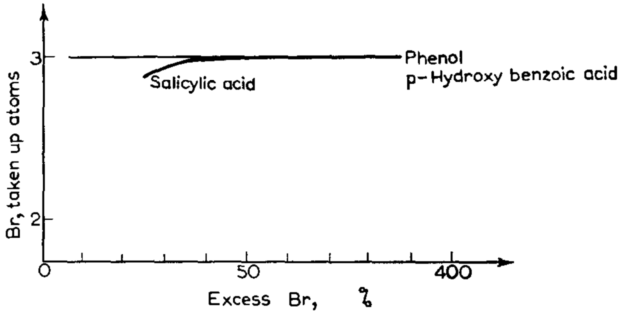

FIG. 1.—Bromination by bromine monochloride. Br taken up, atoms: Excess Br, %

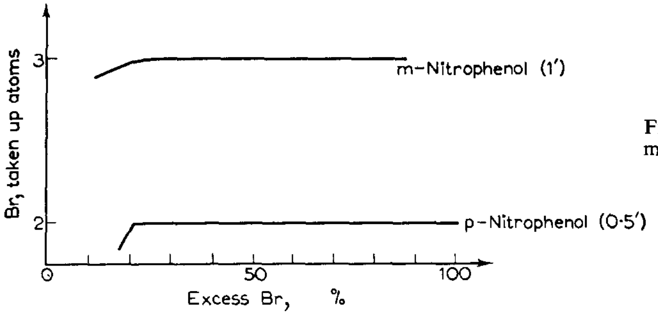

FIG. 2.—Bromination by bromine monochloride. Br taken up, atoms: Excess Br, %

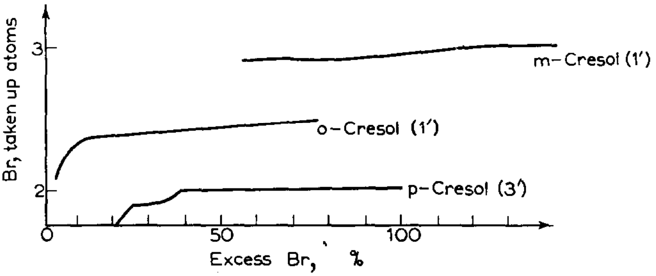

FIG. 3.—Bromination by bromine monochloride. Br taken up, atoms: Excess Br, %

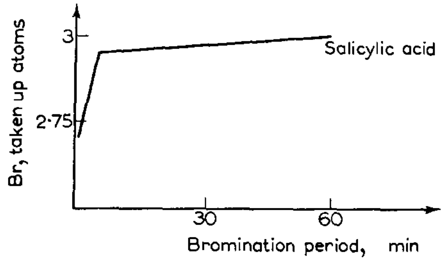

FIG. 4.—Bromination according to Koppeschaar. Br taken up, atoms: Bromination period, minutes

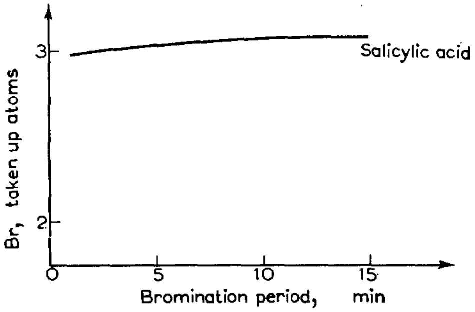

FIG. 5.—Bromination by bromine monochloride. Br taken up, atoms: Bromination period, minutes

Measurements were carried out as follows.

A 0·1N aqueous solution (referred to the component to be determined) was prepared from the test substance. When required, some sodium hydroxide was used in the preparation of this solution. 5–10-ml portions of the stock solution were quantitatively transferred to 300 ml Buchböck bromination flasks and diluted with distilled water to about 80–100 ml. Subsequently, an amount of standard solution corresponding to the planned excess of bromine was added and about 10 ml of 20% hydrochloric acid as an agent of acidification, were placed in the wide part of the neck of the bromination flask. On loosening the stopper, the acid flowed into the flask. After completing the bromination period, potassium iodide was added to the reaction mixture in the same way. On allowing to stand for about 3–5 minutes, the iodine liberated by the excess of bromine monochloride was titrated with 0·1N solution of sodium thiosulphate.

The bromination of phenol, *p*-hydroxybenzoic acid, salicylic acid, *o*-, *m*- and *p*-cresol, and *o*-, *m*- and *p*-nitrophenol was investigated by this method (cf. Tables I–IX and Figures 1–3).

The end-product of the reaction was tribromophenol in the case of phenol, *p*-hydroxybenzoic acid and salicylic acid (equivalent weight 1/6th part of the molecular weight); the corresponding dibromo-product in the case of *p*-cresol and *o*- and *p*-nitrophenol (equivalent weight 1/4th part of the molecular weight); and the corresponding tribromo-product in the case of *m*-cresol and *m*-nitrophenol (equivalent weight 1/6th part of the molecular weight).

Accordingly, 1 ml of standard solution is equivalent to 1·567 mg of phenol, 2·301 mg of *p*-hydroxybenzoic acid, 2·301 mg of salicylic acid, 2·702 mg of *p*-cresol, 3·478 mg of *o*-nitrophenol, 3·478 mg of *p*-nitrophenol, 1·801 mg of *m*-cresol or 2·318 mg of *m*-nitrophenol.

DISCUSSION

It was noted during the present tests that the bromination period required is appreciably reduced when bromine monochloride is applied as a bromination agent instead of the conventional reagent (Table X). This appears most strikingly in the determination of salicylic acid which requires by the Koppeschaar method a bromination period of 60 minutes (Fig. 4) whilst a quantitative bromination is attained by the new method in only two minutes (Fig. 5).

According to our investigations, by the present method a bromination period of 1 minute is necessary for the determination of phenol, *p*-hydroxybenzoic acid, *m*-nitrophenol and *m*-cresol, whereas half a minute proved satisfactory with *o*- and *p*-nitrophenol. A bromination period of two minutes was required for salicylic acid, and three minutes for *p*-cresol. *o*-Cresol could not be determined by bromination with bromine monochloride (as in the Koppeschaar method, an extremely high overconsumption was observed).

It was found at the same time that, whilst the application of bromination periods exceeding the necessary duration did not affect the values obtained in the determination of phenol, *p*-hydroxybenzoic acid and salicylic acid by the Koppeschaar method, high results were obtained in the bromine monochloride procedure.

The correlation of bromination results with the amount of excess bromine monochloride was less close with the new method proposed, provided that properly chosen bromination periods were applied.

Owing to the short bromination periods (1–3 minutes) applied in the bromine monochloride method, the results may also be affected by the volume of solution. With small volumes of solution (20–30 ml), the precipitate formed during bromination may occlude unbrominated molecules which, owing to the relatively short duration of the bromination periods, are not capable of reacting with the reagent. However, in an extremely large volume (200 ml), reaction rates appreciably decrease, due to diminished concentrations, and the otherwise adequate bromination periods prove

TABLE I. BROMINATION OF PHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1N BrCl added, *ml*	Consumed 0·1N $Na_2S_2O_3$ *ml*	Consumed 0·1N BrCl, *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*	Volume of 20% HCl used for acidification
1	8·53	10·03	4·79	5·24	8·21	0·5	91	28·9	
			4·66	5·37	8·42		87	2·96	
			4·59	5·44	8·53	1	84	3·00	
			4·58	5·45	8·54				
			4·58	5·45	8·54	5		3·00	
			4·59	5·44	8·53				
			4·59	5·44	8·53	10		3·00	
			4·59	5·44	8·53				
2	16·92	20·00	9·18	10·82	16·96	1	85	3·00	
			9·16	10·84	16·99				
			9·11	10·89	17·07	5	83	3·03	
			9·10	10·90	17·09				
			8·95	11·05	17·32	60	81	3·07	
			8·94	11·06	17·34				
3	8·53	10·03	7·00	3·03	4·75	1		1·62	5
			5·56	4·47	7·01			2·47	
			4·59	5·44	8·53	1		3·00	10
			4·59	5·44	8·51			3·00	
			4·59	5·44	8·53	1		3·00	15
			4·59	5·44	8·53				
			4·59	5·44	8·53	1		3·00	20
			4·59	5·44	8·53	1			

TABLE II. BROMINATION OF *p*-HYDROXYBENZOIC ACID BY BROMINE MONOCHLORIDE

No.	Substance weighed *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	7·133	10·03	6·92	3·11	7·156	0·5	221	3·01
			6·93	3·10	7·133			3·00
			6·92	3·11	7·156	1		3·01
			6·94	3·09	7·110			3·00
			6·93	3·10	7·133	2		3·00
			6·92	3·11	7·156			3·01
2	14·14	10·03	3·84	6·19	14·24	1	62	3·02
			3·84	6·19				
		20·00	13·83	6·17	14·20	1	224	3·01
			13·82	6·18	14·22			3·02
3	7·133	3·44	0·34	3·10	7·133	1	11	3·00
		3·75	0·65	3·10	7·133	1	21	3·00
		4·03	0·93	3·10	7·133	1	30	3·00
		4·66	1·55	3·11	7·156	1	50	3·01
		5·27	2·17	3·10	7·133	1	70	3·00
		5·89	2·79	3·10	7·133	1	90	3·00
		6·53	3·42	3·11	7·156		110	3·01

TABLE III. BROMINATION OF SALICYLIC ACID BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*	Total volume, *ml*
1	11·34	10·03	5·10	4·93	11·34	1	103	3·00	
			5·11	4·92	11·32			2·99	
			5·10	4·93	11·34	2		3·00	
			5·10	4·93	11·34			3·00	
			5·06	4·97	11·44	5	102	3·03	
			5·04	4·99	11·48			3·04	
			4·97	5·06	11·64	15	98	3·08	
			4·98	5·05	11·62			3·07	
2	22·48	20·00	10·76	9·24	21·26	1	116	2·84	80–100
			10·90	9·10	20·94			2·79	
			10·23	9·77	22·48	2	105	3·00	
			10·23	9·77	22·48			3·00	
3	11·67	10·03	4·95	5·08	11·69	2	98	3·01	
			4·95	5·08	11·69			3·01	
	23·17	20·00	9·95	10·05	23·13	2	99	2·99	
			9·95	10·05	23·13			2·99	
4	23·17	20·00	10·23	9·77	22·48	2	105	2·91	30–40
			10·39	9·61	22·11			2·86	
			9·95	10·05	23·13	2	99	2·99	80–100
			9·91	10·09	23·22			3·01	

TABLE IV. BROMINATION OF *o*-NITROPHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	16·87	10·03	5·10	4·93	17·15	0·5	103	2·03
			5·14	4·89	17·01			2·02
			4·70	5·33	18·54	1	88	2·19
			4·78	5·25	18·26			2·17
			4·52	5·51	19·16	2	82	2·27
			4·48	5·55	19·30			2·28
2	33·45	20·00	10·40	9·60	33·39	0·5	108	2·00
			10·30	9·70	33·73			2·02
						sec		
3	12·63	10·03	6·65	3·38	11·75	15	197	1·86
			6·25	3·78	13·15	30	166	2·08
	16·87	10·03	5·10	4·93	17·15	30	103	2·03
4	25·06	20·00	13·14	6·86	23·26	15	192	1·90
			12·42	7·58	26·36	30	164	2·10
	33·45	20·00	10·30	9·70	33·73	30	106	2·02

TABLE V. BROMINATION OF *m*-NITROPHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	17·40	10·03	2·54	7·49	17·37	1	34	2·99
			2·52	7·51	17·41			3·00
			2·51	7·52	17·44	2	33	3·01
			2·52	7·51	17·41			3·00
		20·00	12·50	7·50	17·39	1	167	3·00
			12·50	7·50	17·39			
2	34·70	20·00	5·01	14·99	34·75	1	33	3·00
			5·03	14·97	34·71			3·00
3	12·32	5·86	0·68	5·18	12·00	1	13	2·92
		6·37	1·10	5·27	12·22	1	21	2·98
		6·87	1·56	5·31	12·31	1	29	3·00
		10·00	4·69	5·31	12·31	1	88	3·00
4	12·32	5·86	0·56	5·30	12·29	2	11	2·99
			0·53	5·33	12·36		10	3·01
		10·03	4·67	5·36	12·43	2	87	3·03
			4·67	5·36				
	24·46	20·00	9·30	10·70	24·81	2	87	3·04
			9·34	10·66	24·72			3·03

TABLE VI. BROMINATION OF *p*-NITROPHENOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1N BrCl added, *ml*	Consumed 0·1N $Na_2S_2O_3$ *ml*	Consumed 0·1N BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	17·58	10·03	4·98	5·05	17·56	0·5	99	2·00
			4·98	5·05	17·56			2·00
			4·96	5·07	17·63	1	98	2·01
			4·95	5·08	17·66			2·01
			4·91	5·12	17·81	2	96	2·03
			4·89	5·14	17·88			2·03
2	17·58	10·03	4·99	5·04	17·53	0·5	99	1·99
			5·00	5·03	17·49			
	34·90	20·00	9·96	10·04	34·92	0·5	99	2·00
			9·95	10·05	34·95			2·00
3	17·42	5·56	0·90	4·66	16·21	0·5	19	1·86
		6·06	1·07	4·99	17·35	0·5	21	1·99
		6·50	1·50	5·00	17·39	0·5	30	2·00
		7·06	2·05	5·01	17·42	0·5	41	2·00
		7·56	2·52	5·04	17·52	0·5	50	2·01
		8·06	3·05	5·01	17·42	0·5	61	2·00
		9·05	4·07	4·98	17·32	0·5	82	1·99
		10·03	5·02	5·01	17·42	0·5	100	2·00
		20·00	14·97	5·03	17·49	0·5	298	2·01

TABLE VII. BROMINATION OF *o*-CRESOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	12·35	10·03	4·62	5·41	14·61	0·5	85	2·37
			4·56	5·47	14·78		83	2·39
			4·36	5·67	15·32	1	77	2·48
			4·38	5·65	15·26			2·47
	13·98	10·03	3·70	6·33	17·10	1	58	2·45
			3·74	6·29	16·99			2·43
			3·48	6·55	17·69	2	53	2·53
			3·47	6·56	17·72			2·53
			2·98	7·05	19·05	5	42	2·72
			2·99	7·04	19·02			2·72
2	12·35	5·00	0·21	4·79	12·94	0·5	4·4	2·09
			0·20	4·80	12·97		4·1	2·10
			0·21	4·79	12·94	1	4·4	2·09
			0·20	4·80	12·97		4·1	2·10
		5·17	0·35	5·22	14·10	1	7	2·28
		6·07	0·72	5·35	14·45	1	13	2·34
		7·06	1·59	5·47	14·78	1	29	2·39
		8·56	2·98	5·58	15·07	1	53	2·44
		10·03	4·36	5·67	15·22	1	77	2·48

TABLE VIII. BROMINATION OF *m*-CRESOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	5·94	10·11	6·79	3·32	5·98	1	200	3·02
			6·80	3·31	5·96			3·01
			6·69	3·42	6·16	2	195	3·11
			6·68	3·43	6·18			3·12
2	12·15	10·11	3·64	6·47	11·65	1	56	2·88
			3·66	6·45	11·62			2·87
		20·00	13·32	6·68	12·03	1	200	2·97
			13·32	6·68				
3	5·94	6·07	2·88	3·19	5·75	1	90	2·91
		7·06	3·80	3·27	5·89		116	2·97
		8·06	4·74	3·32	5·98		143	3·02
		9·06	5·74	3·32	5·98		173	3·02
		10·11	6·80	3·31	5·96		205	3·01

TABLE IX. BROMINATION OF *p*-CRESOL BY BROMINE MONOCHLORIDE

No.	Substance weighed, *mg*	Excess 0·1*N* BrCl added, *ml*	Consumed 0·1*N* $Na_2S_2O_3$ *ml*	Consumed 0·1*N* BrCl *ml*	Substance found, *mg*	Bromination period, *min*	Percentage of excess BrCl: ratio of columns 4 : 5	Amount of Br taken up by 1 mole, *atoms*
1	13·80	10·03	5·37	4·66	12·59	1	115	1·82
			5·37	4·66	12·59			
			4·99	5·04	13·62	2	99	1·97
			4·99	5·04	13·62			
			4·92	5·11	13·80	3	96	2·00
			4·92	5·11	13·80			
			4·46	5·57	15·05	5	80	2·18
			4·46	5·57	15·05			
2	15·78	10·03	4·18	5·85	15·80	3	72	2·00
			4·18	5·85	15·80			2·00
	31·29	20·00	8·40	11·60	31·34	3	72	2·00
			8·43	11·57	31·26			2·00
			8·41	11·59	31·31			2·00
3	27·37	11·07	1·93	9·14	24·69	3	21	1·80
	13·80	6·07	1·25	4·82	13·02	3	26	1·89
	27·37	12·11	2·65	9·56	25·82	3	28	1·89
		13·12	3·36	9·76	26·37	3	34	1·93
	13·80	7·06	1·99	5·07	13·70	3	39	1·99
		8·06	2·99	5·07	13·70	3	58	1·99
		9·06	4·00	5·06	13·67	3	79	1·98
		10·09	5·02	5·06	13·67	3	99	1·99

TABLE X. BROMINATION PERIODS FOR THE BROMINATION OF AROMATIC COMPOUNDS ACCORDING TO KOPPESCHAAR AND BY THE BROMINE MONOCHLORIDE METHOD

No.	Substance	Bromination periods, *min*	
		Koppeschaar method	BrCl method
1	Phenol	5–30	1
2	*p*-Hydroxybenzoic acid	5–30	1
3	Salicylic acid	60	2
4	*o*-Nitrophenol	30	0·5
5	*m*-Nitrophenol	5–30	1
6	*p*-Nitrophenol	5–30	0·5
7	*p*-Cresol	1	3
8	*m*-Cresol	1	1

to be too short. The interfering action caused by extremely large or extremely small volumes of liquid also appears in determinations conducted by the Koppeschaar method. In this case, however, it is of less significance since bromination periods may usually be prolonged; (in general, it is conventional to use, instead of the shortest period necessary, periods 1·5 to 2 times as long): prolonged bromination periods eliminate both errors. In the bromine monochloride method, however, it is not possible to apply prolonged periods of bromination.

To complete our studies, the effect of varying hydrochloric acid concentrations was studied. It was found that correct values were obtained on acidifying with 10–15 ml of 20% hydrochloric acid. Whilst the increase of concentration of hydrochloric acid did not interfere with the results, the application of lower concentrations resulted in values below the actual ones. This may be due to the fact that the decrease of acid concentration reduces the rate of formation of bromine monochloride. In this way, also, elementary bromine liberated in the first stage of preparation of bromine monochloride participates in the substitution reaction. On bromination with elementary bromine, bromide ions form which reduce to bromine some of the bromine monochloride. On bromination with bromine monochloride, chloride ions are formed.

The reaction with bromine monochloride of aromatic compounds which are not brominated by bromine itself was examined. As an example, bromination by bromine monochloride of benzoic and acetylsalicylic acids (the latter without hydrolysis) was attempted and it was found that under the experimental conditions, bromination of these compounds by bromine monochloride was also unsuccessful.

These investigations indicate that on applying bromine monochloride, the range of compounds which can be brominated does not increase, although the rate of bromination increases appreciably.

Increased rates of reaction made possible the application of extremely short bromination periods. This may be of a great practical significance, *e.g.*, in the determination of the components of drug mixtures without previous separation.

The fact that the bromination period of one hour prescribed so far for the determination of salicylic acid could be reduced to only two minutes made possible the precise determination of salicylic acid in the presence of acetylsalicylic acid, thus enabling the investigation of the decomposition of the salts of acetylsalicylic acid. Acetylsalicylic acid cannot be brominated without previous hydrolysis. When, however, a bromination period of one hour, prescribed by Koppeschaar for the determination of salicylic acid, is applied, a partial hydrolysis of acetylsalicylic acid takes place, and salicylic acid formed as a product of this hydrolysis will also be brominated. In contrast, during the bromination period of two minutes required for the bromine monochloride method, practically no decomposition of acetylsalicylic acid occurs, and this source of error is eliminated. Studies carried out in connection with the decomposition of salts of acetylsalicylic acid will be published elsewhere.

Zusammenfassung—Die Bromierung gewisser Phenole durch Bromchlorid wird untersucht, und die Methode wird auf quantitative Messungen angewandt.

Die Anwendung von Bromchlorid vermehrt nicht die Anzahl der Verbindungen, die man bromieren kann, sondern hebt die Geschwindigkeit der Bromierung merklich.

Résumé—On a étudié la bromuration de certains phénols au moyen du chlorure de brome et a utilisé cette méthode comme moyen de dosage.

A partir du bromate et du bromure en quantités équivalentes ($1M$: $2M$), le chlorure de brome a été préparé dans la fiole à bromuration en milieu acide chlorhydrique.

On a trouvé que, bien que l'application du chlorure de brome n'augmente pas le nombre de composés susceptibles d'être bromurés, elle accroît sensiblement la vitesse de bromuration.

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THE COMPLEXOMETRIC TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM. A CRITICAL STUDY

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(*Received* 27 *March* 1958)

Summary—A critical examination has been made at the 0·01*M* level of the performance of various indicators for the titration of calcium in the presence or absence of magnesium with EDTA. The *bis*-azo dye Acid Alizarin Black SN is recommended for the titration of calcium in pure solution, and for solutions where the magnesium/calcium ratio does not exceed 1:12. For higher ratios, quantitative recovery of calcium and satisfactory end-points are only obtained when Calcon is used as indicator.

The range of application of Acid Alizarin Black SN can be extended if 1:2-diamino-propane-N:N′-tetra-acetic acid is used in place of EDTA as titrant.

IN THE original procedure of Schwarzenbach, Biedermann and Bangerter[1] total hardness is determined in the presence of Solochrome Black T as indicator at pH 10; calcium is determined at pH > 12, in the presence of the precipitated magnesium hydroxide, with Murexide as indicator. Several other indicators have since been advocated. The present paper describes an examination we have made of several of these indicators. Where possible the indicators have been used under standardised conditions except for some variation in the reagents used for adjustment of the necessary pH conditions.

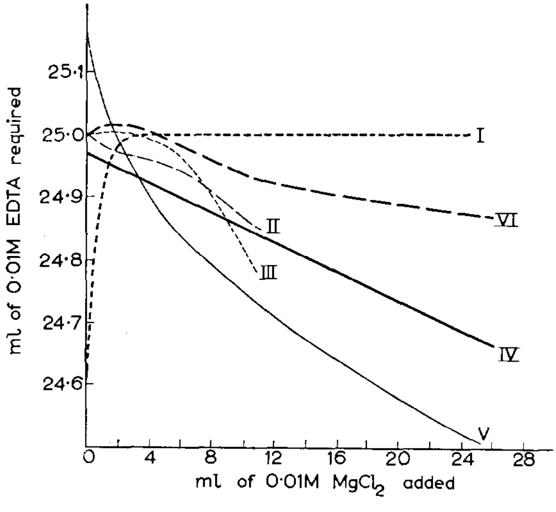

FIG. 1. Recovery of 25·00 ml of 0·01*M* calcium in the presence of magnesium.
I Calcon; II Methyl Thymol Blue; III Acid Alizarin Black SN; IV Murexide; V Calcein; VI Acid Alizarin Black SN with 1:2-Diaminopropane-N:N′-tetra-acetic acid.

Fig. 1 shows the recovery of calcium obtained in the presence of varying amounts of magnesium when using the different indicators. These titrations were carried out at the 0·01M level. The various indicators are also considered separately; details of indicator response and tables of results are given showing the variation in recovery of calcium.

Each entry in the tables represents the mean of ten titrations. A measure of the reproducibility of each indicator may be deduced from the standard deviation. More than 350 determinations were carried out.

Murexide

When no magnesium is present, the pink to purple end-point in the EDTA titration of calcium is sharp but the colour contrast is poor, though it may be improved by screening.[2] Our results show a tendency for low recoveries to occur even in the absence of magnesium, but this may be partly due to personal reactions to the colour change of the indicator.

TABLE I.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, MUREXIDE AS INDICATOR

ml of 0·01M *solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	24·97	0·03
25·00	1·00	24·96	0·03
25·00	2·00	24·95	0·02
25·00	5·00	24·91	0·05
25·00	10·00	24·84	0·05
25·00	25·00	24·68	0·07

The error in the recovery of calcium appears to be proportional to the amount of added magnesium, and the quality of the end-point deteriorates progressively both with regard to sharpness and colour contrast. In these titrations, diethylamine was used as the buffer substance. In our experience this affords a better colour change than the conventional sodium or potassium hydroxide reagents.

Calcein

Calcein[3] screened with thymolphthalein[4] gives a sharp end-point from fluorescent green to dark red in the titration of calcium in pure solution. The recovery of calcium appears to be high when the indicator is titrated to a definite colour change, but this may be due to the presence of impurities in the commercial sample of indicator which we used. When magnesium is present, the end-point is less sharp and the green fluorescence does not entirely disappear, though the dark red colour is very strong in transmitted light. The recovery of calcium falls off markedly as the ratio of magnesium to calcium is increased. The indicator action is also complicated by the occurrence of premature end-points before the equivalence-point. Furthermore, the green fluorescence reappears less than a minute after the end-point.

With this indicator, either sodium or potassium hydroxide was preferred to diethylamine for the adjustment of pH since the last mentioned base tended to cause premature end-points and colour reversion.

TABLE II.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, CALCEIN AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·16	0·07
25·00	1·00	25·06	0·03
25·00	2·00	24·99	0·04
25·00	5·00	24·87	0·03
25·00	10·00	24·75	0·05
25·00	25·00	24·51	0·04

Methyl thymol blue

This substance, which was recently proposed by Körbl and Přibil,[5] gives a sharp, easily detected blue to colourless end-point in the titration of calcium in pure solution. The recovery of calcium appears to be quantitative. When the magnesium/calcium ratio is greater than 1:5, premature end-points occur, but the colour reverts to blue in *ca.* 10 seconds. This reversion also occurs beyond the equivalence-point.

TABLE III.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, METHYL THYMOL BLUE AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·03
25·00	1·00	24·98	0·02
25·00	2·00	24·97	0·02
25·00	5·00	24·96	0·01
25·00	10·00	24·87	0·02
25·00	25·00	—	—

The end-point was judged to be that point in the titration at which the colour reversion no longer occurs quickly—as it does with the first premature end-points. When the magnesium/calcium ratio approached unity, it was not found possible to obtain reproducible results because of the profusion of premature end-points and the repeated reversion of colour even beyond the equivalence-point.

Diethylamine was used as the buffer substance, but caustic soda serves equally well provided that care is taken not to raise the pH much above 12·5. The indicator is permanently blue at higher pH values.

Calcon (B.C.I. No. 202)

Calcon, proposed by Hildebrand and Reilley,[6] does not give a sharp end-point when calcium is titrated with EDTA in the absence of magnesium, or when the magnesium/calcium ratio is less than 1:12. The recovery of calcium is markedly low, *cf.* Table IV. The indicator shows a long purple intermediate shade with a diminishing red shade which finally disappears leaving a pure blue solution *before* the equivalence point, *cf.* Fig. 1. The colour change may spread over 6–8 drops of 0·01*M* titrant. However, the quality of the end-point improves markedly with increasing amounts of magnesium, so that for magnesium/calcium ratios between 1:10–1:5 sharp end-points are obtained and the recovery of calcium appears to be quantitative.

TABLE IV.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, CALCON AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	24·63	0·10
25·00	1·00	24·86	0·10
25·00	2·00	24·99	0·03
25·00	5·00	25·00	0·06
25·00	10·00	24·99	0·07
25·00	25·00	25·01	0·06

In the presence of larger amounts of magnesium, brief premature end-points appear before the equivalence point, but since these revert in 2–3 seconds it is possible to locate the true end-point without much difficulty. Even beyond the equivalence-point, reversion of colour from blue to purple-red occurs after a period of more than 10 seconds. Diethylamine was used as the buffer substance.

Hildebrand and Reilley applied Calcon to the titration of solutions having much higher ratios of magnesium to calcium (10 molar proportions). They comment that the end-point is sluggish when there is a heavy precipitate of magnesium hydroxide.

Acid Alizarin Black SN (B.C.I. No. 337)

In a previous publication, we proposed the use of this *bis*-azo dye for the titration of calcium.[7] In the absence of magnesium, or with magnesium/calcium ratios less

TABLE V.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM, ACID ALIZARIN BLACK SN AS INDICATOR
ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·01
25·00	0·50	24·99	0·03
25·00	1·00	25·00	0·01
25·00	2·00	24·99	0·02
25·00	5·00	24·97	0·05
25·00	10·00	24·81	0·12
25·00	25·00	—	—

than 1:12, a very sharp red to turquoise-blue end-point is obtained and the recovery of calcium appears to be quantitative.

In the presence of larger amounts of magnesium, the end-point response of the indicator becomes less well defined; the colour changes through purple and blue to turquoise-blue. In addition, the recovery of calcium falls below the theoretical value. In the presence of large amounts of magnesium the titration should be carried through to the final shade, but the intermediate colours may spread over 8–10 drops. Brief reversion of colour occurs before the equivalence-point as with the other indicators, but beyond equivalence the end-point is stable for several minutes.

Diethylamine was used as the buffer substance.

Titration of calcium in the presence of magnesium with 1:2-*diaminopropane*-N:N′-*tetra-acetic acid*

As a result of work being carried out in this laboratory on various chelating agents related to EDTA,[8] we have examined the application of 1:2-diaminopropane-N:N′-tetra-acetic acid to this titration. Our examination was confined to the use of Calcon and Acid Alizarin Black SN as indicators, since these appeared to be the most suitable substances in the light of our previous experiments using EDTA. It was found that no better result was obtained when using Calcon—indeed we prefer the use of EDTA in conjunction with the indicator, but the performance of Acid Alizarin Black SN was considerably improved.

TABLE VI.—TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM WITH 1:2-DIAMINOPROPANETETRA-ACETIC ACID, ACID ALIZARIN BLACK SN AS INDICATOR

ml of 0·01*M solutions*

Calcium taken	Magnesium added	Calcium found	Standard deviation
25·00	0·00	25·00	0·00
25·00	1·00	25·00	0·03
25·00	2·00	25·02	0·04
25·00	5·00	25·01	0·05
25·00	10·00	24·93	0·06
25·00	25·00	24·88	0·08

Very sharp end-points and quantitative recoveries of calcium were obtained when the magnesium/calcium ratio did not exceed one fifth. Thereafter, increasingly large amounts of magnesium caused less sharp end-points and low recoveries of calcium. It would appear from Fig. 1 that slightly high results are obtained for low magnesium contents, but it must be stressed that the results shown are the arithmetic mean titres and the divergence from theory is within the limits of measurement of the 50-ml burettes used in these experiments.

EXPERIMENTAL

Reagents

0·01*M EDTA:* Standardised against pure magnesium metal using Solochrome Black 6B at pH 10 as indicator.[9]

0·01*M* *Calcium chloride:* Prepared from A.R. calcium carbonate by dissolution in a slight excess of hydrochloric acid.

0·01*M* *Magnesium Chloride:* Prepared from pure magnesium metal.

Buffers: Diethylamine
2*N* Sodium or potassium hydroxide

Indicators: Calcon—0·5% Ethanolic solution
Murexide—1% Dispersion in sodium chloride.
Calcein—1% Calcein, 0·6% thymolphthalein dispersion in potassium chloride
Methyl Thymol Blue—1% Dispersion in potassium nitrate
Acid Alizarin Black SN—2% Dispersion in sodium chloride.

Procedure

25·00 ml of 0·01*M* calcium chloride solution were pipetted into a 250-ml conical flask and the requisite amount of magnesium chloride solution was added from a burette. To every 25 ml of this test solution were added 5 ml of diethylamine or 5 ml of alkali hydroxide. The mixture was shaken and allowed to stand for 5 minutes. A sufficient amount of the appropriate indicator was then added to impart the necessary colour to the solution and the titration was carried out with 0·01*M* EDTA to the end-point. Ten determinations were made for each molar ratio of calcium to magnesium and the mean recovery and standard deviation were recorded in each case.

DISCUSSION

As a result of these studies it appears to us that the conventional Murexide indicator for the titration of calcium in the presence of magnesium is less suitable than some of the newer indicators both on the grounds of low recoveries of calcium and the quality of the end-point. The presence of appreciable amounts of magnesium causes a deterioration in the quality of the end-point of all these indicators except Calcon and favours low recoveries. The behaviour of Calcon is unsatisfactory in the absence of magnesium hydroxide, but is considerably improved in its presence. For calcium in the absence of magnesium all the other indicators examined, except possibly Calcein and Murexide, are satisfactory, but the most precise and clear-cut end-point is obtained with Acid Alizarin Black SN. This indicator is particularly useful in that it functions best in the region of magnesium/calcium ratios where Calcon cannot be applied very successfully, *cf.* Fig. 1. Accordingly we recommend that Acid Alizarin Black SN be used for the titration of calcium in pure solution and for magnesium/calcium ratios less than 1:12 (0·01*M* solutions); for higher ratios of magnesium to calcium, Calcon should be applied.

The occurrence of premature end-points is almost certainly due to the co-precipitation of calcium with the magnesium hydroxide, but the reversion of colour which occurs even after the equivalence-point with those indicators which are capable of responding to magnesium ions with a high degree of sensitivity, *viz* Methyl Thymol Blue, Calcein and Calcon, suggests that the magnesium takes part in the reaction either by direct solution of the hydroxide precipitate or by kinetic exchange with the chelated calcium in the solution.

The indicator of Patton and Reeder[10] was not included in this comparison, because in spite of its excellent colour change in the titration of calcium in the presence of magnesium, in our experience it is somewhat unstable in strongly alkaline solution.

The extension of the range over which Acid Alizarin Black SN gives a sharp end-point with quantitative recoveries of calcium when 1:2-diaminopropane-N:N′-tetra-acetic acid is used as titrant is interesting, but in view of the excellent response of Calcon with EDTA in this extended region, there is little advantage to be gained.

Acknowledgements—We are grateful to the Clayton Aniline Company for the award of a research grant and for the gift of a sample of Acid Alizarin Black SN.

Zusammenfassung—Es wurde eine kritische Untersuchung verschiedener Indikatoren für die Titration von Calzium mit $0{\cdot}01M$ Lösung von ÄDTA in Anwesenheit oder Abwesenheit von Magnesium gemacht. Der *bis*-azo Farbstoff Acid Alizarin Black SN wird für die Titration von Calzium in reiner Lösung vorgeschlagen sowie für Lösungen in denen das Magnesium/Calzium Verhältnis 1:12 nicht übersteigt. Bei Größeren Verhältnissen wird nur dann Calzium quantitativ erfasst und eine gute Endpunkt erhalten, wenn Calcon als Indikator gebraucht wird.

Man kann den Anwendungsbereich von Acid Alizarin Black SN ausdehnen, wenn 1:2-Diaminopropan-N:N′-Tetraessigsäure and Stelle von ÄDTA als Masslösung gebraucht wird.

Résumé—Un examen critique a été fait à partir des solutions $0{\cdot}01M$ du fonctionnement de divers indicateurs utilisés pour le titrage du calcium, soit suel, soit en présence de magnésium, au moyen de l'EDTA. Le colorant *bis*azoïque "Acid Alizarin Black SN" est recommendé pour le titi age du calcium en solution pure, et pour des solutions où le rapport magnésium/calcium ne dépasse pas 1:12. Où les rapports sont plus hauts la récupération quantitative du calcium et des fins de réaction satisfaisantes ne sont obtenues qu'en utilisant comme indicateur le calcon.

On peut porter plus loin les limites d'application de l'Acid Alizarin Black SN en remplaçant l'EDTA comme solution titrante par l'acide 1:2-diamine-propane-N:N′-tetracétique.

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Talanta, 1958, Vol. 1, pp. 245–248, Pergamon Press Ltd., London.

AN IMPROVED ALTERNATING CURRENT POLAROGRAPH

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(*Received* 2 *December* 1957)

Summary—Results obtained with the a.c. bridge polarograph devised by the authors are given.

THE polarogram obtained instantaneously by means of the oscillograph could offer a versatile technique in rapid polarographic analysis or in following chemical reactions. But this technique has been faced with troublesome problems arising both from the difficulty of construction of a suitable oscillograph and from theoretical defects based on diffusion phenomenon.

In such oscillographic polarography, sine-wave, saw-tooth-wave, or triangle-wave a.c. current has been applied to the polarographic cell and the mechanism of chemical reaction on the surface of the electrode has been studied.[1–5]

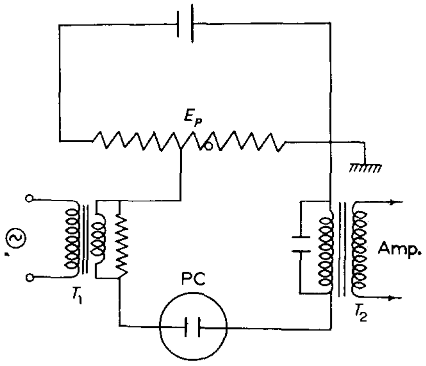

FIG. 1. Principle of a.c. polarograph (MacAleavy).

R. H. Müller[6] measured the a.c. current in the polarographic current by superimposing a.c. voltage on the d.c. voltage. J. Boeke[7] carried out the same measurement by observing the figure shown on a Brown tube (a.c. voltage applied as abscissa and a.c. current as coordinate) and found the value of the half-wave potential from the change of the figure with gradual change of applied d.c. voltage. He also determined the amount of the substance by measuring the resistance at the half-wave potential by means of a Kohlrausch's bridge.

So-called a.c. polarography is different from the oscillopolarography just described. One measures the a.c. current separated from d.c. current flow with an ammeter when a weak a.c. voltage was applied on top of the d.c. voltage to the polarographic cell. Such a.c. polarography has recently been developing in both theory and application, especially in the field of chemical analysis.

An example of the circuit used in a.c. polarography is illustrated in Fig. 1 (MacAleavy's circuit).[17] The a.c. voltage is applied to the polarographic cell through the transformer T_1 and the a.c. component in the electrolytic current is separated through the transformer T_2, amplified and then measured.[9,10]

B. Breyer,[11] J. E. B. Randles[12] and others have developed the theory of this type of polarography and also its practical application. P. Delahay *et al.*[13] instituted the vector method in order to compensate for the differential capacity due to the resistance of the cell solution and the electric double layer.

Graham[14] also derived a fundamental equation of a.c. polarography based on theoretical considerations of the rate of the electrode reaction. Ishibashi and Fuginaga[15] have proposed a differential polarograph which uses a rectangle-wave as a.c. source. Tachi and Senda[16] recorded an a.c. polarogram, by picking up the a.c. component from transformer T_2, rectifying to d.c. current and leading this to a conventional d.c. polarograph.

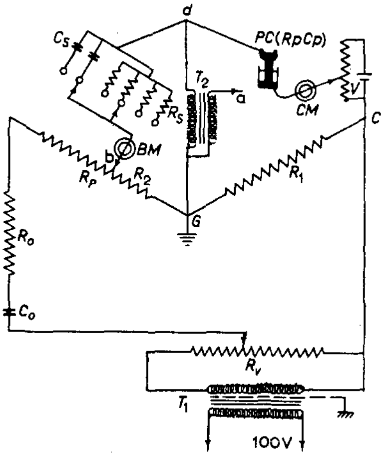

FIG. 2. Principle of a.c. polarography. $R_x = 16{\cdot}7\,\Omega$, $R_1 = 16{\cdot}7\,\Omega$ (and $+33{\cdot}3\,\Omega$), $R_s =$ 100 Ω, 200 Ω, 300 Ω, 500 Ω, 2, 3, 5 $K\Omega$, $C_s = 0{\cdot}1, 0{\cdot}2, 0{\cdot}5, 1, 2, 4\,\mu$F, PC = polarographic cell, E_p 0–2·5 V., T_2 = input trans. (1/10), BM = two-phase balancing motor, CM = synchronous motor.

A.c. polarography is the measurement of the fluctuating phenomenon during the dropping of mercury just as in d.c. polarography. Therefore, it is certain that a recording method is the most straightforward and effective one in a.c. polarography for measuring the fluctuating phenomenon precisely.

In measuring the a.c. current by means of MacAleavy's circuit or a related one, the a.c. voltage superposed on the d.c. voltage should be kept constant. Even though this is done, the a.c. voltage on the surface of the dropping mercury (electric double layer) may change the amplitude and phase of a.c. current in accordance with the gradually changing voltage of d.c., since a change of the Faradaic impedance on the surface of the electrode occurs so that more a.c. current flows, resulting in a depression of the a.c. voltage. Thus it is certain that in a.c. polarography the relationship between the a.c. current and the concentration of the substance to be reduced may deviate from a linear relationship.

With a view to removing the above difficulties of a.c. polarography, the present authors have tried to apply an a.c. bridge and after much investigation have succeeded in constructing a very versatile polarograph, which may be called an "a.c. polarograph with a.c. bridge". Fig. 2 illustrates the principle of this polarograph, which is pen-recording with automatic balance.

In this instrument the polarographic cell PC, standard resistance R_S, the variable slide resistance R_2 and the fixed resistance R_1 form an a.c. bridge, and the minute and definite a.c. voltage is superimposed on the gradually changing d.c. voltage applied to the polarographic cell. When the d.c. voltage reaches a certain voltage and at the same time the electrolytic current begins to flow suddenly, the conductivity of the solution in the polarographic cell reaches a maximum value.

The a.c. bridge cannot retain balance when the conductivity changes in this way. Thus generated unbalanced a.c. current, subsequently amplified, passes to the two-phase balancing motor, and moves the variable slide resistance R_2 until the a.c. bridge is again balanced. The movement of the slider indicates the conductivity of the polarographic cell and is written on the chart which is synchronised with gradually increasing voltage of d.c.

When the a.c. voltage E changes differentially, dI/dE (where I is the electrolytic a.c. current) is given as a true conductivity, measured precisely by the bridge, if we correct the minute change of the capacity of the small electrode by means of a condenser in parallel with a standard resistance.

In Fig. 2, the a.c. source, either 50 or 60 c/min, is applied to transformer T_1 and its output is moderated to a selected voltage by adjusting R_V, and to a suitable phase by means of the condenser C_0 and the resistance R_0. The values of C_0 and R_0 are determined in order to intersect the output from the amplifier in a direction rectangular to the a.c. source (100 V). In the a.c. circuit bridge the following relationship is thus established:

$$R_2/R_S = R_1/R_P$$

where R_P is the equivalent internal resistance of the polarographic cell. Changing the form of the above formula,

$$R_2 = R_S \,.\, R_1/R_P$$

the indicating resistance R_2 is seen to be proportional to the reciprocal of the internal resistance of the polarographic cell, $1/R_P$, and since $1/R_P$ corresponds to dI/dE, R_2 indicates the value of dI/dE.

In practice the a.c. voltage superimposed in the polarographic cell is less than 50 mV, when the d.c. voltage changes within 0·05–0·2 V. When the changing range of the a.c. voltage is within 1–100 mV, depending upon the change of either the resistance R_1 or a.c. current flowing through R_1 and R_r, a precise polarogram can be drawn.

The synchronous motor of the potentiometer(V) for which applies the d.c. voltage changes continuously and is connected with the motor of the recorder. D.c. current flows from the potentiometer V, through the electrolytic cell PC, the primary side of the transformer T_2, and resistance R_1, and returns to V; the resistance of the primary side of T_2 and resistance R_1 are kept small in order to make the most of d.c. voltage charge on the polarographic cell; the slide resistance of the potentiometer V is assumed to be negligible in comparison with R_P.

The unbalanced a.c. current generated in the secondary side of T_2 is amplified by means of the amplifier shown in Fig. 3, in which the input of a.c. voltage is amplified by the vacuum tubes V_1 and V_2 and is led into one phase of the two-phase balancing motor BM. If the capacity of the bridge is balanced, the imaginary part of the output current is negligible, so that the output intersects the a.c. source rectangularly, resulting in revolution of the balancing motor. It is necessary to connect the output to the slider (b) in order to rotate the balancing motor and thus to balance the bridge.

The maximum conductivity of a.c. current appears just at the half-wave potential of the d.c. polarogram. Therefore, it may be concluded that the a.c. polarogram approaches the ideal differential curve as the superposed a.c. voltage becomes smaller and smaller. Furthermore, the fluctuating voltage of the a.c. source has little effect on an a.c. polarogram and therefore on the determination of a reducible substance by polarography.

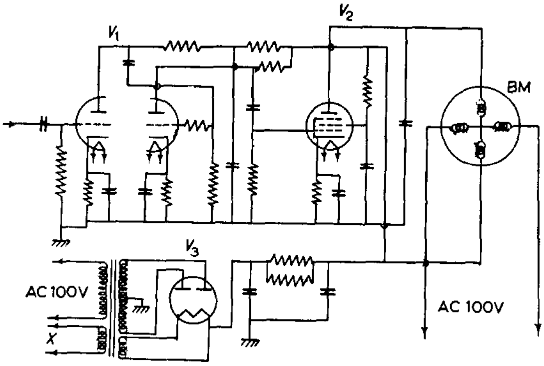

Fig. 3. A.C. amplification circuit.

Results obtained by an a.c. polarograph are more exact than those by d.c. polarography in chemical analysis, because the presence of more easily reducible substances than the substance to be determined has much less influence than in d.c. polarography. Some examples are shown in Figs. 4–8.

The a.c. polarograph, now available in Japan, is constructed as shown in Fig. 9.

Zusammenfassung—Die mit dem von den Verfassern entwickelten Wechselstrombrücke-Polarographen erreichten Resultate werden angegeben.

Résumé—On donne des résultats obtenus à l'aide du polarographe à pont pour courant alternatif, inventé par les auteurs.

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FIG. 4. A mixed solution of Tl and Pb ions in 0·2M H_3PO_4
Left: $Pb(NO_3)_2$ $M/2500$ and $TlNO_3$ $M/2000$ (Voltage unit 0·1 V)
Centre: $Pb(NO_3)_2$ $M/2500$ and $TlNO_3$ $M/2000$ (Voltage unit 0·05 V)
Right: $Pb(NO_3)_2$ $M/2000$ and $TlNO_3$ $M/1000$ (Voltage unit 0·05 V)

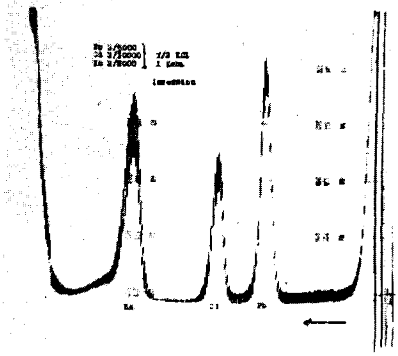

FIG. 5. A mixed solution of Pb, Cd and Zn ions in 0·5N KCl
$Pb(NO_3)_2$ $M/5000$, $CdSO_4$ $M/10000$ and $ZnSO_4$ $M/2000$

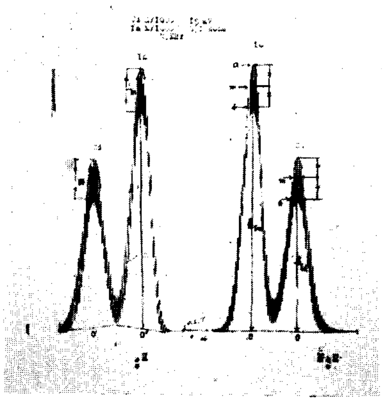

FIG. 6. A mixed solution of Cd and In ions in 1N KBr
$CdSO_4$ $M/1000$ and $In(NO_3)_3$ $M/1000$

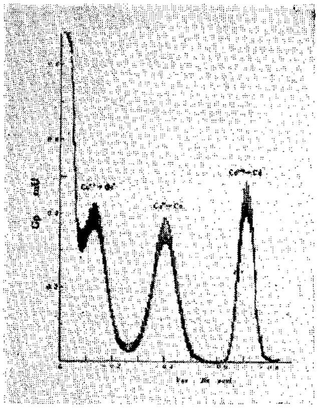

FIG. 7. A mixed solution of Cd and Cu ions in 1N NH_4OH and 1N NH_4Cl : $CdSO_4$ $M/2000$ and $CuSO_4$ $M/1000$

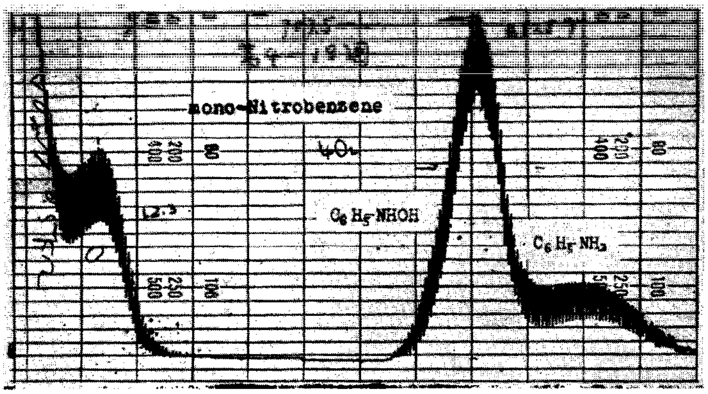

FIG. 8. Mononitrobenzene

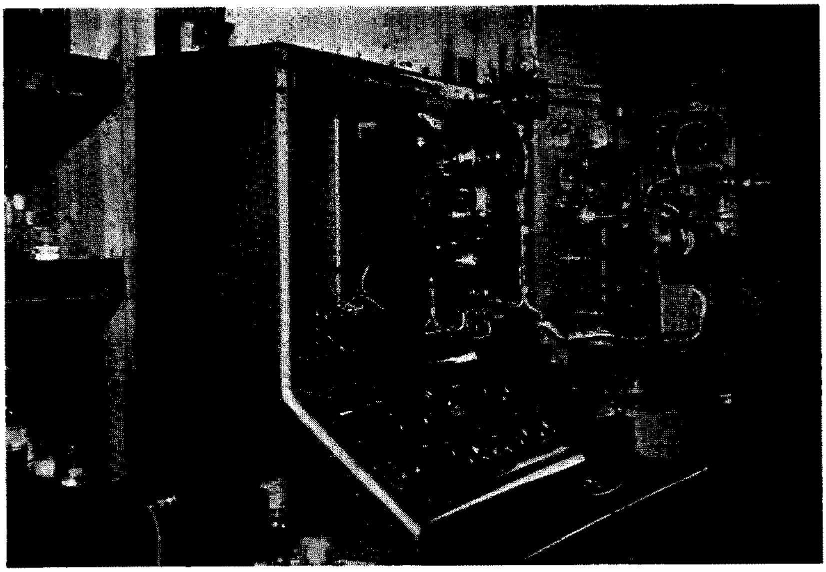

FIG. 9. A view of the self-recording A.C. Bridge Polarograph invented by Authors and sold by Yanagimoto Co., Kyoto, Japan.

Talanta, 1958, Vol. 1, pp. 249–251, Pergamon Press Ltd., London.

THE ANALYTICAL CHEMISTRY OF THE PYRIDINE THIOCYANATES—I

THE SEPARATION OF COBALT AND NICKEL BY SOLVENT EXTRACTION

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(*Received* 23 *April* 1958)

Summary—A procedure is described for the separation of cobalt and nickel as pyridine thiocyanates using solvent extraction. After separation the metals are determined colorimetrically in the extracts.

REFERENCE to the pyridine thiocyanates of cobalt and nickel in the literature is not new, dating in some cases from the end of the last century.[1,2,3] All of these papers, however, deal with methods for the preparation of the pyridine thiocyanates of the metals and have no analytical significance.

Duval,[4] in his book on thermogravimetric analysis, however, describes the thermogravimetric behaviour of nickel pyridine thiocyanate, showing that it provides a suitable weighing form for the determination of the metal. In recent years, the blue colour formed by cobalt thiocyanate in acetone and other solvents has been used by several workers for the determination of cobalt.[5]

Sharp and Wilkinson,[6] in developing a method for obtaining nickel-free cobalt salts, used ^{57}Ni and ^{60}Co tracers to investigate the separation of the two metals as thiocyanates by solvent extraction. Apart from these investigations, however, it would appear that the analytical value of the pyridine thiocyanates of cobalt and nickel has not been examined to any extent.

This paper describes a procedure for the separation and determination of cobalt and nickel by the formation of the pyridine thiocyanates.

PRELIMINARY INVESTIGATIONS

Under suitable conditions, cobalt and nickel form pyridine thiocyanates readily. The structure for the cobalt complex has been given[1] as $Co\ py_4\ (SCN)_2$ and, for that of nickel[2] as $Ni\ py_4\ (SCN)_2$.

The conditions under which these compounds formed were examined. In the case of cobalt it was found that, if excess thiocyanate is added to a cobalt solution, and the pH is adjusted to 2·5, slow addition of pyridine causes precipitation of cobalt pyridine thiocyanate when the pH has risen to a value of 5·6.

On the other hand, if excess thiocyanate is added to a nickel solution and the same procedure is followed, the nickel pyridine thiocyanate begins to form at pH 4·2 and precipitation is complete at pH 4·6.

Both compounds are very soluble in organic solvents, and it was found possible to effect a separation of the two metals on the basis of these preliminary observations.

As a means of determining the nickel present in the chloroform extract, the absorption spectrum of nickel pyridine thiocyanate in chloroform was determined.

This is shown in Fig. 1. The maxima at 560 mμ and 580 mμ were found to be too small to be of value and measurements were, therefore, carried out at 320 mμ.

For known amounts of nickel a calibration curve was prepared. From this curve the minimum amount of nickel which can be determined with certainty is 100 μg.

On extraction of the cobalt pyridine thiocyanate complex with methyl *iso*butyl ketone (Hexone) the colour of the extract is blue. The absorption spectrum of the solution is shown in Fig. 2. The maximum at 620 mμ is very suitable for measurement and was used throughout. Comparison of the absorption spectrum of this solution with that obtained by extracting cobalt thiocyanate from an aqueous solution between pH 4 and 6 with Hexone showed complete identity. It would appear, therefore, that it is cobalt thiocyanate which is extracted by Hexone.

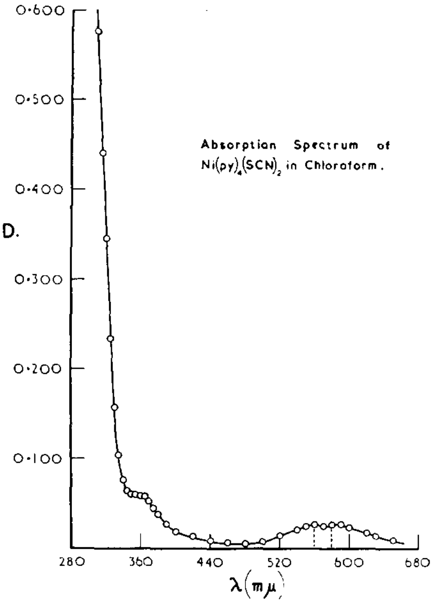

FIG. 1—Absorption spectrum of nickel pyridine thiocyanate in chloroform.

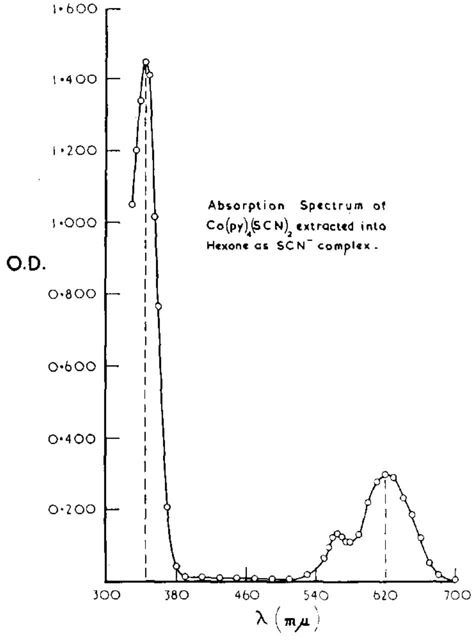

FIG. 2.—Absorption spectrum of cobalt thiocyanate complex in methyl *iso*butyl ketone.

For known amounts of cobalt a calibration curve was prepared. From this curve the minimum amount of cobalt determinable was 50 μg.

PROCEDURE

Preparation of the nickel complex

1. To about 20 ml of the solution for analysis, which should contain not less than 50 μg cobalt and 100 μg nickel, add 0·5 ml (excess) of a 40% solution of potassium thiocyanate. Make the pH 2·5–3·0 by means of hydrochloric acid.
2. Adjust the pH to 4·6 by the slow addition of pyridine. Nickel pyridine thiocyanate precipitates.
3. Extract the precipitate twice with 10 ml portions of chloroform and make up to 25 ml. This solution contains all the nickel present in the original sample. Under these conditions of precipitation, cobalt, if present, does not form a pyridine thiocyanate and probably exists in solution as cobalt thiocyanate which is not extracted into chloroform.

Determination of nickel

1. Filter the chloroform-extract and pour into the absorption cell of the spectrophotometer. This operation removes small globules of water which are sometimes present.

2. Compare the optical density of this solution against chloroform and calculate the amount of nickel in the solution from the calibration curve.

Preparation of the cobalt complex

1. To the aqueous layer remaining after extraction of nickel (which contains potassium thiocyanate, a trace of pyridine and cobalt, if present) add hydrochloric acid until the pH of the solution is in the region 2·5–3·0.
2. Add pyridine slowly to this solution until the pH is 5·6. Cobalt pyridine thiocyanate precipitates.
3. Extract this precipitate with two 10-ml portions of Hexone and make the volume to 25 ml with Hexone.

Determination of cobalt

1. Filter the Hexone-extract and pour into the absorption cell of the spectrophotometer.
2. Compare the optical density of this solution against Hexone, and from the calibration curve determine the amount of cobalt present.

RESULTS

To test the validity of the proposed method a number of "unknown" mixtures were analysed by one of us (J. H. W. F.). The results are recorded in Table I. Where the experimental results differ from the actual composition, the true are recorded in parentheses.

TABLE I

No. of sample	Co μg	Ni μg
1	1	100
2	50	trace (50)
3	50	975 (1000)
4	995 (1000)	105 (100)
5	250	—

The results, for cobalt in particular, are very satisfactory. The procedure is rapid and requires no special technique on the part of the operator.

Acknowledgement—One of us (J. H. W. F.) acknowledges gratefully a grant from the Physical Chemistry Group, Imperial Chemical Industries Limited, (Billingham Division) which enabled him to take part in this work.

Zusammenfassung—Es wird ein Extraktionsverfahren zür Trennung von Kobalt und Nickel als Metall–Pyridin–Rhodanid–Komplexe beschrieben. Die Metalle sind in den Extrakten kolorimetrisch bestimmbar.

Résumé—Description d'un procédé pour effectuer la séparation par extraction au moyen d'un solvant du cobalt d'avec le nickel sous forme de thiocyanates pyridiques. Après séparation on dose par colorimétrie les métaux dans les extraits.

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Talanta, 1958, Vol. 1, pp. 252–255. Pergamon Press Ltd., London.

DIFFERENTIATION OF ORGANIC ACIDS IN SPOT TEST ANALYSIS

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(*Received* 30 *April* 1958)

Summary—Halogen hydracids are released when aliphatic and aromatic polycarboxylic acids, arylalkyl carboxylic acids or aromatic mono carboxylic acids are heated at 160° along with alkali or ammonium halides. *o*-Nitrophenol shows the same behaviour and can thus be distinguished from its isomers. Aliphatic monocarboxylic, hydroxamic and sulphonic acids are without effect.

The detection of the released halogen hydracid by means of indicator paper (or by the demasking of silver ferrocyanide) makes possible a procedure for revealing the presence of effective organic acids. Microanalytical limits of detection were attained employing spot test techniques.

A SPOT test for succinimide was recently described[1] based on the production of pyrrole through distillation with zinc dust.[2] The product can be identified by means of a colour reaction with *p*-dimethylaminobenzaldehyde.[3] While working on this test it was found that pyrrole is likewise formed when a mixture of succinic acid and ammonium chloride is distilled with zinc dust; and accordingly a test for succinic acid was developed on this basis. It was assumed that when these materials are heated together they undergo metathesis to yield hydrogen chloride and ammonium succinate, which then loses water to yield succinimide. This supposition was confirmed in that acid vapours (change of indicator paper) are evolved when ammonium chloride is heated to 160° along with succinic acid (m.p. = 189°). This finding must be due to the release of hydrogen chloride since at this temperature there is no volatilization of succinic acid nor is ammonium chloride thermally decomposed with production of hydrogen chloride. This release of hydrogen chloride was likewise observed when succinic acid was heated with sodium chloride, potassium chloride, calcium chloride and other alkaline-earth chlorides.

The production of hydrogen chloride from its salts on heating at 160° in the presence of succinic acid is undoubtedly related to the fact that hydrogen chloride is volatile at this temperature in contradistinction to succinic acid and its salts. Since this difference also is true of other halogen hydrides, it could be expected that heating a mixture of an alkali halide and a nonvolatile organic acid (HAc) should give the reaction

$$\text{MeHal} + \text{HAc} \rightarrow \text{MeAc} + \text{HHal}$$

if Me = Na, K, NH_4 and Hal = Cl, Br, I.

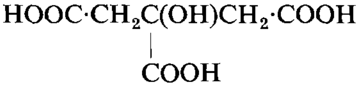
The occurrence of this reaction was tested with mixtures of alkali halides and organic acids. The mixtures were heated to 160° and the vapours tested for halogen hydracid with indicator paper (Merck universal indicator paper). The acids tested included aliphatic and aromatic monocarboxylic acids, arylalkyl carboxylic acids, sulphonic acids, hydroxamic acids, and aliphatic and aromatic polycarboxylic acids.

Surprisingly, the release of halogen hydracid proved to be characteristic of aliphatic and aromatic polycarboxylic acids, arylalkyl carboxylic acids, and aromatic monocarboxylic acids. There is no relation between this effect and the melting points of organic acids and their dissociation constants in solution. Therefore it appears that the active acids are far stronger acids in their melts or in the vicinity of their melting points than when dissolved. It seems that this increase in acidity does not occur at all or occurs only to a much less extent in the case of monocarboxylic, sulphonic and hydroxamic acids.

The reactions of molten or solid organic acids resulting in the liberation of halogen hydracid always occur on the surface of the solid alkali halide. Although the limited reaction theatre is a handicap to any extensive reaction, the release of hydrogen chloride from sodium chloride by tiny amounts of monocarboxylic aromatic, di- and tri-carboxylic aliphatic, and arylalkyl carboxylic acids not only occurs to an adequate extent but is so rapid that the effect on indicator paper can serve as a test for the acids of the type just noted.

Procedure. A small quantity of the sample or a drop of its solution is placed in a micro test tube and several cg of sodium chloride added. After complete volatilization of the solvent, if necessary, the test tube, covered with a strip of moist indicator paper (Merck Universal Indicator Paper), is plunged into a glycerol bath previously heated to 160°. The colour of the indicator will change within 2–5 minutes at the outside if active acids are present.

The following acids gave a positive response:

Oxalic acid	$HOOC\cdot COOH$
Malonic acid	$HOOC\cdot CH_2\cdot COOH$
Succinic acid	$HOOC\cdot CH_2CH_2\cdot COOH$
Malic acid	$HOOC\cdot CHOH\cdot CH_2\cdot COOH$
Maleic acid	$HOOC\cdot CH{=}CH\cdot COOH$
Tartaric acid	$HOOC\cdot CHOH\cdot CHOH\cdot COOH$
Adipic acid	$HOOC(CH_2)_4COOH$
Pimelic acid	$HOOC(CH_2)_5COOH$
Azelaic acid	$HOOC(CH_2)_7COOH$
Citric acid	 $HOOC\cdot CH_2\underset{\substack{\vert\\ COOH}}{C}(OH)CH_2\cdot COOH$
Benzoic acid	$C_6H_5\cdot COOH$
Phenyl acetic acid	$C_6H_5\cdot CH_2\cdot COOH$
Cinnamic acid	$C_6H_5\cdot CH{=}CH\cdot COOH$
Mandelic acid	$C_6H_5\cdot CHOH\cdot COOH$
Salicylic acid	$C_6H_4\cdot OH\cdot COOH$ (1: 2)
Phthalic acid	$C_6H_4(COOH)_2$ (1: 2)

An estimate of the sensitivity of the test is provided by the finding that 10 μg of pimelic or mandelic acids, 20 μg of adipic and 100 μg of benzoic acid respond definitely when tested by this procedure.

The following acids did not release hydrogen chloride under the stated conditions: caprylic, capric, lauric, myristic, palmitic, stearic, sulphanilic, 1:5-naphthol sulphonic, anthraquinone-1-sulphonic, anthraquinone-1:5- and -2:6-disulphonic acids.

These findings show that the procedure is suitable for revealing the presence of dicarboxylic acids in mixtures with higher fatty acids, and also for differentiating aliphatic and aromatic monocarboxylic acids. If alkali or alkaline earth salts of organic acids are presented for examination, a little sodium chloride should be added and the mixture then taken to dryness after introducing an excess of dilute hydrochloric acid. The residue is then kept at 120° for 10 minutes to remove the unused hydrochloric acid. If this preliminary treatment is conducted in a micro test tube, the process of heating to 160° and testing the vapour with indicator paper can be accomplished without transfer.

When this procedure is applied, it should be noted that volatile monocarboxylic acids (formic, acetic, propionic, lactic, etc.) will change the indicator paper and thus simulate the release of hydrogen chloride. However, vapours of the latter can also be tested with paper impregnated with silver ferrocyanide and ferric sulphate.[4] The following reaction occurs followed by the formation of prussian blue; the presence of hydrogen chloride is thus established:

$$Ag_4Fe(CN)_6 + 4Cl^- \rightarrow 4AgCl + [Fe(CN)_6]^{4-}$$

Procedure. As before with substitution of silver ferrocyanide-ferric sulphate paper for the acid-base paper.

Reagent paper: Silver ferrocyanide is prepared by adding excess silver nitrate to neutral potassium ferrocyanide solution. The precipitate is washed thoroughly and dissolved in ammonium hydroxide. Quantitative filter paper is bathed in the ammoniacal solution and dried in a current of warm air. The $Ag_4Fe(CN)_6$ remains in the pores of the paper. The paper keeps if stored out of contact with the air.

Trinitrophenol (picric acid), because of its strong acidic nature, releases hydrochloric acid when treated with sodium chloride under the test conditions. 2:4-Dinitrophenol and *m*- and *p*-nitrophenol are inactive, whereas *o*-nitrophenol behaves like the above-mentioned active acids. Thus 5 μg of *o*-nitrophenol may be identified. The behaviour of *o*-nitrophenol permits a sure distinction from its isomers. In a mixture of *o*- and *p*-nitrophenols it was possible to detect 20 μg of *o*-nitrophenol in the presence of 1000 μg of the *p*-isomer.

The behaviour of *o*-nitrophenol and the non-reactivity of its isomers and of 2:4-dinitrophenol show that the action on sodium chloride does not depend on the acidity in solution but on the enhanced acidity when melted, as was assumed before.

Zusammenfassung—Bei Erhitzung von Alkalihaliden mit organischen Säuren auf 160° wurde festgestellt, dass alifatische Monocarbonsäuren, Hydroxamsäuren, aci-Nitroverbindungen und Sulfosäuren ohne Einwirkung sind. Hingegen erfolgt Abspaltung von Halogenwasserstoff durch Polycarbonsäuren, *o*(1)Hydroxycarbonsäuren, sowie Monocarbonsäuren die eine —CH=CH— Gruppe in Nachbarschaft zur COOH— Gruppe enthalten.

Der Nachweis, des aus Natriumchlorid freigelegten Chlorwasserstoffes durch Indikatorpapier (oder Demaskierung von Silberferrocyanid) ermöglicht den Nachweis von wirksamen organischen Säuren. In der Arbeitsweise der Tüpfelanalyse werden mikroanalytische Empfindlichkeiten erreicht.

Résumé—Les hydracides halogènes sont libérés lorsqu'on chauffe avec des halogénures alcalins ou ammoniacaux à 160° les acides polycarboxyliques aliphatiques et aromatiques, les acides carboxyliques arylalkyls ou les acides mono-carboxyliques aromatiques. L'*o*-nitrophénol se comporte de la même façon, ce qui permet de le distinguer de ses isomères. Les acides mono-carboxyliques aliphatiques, hydroxamiques et sulfoniques sont sans effet.

La détection de l'hydracide halogène libéré au moyen de papier indicateur (ou en démasquant

le ferrocyanure d'argent) permet un procédé qui sert à révéler la présence d'acides organiques effectifs. Utilisant des techniques d'analyse à la touche on a pu arriver à des limites de détection microanalytiques.

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THE ORIGINS OF QUANTITATIVE INORGANIC ANALYSIS*

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(*Received* 27 *July* 1958)

Summary—Analytical chemistry owes much to men such as Bergman, Klaproth and Berzelius, who pioneered the analysis of natural materials and developed a systematic approach in spite of incomplete knowledge of the nature of chemical composition.

> "*When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a mean and unsatisfactory kind. It may be the beginning of knowledge but you have scarcely in your thought advanced to the state of a science.*"—LORD KELVIN

FROM the earliest days when men extracted metals from their ores, those who practised the art were interested in the "analysis" of different ores to discover which yielded the most metal. It was not analysis as we understand it to-day, the separation of the required metal rarely being complete with the simple dry methods then in use.

Agricola, in his *De re metallica* (1556) describes a considerable number of methods of analysis, many of which, modified to ensure complete extraction, are still in use. He gives full descriptions of the apparatus employed, which included balances enclosed in glass cases and a very wide range of crucibles and furnaces.

Alloys containing gold, silver and copper were analysed mainly by comparing the marks which they made on a "touchstone" (a dense flint) with those produced by standard alloys. Other than the parting of gold and silver with nitric acid, wet methods were rarely used, although several qualitative colorimetric methods were known such as the detection of iron in verdigris with extract of nutgalls. Although very highly developed, metallurgy was essentially an empirical art, and there was little effort at seeking an explanation of the ways in which metals could be extracted, or of the differences between ores of the same metal.

The search for an explanation of the composition of matter included the early theory of the four elements of earth, air, fire and water, followed by the "philosophic principles" of sulphur, salt and mercury. In their search for the elixir of life and the philosophers' stone, the alchemists, bemused by their own philosophy, were more interested in the outward appearance of their materials than in their chemical composition. The allegorical way in which their work was recorded makes the study of it very difficult, but the knowledge that was built up was enormous, although of little value until an understanding of chemical composition began to emerge at the beginning of the sixteenth century. Stillman, speaking of alchemists at that time,

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* Paper presented at a symposium on the History of Analytical Chemistry, organised by the Midlands Section and the Western Section of the Society for Analytical Chemistry, and held at Shrewsbury on 16–17 May 1958.

says "not only were methods of quantitative analysis lacking but there existed no hypothesis in their philosophy which could have suggested the possibility of such methods."

When chemists became interested in the application of their compounds in medicine, a certain amount of analysis became essential. Antimony was one of the earliest metals so used and the early uncertainty of the antimony content of various preparations caused a certain amount of ill-feeling.

The analysis of minerals and naturally occurring waters was attempted as a means of classification. The systematic use of the balance spread rapidly. Facts were built into theories which in turn suggested further directions for investigation. Chemistry had emerged as a fully qualified science in the terms of Lord Kelvin's definition.

Boyle, often referred to as "The Father of Chemistry", displayed the inability of the alchemists to produce a coherent theory to explain the facts they knew, but could not offer a new theory, only a way in which it must be sought, through the discovery of natural laws. Joseph Friend, a professor of chemistry at Oxford, said in 1712, "Chemistry has made a laudable progress in experiments but we may justly complain that little advances have been made towards the explication of them. . . . Nobody has brought more light to the art than Mr. Boyle, who, nevertheless, has not so much laid a new foundation of chemistry as he has thrown down the old".

The fundamental concept, upon which the whole structure of chemistry is based, is that of conservation of matter. Many chemists had tacitly assumed this but it was not until 1756 that it was formally expressed by Lomonossof.

In view of the long history of metallurgy it is not surprising that the first great theory dealt with the oxidation of metals and the reduction of the oxides. That some metals gained in weight when heated in air was known at least as early as the eighth century A.D. As soon as the balance came into regular use a number of metals were studied and the Phlogiston theory was put forward by Becher (1635–1682) and later developed by Stahl (1660–1734). Although the basis of the theory was incorrect it did correlate a wide number of phenomena. That Lavoisier later showed that this theory did not offer a correct explanation of the reactions in no way diminishes the important part it played as the first attempt to explain a number of related reactions.

The study of minerals and natural waters exercised the minds of most of the early analysts of whom three made outstanding contributions. Torbern Olaf Bergman (1735–84), a professor at Uppsala, made many analyses but his methods of separation were often very poor. Martin Heinrich Klaproth (1743–1817), the first professor of chemistry at Berlin introduced many improvements and tried to produce general rules for the analysis of these materials. Jons Jacob Berzelius (1779–1848), professor of chemistry at Stockholm, carried out a considerable amount of analysis, often with high accuracy. The main importance of his work, in relation to the general theory of chemistry, was to apply current ideas of structure to the analytical results obtained, both by himself and others.

The work of these three must be viewed against the background of general knowledge existing at the time. During the lives of Bergman and Klaproth the role of metals in minerals was fairly clear but the different valencies of some metals were not understood and many confusions existed with closely related elements. The role of non-metallic elements was not at all clear, particularly in the case of chlorides where the acid was believed to contain oxygen.

Proust's law of constant composition was published in 1800, followed rapidly by the work of Dalton on multiple proportions and on his *New System of Chemical Philosophy* or Atomic Theory. From these ideas Berzelius tried to deduce the composition of minerals.

The main aim of these early workers was to establish a system of classification of minerals from their chemical composition. The identification of constituents by heating with a blowpipe on charcoal arose from the work of Pott (1692–1777) who was asked by the King of Prussia to discover the ingredients from which Saxon porcelain was made and tried fusing various mixtures of likely constituents. This work, in the words of Thomas Thomson "gradually led to the methods of examining materials by the blowpipe. These methods were brought to the present state of perfection by Assessor Gahn of Fahlun, the result of whose labours has been published by Berzelius in his treatise on the blowpipe".

Cronstedt (1727–1765) divided minerals into earths, bitumens, salts and metals, but carried out little chemical analysis. Bergman was the first man to attempt to lay down systematic rules for the chemical analysis of minerals and natural waters. He analysed a number of local waters paying close attention to the colours given with a variety of natural dyes. He distinguished between carbonates and bicarbonates and usually boiled his samples to see what was deposited. Methods of separation were very simple, alcohol was often used for extraction of salts such as calcium chloride, while iron was often separated from metals such as calcium and magnesium by igniting the nitrates to oxides and extracting with dilute nitric acid.

Few reagents were in use for separating metals other than the common acids and alkalies; potassium ferrocyanide was sometimes used to precipitate iron, and oxalic acid to precipitate calcium. The reaction of oxalic acid (produced by the action of nitric acid on sugar) with all the known metals was described by Bergman. That it was not more regularly used to separate calcium may be due to lack of knowledge of how to separate other metals, or prevent their interference. It was not known then that magnesium may be retained in solution with a sufficient concentration of ammonium salts.

Having analysed a water, Bergman usually synthesised it to see if the mixture had the same properties of specific gravity, taste, etc.

In the analysis of minerals, the majority of which would not dissolve in acids, Bergman showed that fine crushing and fusion with sodium carbonate in iron crucibles, followed by leaching with hydrochloric acid, would bring most minerals into solution. The introduction of iron from the crucible was a serious drawback.

The separation of silica by evaporation with hydrochloric acid was usually followed by treatment with ammonia to precipitate iron, aluminium, etc. The solution was then treated with alkali carbonate. Metals such as copper were precipitated as metals, while antimony was separated by evaporation with nitric acid. Chloroplatinic acid was known as a reagent for separating sodium and potassium.

The role of acid radicles in minerals was little understood. In a footnote, Cullen, who made an English translation of Bergman's *Physical and Chemical Essays*, states "Mr. Kirwan considers the acids as pure, and totally free from water; whereas Professor Bergman considers them in a state of considerable concentration indeed, but as containing a very large proportion of water".

It was Klaproth who, in the words of Thomas Thomson, "first systematised chemical analysis and brought the art to such a state that the processes followed could be imitated by others with nearly the same results."

Klaproth always described the source, physical appearance and gravity of his specimens since he considered that many discrepancies occurred between results obtained by different analysts due to varying degrees of contamination. In an account of his work published in 1801 he gives first an account of the behaviour of more than a hundred minerals when heated in charcoal and in clay crucibles, covered respectively with lids of the same material. He was one of the first to use charcoal crucibles. He gives detailed descriptions of changes in appearance, or chemical reactions such as the separation of iron, and whether any change in weight takes place.

One of the difficulties encountered by Klaproth was the contamination of samples from the flint mortar that he used. To allow for this he analysed the flint, then weighed the mortar before and after use, and deducted the appropriate values from his results.

For samples insoluble in acid, fusion with alkali carbonate or hydroxide was employed, usually in a silver crucible. When employing a hydroxide the sample was often mixed with a strong aqueous solution of the alkali, the mixture gradually dried, and then fused. The methods of separation employed were largely those used by Bergman but several new methods were introduced including the use of succinic acid for the separation of iron from manganese. Hydrogen sulphide was sometimes used, mostly in qualitative tests, but occasionally in quantitative work as in the separation of iron from the rare earths.

One change which Klaproth introduced was to report results as he found them instead of the previous practice of applying a factor to bring the sum of the results to 100%.

The following examples are typical of analyses carried out by Klaproth:

Analysis of red silver ore

1. Treat with nitric acid. Filter.
2. Treat filtrate with hydrochloric acid. Filter. Weigh silver chloride. Treat the filtrate with barium chloride and weigh barium sulphate.
3. Treat the residue from 1 with *aqua regia*, dilute a little and filter. Residue contains sulphur and silver chloride.
4. Dilute filtrate and digest to separate antimony as oxide. Filter. Weigh oxide and reduce with carbon.
5. Treat filtrate with barium chloride and weigh barium sulphate. Result from 500 grains (32.2 g.)

Silver	300
Antimony	101·5
Sulphur	58·5
Concrete sulphuric acid	40
	500

Analysis of Bohemian garnet

1. Fuse with caustic potash, leach with water and filter.
2. Allow filtrate to stand. Hydrated oxide of manganese separates out. Filter.
3. Treat solution with hydrochloric acid to separate silica, then precipitate aluminium with ammonia.
4. Treat residue from 1 with hydrochloric acid to separate silica.

5. Treat filtrate with ammonia to precipitate iron and aluminium.
6. Treat filtrate with sulphuric acid. Separate calcium and magnesium sulphates.
7. Treat residue from 5 with hydrochloric acid. Precipitate iron as ferrocyanide then aluminium as hydroxide.

Result from 200 grains (13 g)	
Silica	80
Alumina	57
Oxide of iron	33
Magnesia	20
Lime	7
Oxide of manganese	0·5
	197·5

Of the acid radicles, carbonate was usually estimated from the loss in weight on treatment with acids, but for one sample of soda from Egypt the amount of nitric acid required for neutralization was weighed and the acid standardised in a similar way against pure sodium carbonate.

Methods of calculating acid radicles were closely linked with existing ideas of the composition of compounds. Sulphur in the form of sulphate could be estimated very accurately but there was little knowledge of how the sulphur existed in the compound, so that sulphidic minerals were often reported to contain sulphate, since that was found due to some of the sulphide being oxidised completely during analysis. Even then there were difficulties. In early work sulphuric acid was calculated in terms of free acid. Later reports are calculated in terms of "concrete sulphuric acid", *i.e.* acid free from water (sulphur trioxide).

This method of calculation led Klaproth into difficulties when dealing with chlorides. He reasoned as follows:—"100 parts of metallic silver yield 133 parts of muriated silver. But as this metal, to be rendered soluble in acids, takes up 12½ parts of oxygen, these must be subtracted so that of this increase by 33 parts, there remain 20½ for the muriatic acid".

Berzelius classified the components of minerals as electronegative and electropositive bodies and sought to show that the components were present in simple proportions. He knew that some oxides could behave as acids or bases according to the substances with which they were combined. He paid great attention to the state of oxidation of metals such as iron and manganese to arrive at the correct amount of oxygen which should be allocated to them.

The desire to find a formula to fit each substance led Berzelius into errors such as the following: "The small proportion of iron in this substance (graphite) long induced me to suppose it to be pure carbon mechanically blended with a little of the carburet of iron. But as the proportion of carbon in the artificial black lead, which crystallises during the fusion of cast iron, exceeds 90%, this body must therefore be a chemical combination, because we cannot suppose that an elementary body can separate itself from all combination with another from the mere disposition to crystallisation. Besides, it is known that the crystallising hydrargyret (amalgam) of potassium does not contain full three per cent of potassium, though it is beyond all doubt a chemical combination. This demonstrates that the maximum of particles (atoms, volumes) of a body which can be combined with a single particle of another must be very great. For if, according to the analysis of Saussure, the pure native graphite of Cornwall contains 96 parts carbon for 4 parts iron, and if the artificial, according to Berthollet, contains 91 parts carbon for 9 parts iron, one particle of iron in the first instance is combined with 208, and in the second with 98 particles of carbon, or, allowing for a trifling error in the analysis, the former may be Fe + 200C and the latter Fe + 100C".

When seeking a formula for a mineral whose components were oxides, the only facts needed were the proportion of oxygen in the oxides. This was not always easy, except where the metals had been isolated. By the comparison of the combining proportions of bases with various acids, particularly sulphuric acid where the ratio of sulphur to oxygen was known, Berzelius correctly deduced the composition of most oxides from which he calculated atomic weights, tables of which he published in 1814, 1818 and 1826. In the two earlier tables there are many oxides with twice the correct number of oxygen atoms, *e.g.* FeO_2 and FeO_3 because Berzelius considered that the simplest binary compounds must contain one atom of one element combined with 1, 2, 3... atoms of the other. Following the work of Dulong and Petit on atomic heats (published in 1819) Berzelius corrected most of these errors but still retained his orginal formulae of the alkaline oxides, *e.g.* KO, NaO although these gave atomic weights double those deduced from the specific heats. The accuracy of some of the values used by Berzelius for the oxygen content of oxides may be judged from the examples in Table I.

Table I. Oxygen content of oxides

Oxide	According to Berzelius	Modern Value
Silica	49·6	53·3
Alumina	46·7	47·1
Magnesia	38·0	39·7
Lime	28·0	28·5
Baryta	10·5	10·4
Soda	25·7	25·8
Potash	17·0	17·0

Berzelius took the results of many analyses of minerals, some of his own, but others from all sources, and calculated the amount of oxygen contributed by each basic or acidic oxide. Taking the lowest value as unity and reducing higher values accordingly he obtained an empirical formula, calculated what the composition would be, and compared it with the results found.

The following example shows the method:

Composition of Byssolite

Calculated by Berzelius from an analysis by Vauquelin

					Calculated composition	
Silica	47·0	contains oxygen	23·6	≡	8	48·00
Magnesia	7·3		2·8		1	7·86
Lime	11·3		3·2		1	10·70
Oxide of iron	20·0		6·1		2	19·36
Oxide of manganese	10·0		3·0		1	9·68

Similar methods were employed for compounds of other types, *e.g.* sulphides.

The work of Bergman, Klaproth and Berzelius shows that many analyses could be carried out with a high degree of accuracy, but methods of separation were often inadequate. Beginning with Berzelius, attempts were made to relate the results obtained from the analysis of natural materials to the rapidly developing ideas on the structure of chemical compounds. Chemical analysis was given a sound basis for the great progress which was made in following years.

Zusammenfassung—Die analytische Chemie verdankt viel solchen Männern wie Bergman, Klaproth und Berzelius, die zu der Analyse von natürlichen Stoffen den Weg bahnten und eine systematische Annäherung entwickelten, trotz einer unvollkommenen Kenntnis von der Natur der chemischen Komposition.

Résumé—La chimie analytique doit beaucoup aux hommes tels que Bergman, Kloproth et Berzélius qui pionnèrent l'analyse de matières naturelles et developèrent un rapprochement systématique, malgré une connaissance imparfaite de la nature de la composition chimique.

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THE EXTRACTION OF ZIRCONIUM WITH TRI-*n*-OCTYLPHOSPHINE OXIDE AND ITS DIRECT DETERMINATION IN THE ORGANIC PHASE WITH PYROCATECHOL VIOLET

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(*Received* 15 *April* 1958)

Summary—A sensitive colorimetric method for the determination of zirconium has been developed for use in organic extracts which contain tri-*n*-octylphosphine oxide (TOPO) in *cyclo*hexane. The method is based on the absorbance of the zirconium-pyrocatechol violet complex in a TOPO-*cyclo*hexane-ethyl alcohol medium at a wavelength of 655 mμ. The molar absorbance index for this complex at 655 mμ is about 40,000. The complex conforms to Beer's law up to a concentration of 1.0 μg of zirconium per ml. When zirconium is extracted from a chloride medium, this method is useful for the determination of zirconium in the presence of large amounts of aluminium, uranium, vanadium, iron, and chromium; moderate amounts of thorium do not interfere. Molybdenum, titanium, and hafnium interfere with the method. The procedure is applicable in the presence of milligram amounts of phosphate and sulphate ion. When zirconium is extracted from a nitrate medium, the method is useful for the determination of zirconium in the presence of aluminium, titanium, molybdenum, vanadium, iron and chromium; however, uranium, thorium, and hafnium interfere. Microgram amounts of phosphate and sulphate ion can be tolerated. This method has the common advantage of most extraction methods in that zirconium which is present in an aqueous sample can be extracted into a smaller organic volume. The coefficient of variation for the determination of zirconium by this method is less than 3%.

INTRODUCTION

TRI-*n*-OCTYLPHOSPHINE oxide (TOPO) in non-polar solvents has been shown by White and Ross[6] to be an effective reagent for the extraction of zirconium from either hydrochloric or nitric acid solutions. The extraction of zirconium can be extended to other acidic media by the addition of sufficient nitric or hydrochloric acid prior to extraction with TOPO. For example, zirconium can be readily extracted with $0.01M$ TOPO in *cyclo*hexane from $1M$ H_2SO_4 which is made $7M$ with respect to hydrochloric acid. It has further been shown, in the colorimetric determination of chromium with diphenylcarbazide[4] and the colorimetric determination of uranium with dibenzoylmethane,[2] that the metal ion in the organic-TOPO phase will undergo reactions such that a colorimetric determination of the metal ion can be made directly in the organic extract. Through combination of extraction with TOPO and the use of a chromogenic reagent, such as pyrocatechol violet, which is one of the most sensitive reagents for the colorimetric determination of zirconium[1,8] in aqueous solutions, a selective and sensitive colorimetric method has been developed for the determination of zirconium in the organic extract.

EXPERIMENTAL

Absorbance spectra

The partial absorbance spectra of the zirconium-pyrocatechol violet complex in a TOPO-*cyclo*hexane-absolute ethanol medium is shown in Figure 1. The maximum

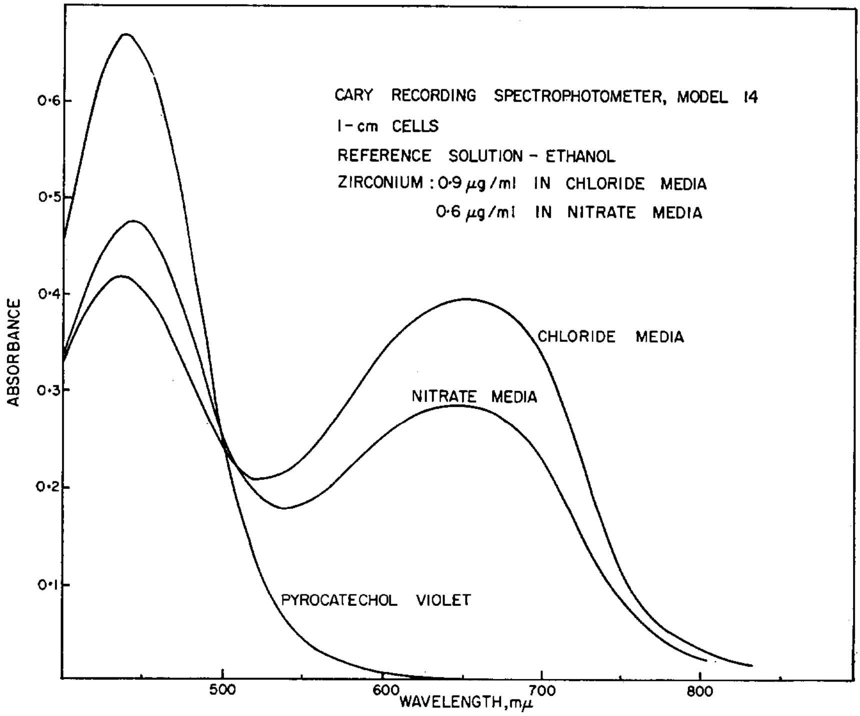

FIG. 1. Absorption spectra of zirconium-pyrocatechol violet complex in TOPO-*cyclo*hexane-ethanol.

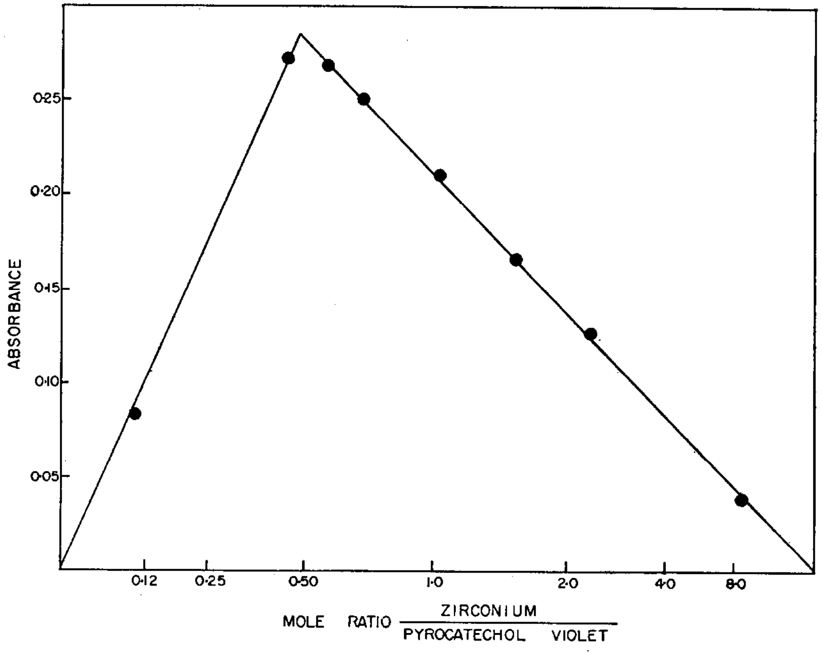

FIG. 2. Molar combining ratio of zirconium and pyrocatechol violet in ethanol.

absorbance of the complex occurs at a wavelength of 655 mμ. The absorbance of a solution which contains all reagents except zirconium is essentially zero, less than 0.005 absorbance units, at this wavelength.

The absorbance of the zirconium-pyrocatechol violet complex in the TOPO-*cyclo*hexane-ethyl alcohol medium conforms to Beer's law up to a concentration of one μg of zirconium per ml. The reciprocal of the slope of the calibration curve is 2.27 μg zirconium per ml per unit absorbance in the hydrochloric medium. The molar absorbance index of the complex at a wavelength of 655 mμ is about 40,000.

Metal-ligand ratio

Stoichiometry of the zirconium-pyrocatechol violet complex in ethanol. The method of continuous variation[3] was applied to the zirconium-pyrocatechol violet complex in ethanol in order to determine its composition. As shown in Figure 2, the complex contains two moles of pyrocatechol violet to one mole of zirconium.

Order of addition of reagents

In order to obtain maximum colour development, no change should be made in the order of addition of reagents as described in the procedure. Low absorbances were observed when the pyrocatechol violet was added directly to the *cyclo*hexane, and also when the test portion was added to either the pyrocatechol violet or the pyridine, or to a mixture of the two. The addition of absolute ethanol to the test portion of the extract is necessary to maintain complete miscibility of pyrocatechol violet and pyridine with the *cyclo*hexane in the test portion.

Effect of water on formation of complex

Absolute ethanol is preferred as the diluent since the absorbance of the test solution is decreased by approximately 20% if 95% ethanol is used. A similar order of decrease in absorbance of the final test solution resulted from the use of a solvent which contained absolute ethanol and known amounts of water. For example, for 1% water in the ethanol the resultant absorbance of the zirconium-pyrocatechol violet complex was lower by 5% than in absolute ethanol diluent. Although no elaborate precautions are necessary to minimize the absorption of water by the absolute ethanol, the solvent should not be exposed to air for unduly long periods of time.

The interference of water in this method is apparently due to some reaction of water which prevents full colour development of the complex since the effect of water on the absorbance of the zirconium-pyrocatechol violet complex is negligible if the water is added after the complex has been formed.

Reagent stability

Solutions of pyrocatechol violet in absolute ethanol should be prepared fresh daily. The use of a solution of the chromogenic reagent which is one day old will cause a decrease in the absorbance of the resultant complex of approximately 10%. This effect is apparently due to the slow decomposition of pyrocatechol violet when dissolved in ethanol. The absorption spectra, from 350 to 750 mμ, of such a solution when measured with respect to time shows no unique changes in general form, but rather there is a gradual, uniform decrease in the absorbance at all wavelengths.

The pyridine concentration of the final test solution can vary from 12 to 28 v/v%.

Lower or higher concentrations result in incomplete development of the complex. The absorbance of a reference solution which contains no zirconium is likewise completely independent of pyridine concentration over the range from 8 to 40 v/v % of this organic base in the final test solution.

Stability

The colour of the zirconium-pyrocatechol violet complex develops immediately and is stable for a period of two hours. As the concentration of zirconium and TOPO in the test solution is increased, the stability of the resultant colour is decreased somewhat. After a period of two hours the test solutions will gradually change in their absorbance, and the zirconium-pyrocatechol violet complex will precipitate from solution. These results are shown in Table I.

TABLE I.—STABILITY OF THE ZIRCONIUM-PYROCATECHOL VIOLET COMPLEX IN A TOPO-*cyclo*HEXANE-ETHYL ALCOHOL MEDIUM
Final volume, 25 ml

Zirconium *μg/ml*	TOPO *mmoles/25 ml*	Absorbance		
		0.0 *hr*	1.0 *hr*	2.0 *hr*
0.16	0.01	0.074	0.077	0.086
0.32	0.01	0.132	0.131	0.138
0.32	0.01	0.140	0.140	0.144
0.63	0.01	0.278	0.280	0.296
0.63	0.02	0.278	0.283	—[a]
1.26	0.02	0.565	0.557	—[a]

[a] Precipitate present in two hours.

Diluents

The maximum amount of zirconium in the test aliquot should be 125 μg. In case of larger amounts dilution should preferably be made with 0.01*M* TOPO. These dilutions are stable at least 24 hours. *cyclo*Hexane can also be used for this dilution if the final concentration of TOPO in the test solution is maintained within the range of 0.003 to 0.03 mmoles/25 ml.

The best diluent for use in the development of the colour of the zirconium-pyrocatechol violet complex is absolute ethanol. Of other diluents tested, such as benzene, *cyclo*hexane, dioxane, 95% ethanol, acetone, amyl alcohol, butyl acetate, and methyl *iso*butyl ketone, all resulted in a decreased sensitivity of the method, and many resulted in rapid precipitation of the complex.

Composition of non-aqueous solution

The concentration of *cyclo*hexane in the final 25-ml volume must be less than 20 v/v %; in higher percentages, the complex precipitates. In order to maintain a miscible solution the volume ratio of *cyclo*hexane to ethanol should never exceed one.

The amount of TOPO in the final volume should be in the range of 0.003 to 0.04 mmoles. If a larger amount of TOPO is present, the absorbance of the complex is decreased by about 5%.

Extraction from acidic chloride solutions

In addition to zirconium, such metals as uranium, titanium, iron, thorium, and chromium are extracted, under certain conditions, by TOPO.[5] Since ions of these metals also react with pyrocatechol violet, steps were necessary either to prevent their extraction or to minimise their interference in the organic solution.

The addition of ammonium thiocyanate to the acidic aqueous solution before extraction was found to be beneficial. The extraction of zirconium from 7*M* hydrochloric acid, and the resultant colour formation of zirconium in the extract with pyrocatechol violet is unaffected by a concentration of ammonium thiocyanate in the aqueous phase from 10 to 200 mg/ml. These results are shown in Table II.

TABLE II.—EFFECT OF AMMONIUM THIOCYANATE ON THE EXTRACTION OF ZIRCONIUM AND ITS DETERMINATION WITH PYROCATECHOL VIOLET

Aqueous Phase, 7*M* HCl		Zirconium, *μg/ml*	
Volume, *ml*	NH_4CNS, *mg/ml*	Present in Aqueous Phase	Found
5	10	7.9	8.0
5	20	7.9	7.9
5	40	7.9	8.0
5	80	7.9	7.8
5	140	7.9	8.0
5	200	7.9	8.0
5	320	7.9	7.2
10	[illegible]0	3.9	4.0
10	140	3.9	3.8
25	140	1.6	1.6

Up to 200 mg/ml of NH_4CNS can be tolerated; the results were low when 320 mg were present in the aqueous phase. In the highly acidic aqueous phase, ammonium thiocyanate decomposes to form, among other things, polymerised thiocyanic acids and hydrogen cyanide.[7] The decomposition products of this salt will eventually, within one to two hours, depending on temperature and other factors, make the removal of a test portion of the extract impractical. The extraction container will always contain hydrogen cyanide gas in varying concentrations, and precautions should be exercised in the handling of these containers.

The extraction of uranyl ions is essentially eliminated by the presence of thiocyanate ion.[6] Uranium normally extracts quite readily from 7*M* hydrochloric acid into solutions of TOPO.[8] However, only 0.8 % of uranyl ion, at a 200 μg/ml concentration level, is extracted from 7*M* hydrochloric acid if the concentration of ammonium thiocyanate is 80 mg/ml. A four-fold increase in the uranium thiocyanate concentration level will reduce the extraction of uranium to 0.02 %. At the concentration level of ammonium thiocyanate that is recommended in the procedure, 140 μg/ml, uranyl ion extracts to the extent of 0.2 %.

No evidence of ferric ions was found in the organic phase when the extraction was conducted from aqueous solution which contained thiocyanate. The extraction of either vanadyl or vanadate ion is apparently grossly hindered by thiocyanate ion in

Table III.—Effect of cations on the determination of zirconium with pyrocatechol violet in a TOPO-*cyclo*hexane-ethyl alcohol medium

Equilibration time—10 minutes
Aqueous phase—5 ml 7*M* HCl
140 mg NH_4CNS/ml

Aqueous phase

Cation		Zirconium, *µg/ml*	
	µg/ml	Present	Found
Al^{3+}	130	11.8	12.2
	260	11.8	12.3
UO_2^{2+}	50	7.9	8.0
	100	7.9	8.0
Fe^{3+}	20	7.9	7.9
	100	7.9	8.0
Cr^{6+}	25	11.8	11.6
	50	11.8	11.6
	100	11.8	11.9
V^{4+}	100	11.8	11.8
	200	11.8	11.7
	600	7.9	7.7
	6000	7.9	7.8
	6000	15.8	16.1
V^{5+}	600	7.9	8.0
	600	15.8	16.6
	1200	7.9	8.0
	1200	11.8	12.1
Th^{4+}	10	11.8	11.9
	20	11.8	12.1
	25	11.8	12.3
	50	11.8	12.7
	100	11.8	13.3
Mo^{6+}	20	11.8	13.0
	30	11.8	14.4
	40	11.8	15.0
Ti^{4+}	3.7	7.9	12.0
	7.4	7.9	16.2
	14.8	11.8	27.7
Hf^{4+}	12.4	0.0	6.2 (Hf = 12.2)
	35.8	0.0	19.2 (Hf = 37.7)

the aqueous phase. Titanium, however, extracts as an intensely yellow thiocyanate complex into TOPO from aqueous solutions which contain thiocyanate ion.

The addition of thiocyanate to the aqueous phase prior to the extraction of zirconium, therefore, leads to quantitative separation from uranium and iron.

Effect of diverse ions

The effect of various cations on the determination of zirconium was studied. An aqueous solution which contained both zirconium and the cation to be studied, in 7*M* hydrochloric acid, was treated according to the procedure that was described previously. The results of this investigation are presented in Table III.

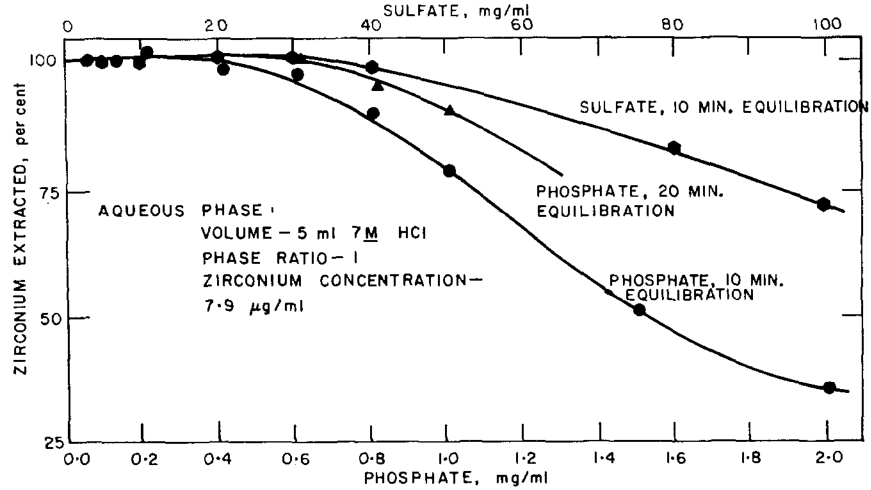

FIG. 3. Effect of phosphate and sulphate ion on the extraction of zirconium and its determination with pyrocatechol violet.

This method is particularly suited for the determination of zirconium in the presence of large concentrations of aluminium, dichromate, ferric, uranyl, vanadyl, and vanadate ions. At the level of concentration shown in Table III these ions cause no significant error in the determination of zirconium. The tolerance to the other ions which were mentioned is probably much better than shown; however, higher concentrations of these ions were not studied. The alkali metals, alkaline earths, rare earths, lead, nickel, cobalt, arsenic, ferrous iron, and indium do not extract into solutions of TOPO from aqueous solutions which are 7*M* in HCl; therefore, these elements will not interfere with the determination of zirconium by this method.

Small quantities of thorium, molybdenum, titanium, and hafnium interfere. An error of 5% will result if the thorium/zirconium weight ratio is as high as four. At a weight ratio of one, molybdenum will cause a 5% error.

Titanium causes serious interference in this determination, since it is extracted along with zirconium and forms a blue complex with pyrocatechol violet. The presence of even submicrogram amounts of titanium, however, in the aqueous phase can readily be detected by visual observation of the resultant organic extract. Titanium is extracted as a yellow thiocyanate complex; less than 0.5 μg of titanium in 5 ml of the organic phase can be detected by the coloration it imparts to the extract.

This behaviour of titanium is being investigated as a basis for a determination of this element.

The method is apparently equally sensitive to zirconium or hafnium on a molar basis.

This method has quite a high tolerance to phosphate ion as shown in Fig. 3. Under the conditions of the procedure, up to 600 μg of phosphate per ml can be tolerated in the aqueous phase with less than a 5% error in the resultant determination of 7.9 μg of zirconium per ml. If the equilibration time is increased from 10 to 20 minutes 800 μg of phosphate per ml can be tolerated at the same error.

Up to 1.5 mmoles of sulphate ion can be tolerated in 5 ml of $7M$ hydrochloric acid with an error of less than 5%.

The combination of sulphate and thiocyanate ions in the aqueous phase depresses the extraction of zirconium with TOPO.

The effect of other anions on this method was not specifically studied; however, no trouble has been encountered with small concentrations of nitrate or perchlorate ions when these were present in some aqueous samples. Large amounts of nitrate in this strongly acid aqueous phase will result in serious decomposition of the thiocyanate ion.

In comparing the effect of diverse ions on this non-aqueous method and on the aqueous method of Young, French, and White,[9] large amounts of aluminium, iron, and vanadium do not interfere with the non-aqueous method. Iron can be tolerated only to a limited degree in the aqueous method; aluminium and vanadium interfere quite seriously. This non-aqueous method exhibits a tolerance to phosphate ion; phosphate interferes with the aqueous method. However, the aqueous method can tolerate larger amounts of thorium and is more independent of sulphate ion concentration than is the non-aqueous method. Titanium causes serious interference in both methods.

Applications

This method has been applied to the routine determination of microgram quantities of zirconium in solutions which contain small amounts of phosphate and extremely large amounts of vanadyl or vanadate ions. The quadrivalent vanadium solutions were $1M$ with respect to sulphuric acid; the solutions of quinquevalent vanadium were up to $3M$ with respect to perchloric acid. Typical results that were obtained on synthetic samples are presented in Table IV.

Zirconium can be determined in this type of sample with a coefficient of variation of 2%. The slight positive bias shown for the data in Table IV does not appear to have any significance.

No further applications of this method have been made as yet; however, it should be quite useful for the determination of zirconium in aluminium, uranium, iron, rare earths, and certain phosphates, to mention only a few possibilities.

Extraction from acidic nitrate solutions

Fewer elements are extracted by TOPO from acidic nitrate solutions. Essentially only zirconium, uranium, thorium, and tin are extracted. Hence, the method should be less subject to interferences due to mutual extraction from nitric acid solution than from hydrochloric acid solutions. Ross and White[6] reported, however, that based

TABLE IV.—TYPICAL RESULTS FOR THE DETERMINATION OF ZIRCONIUM WITH PYROCATECHOL VIOLET IN THE PRESENCE OF VANADIUM, PHOSPHATE AND OTHER IONS

Aqueous phase: Volume—5 ml 7*M* HCl
140 mg NH_4CNS/ml

Vanadium		Millimoles		Phosphate *µg*	Zirconium Found, *µg*
Valence State	*mg*	SO_4^{2-}	ClO_4^-		
0.00 *µg* of zirconium present					
4	30	0.2	—	—	0.9
5	6	—	5.5	—	1.2
39.4 *µg* of zirconium present					
4	3	0.02	—	—	38.2
4	30	0.2	—	—	38.8
5	3	—	—	—	39.7
5	6	—	2.8	—	40.8
5	6	—	5.5	—	40.0
5	6	—	5.5	310	40.0
				Average	39.6 ± 2%
59.1 *µg* of zirconium present					
5	6	—	2.8	—	59.7
5	6	—	5.5	—	61.0
				Average	60.3
78.8 *µg* of zirconium present					
4	30	0.2	—	—	79.4
5	3	—	—	—	82.0
				Average	80.7

TABLE V.—EFFECT OF CATIONS ON THE DETERMINATION OF ZIRCONIUM WITH PYROCATECHOL VIOLET IN A TOPO-*cyclo*HEXANE-ETHYL ALCOHOL MEDIUM

Equilibration time—10 minutes
Aqueous phase—5 ml 7*M* HNO_3

Aqueous phase

Cation		Zirconium, $\mu g/ml$	
	$\mu g/ml$	Present	Found
Cu^{2+}	100	11.8	11.7
Fe^{3+}	50	11.8	12.1
	100	11.8	12.2
	200	11.8	12.1
Mo^{6+}	100	11.8	12.1
	200	11.8	12.1
V^{4+}	600	7.9	7.8
	1800	7.9	7.9
	3000	7.9	8.3
V^{5+}	400	7.9	7.9
	800	7.9	8.2
	1200	7.9	8.0
Ti^{4+}	45	11.8	11.8
	90	11.8	12.2
	180	11.8	13.1
Th^{4+}	6	7.9	7.8
	12	7.9	8.3
	18	7.9	8.9

on a TOPO/zirconium molar combining ratio of 2, complete extraction of 100 μg of zirconium from nitric acid requires a molar ratio of excess TOPO of at least 25 in sharp contrast to a figure of 2 for similar extraction from hydrochloric acid. Their results were confirmed in this study.

The extraction of about 100 μg of zirconium is quantitative only when 1 mmole of TOPO is used.

Effect of diverse ions

The effect of various cations on the determination of zirconium was studied. An aqueous solution which contained both zirconium and the cation to be studied in 7*M* nitric acid was treated according to the procedure that was described in this report. The results of this investigation are presented in Table V.

The determination of zirconium in nitric acid medium is unaffected by large amounts of copper, ferric ion, sexivalent molybdenum and vanadium. The alkali metals, alkaline earths, aluminium, rare earths, lead, nickel, cobalt, arsenic, and indium do not extract into solutions of TOPO from aqueous solutions which are

7*M* in NHO_3; therefore, these elements will not interfere with the determination. Thorium interferes with the determination of zirconium. Weight ratios of thorium to zirconium of more than 1.5 cause an error in the subsequent determination of zirconium of at least 5%.

As shown in Table V, titanium in a weight ratio of titanium to zirconium of as high as 10 causes only slight interference with the determination of zirconium. Larger concentrations of titanium do interfere even though the extraction coefficient for titanium is low in a nitrate medium. If the original organic phase is backwashed with 7*M* nitric acid, however, weight ratios of titanium to zirconium of 100 and more are tolerated by the method.

TABLE VI.—EFFECT OF VARIOUS ANIONS ON THE EXTRACTION OF ZIRCONIUM IN A NITRATE MEDIUM AND ITS SUBSEQUENT DETERMINATION WITH PYROCATECHOL VIOLET

Equilibration time—10 minutes

Aqueous phase—5 ml 7*M* HNO_3

Aqueous phase

Anion			Zirconium, *μg/ml*	
	M	*μg/ml*	Present	Found
Cl^-	0.2		7.9	7.9
	0.4		7.9	7.7
	0.6		7.9	7.8
	0.8		7.9	7.6
SO_4^{2-}	0.3		7.9	4.4
	0.6		7.9	2.5
	1.2		7.9	1.2
PO_4^{3-}		50	7.9	7.7
		100	7.9	7.0
		200	7.9	6.0

The effect of various anions on this determination of zirconium is summarized in Table VI. Chloride ion, as hydrochloric acid, caused no effect on the extraction or determination of zirconium. Sulphate ion, as sulphuric acid, caused serious interference with this method for the determination of zirconium; it is probable that this interference is due to incomplete extraction of zirconium in the presence of sulphate ion. Phosphate ion in concentrations up to approximately 50 μg/ml do not interfere with this method. Larger concentrations of phosphate ion, however, are not tolerable; again this effect is probably due to incomplete extraction of zirconium from the aqueous phase.

Comparison of the effect of diverse ions on the non-aqueous determination of zirconium in chloride or nitrate medium

A re-examination of the effect of various diverse ions on extraction of zirconium with TOPO and its subsequent determination with pyrocatechol violet point up the utility of this general method. Of the possible interferences that have been mentioned, alkali metals, alkaline earths, rare earths, aluminium, iron, chromium, vanadium, lead, nickel, cobalt, arsenic, and indium do not affect the determination of zirconium regardless of the possible acid which may be present in aqueous phase. The choice of making the initial aqueous sample 7*M* with respect to nitric or hydrochloric acid should be based on the presence in the aqueous sample of thorium, uranium, molybdenum, titanium, sulphate and phosphate ions. In extracting from a chloride-thiocyanate medium, the interference of uranyl ions is eliminated; relatively large concentrations of phosphate and sulphate ions can be present; and thorium can be tolerated up to a weight ratio of thorium to zirconium of four. Titanium and molybdenum interfere seriously with the application of this method to a chloride medium. In extracting from a nitrate medium, the interference of molybdenum and titanium can be completely eliminated. The tolerance of the method, in a nitrate medium, to thorium, phosphate, and sulphate ion is much reduced; uranyl ions will likewise extract and interfere with the subsequent determination of zirconium.

PROCEDURE

Extraction from hydrochloric acid solution

The solution to be extracted is first made approximately 7*M* with respect to hydrochloric acid; at this point the volume of the aqueous phase should be no greater than 25 ml and should preferably contain less than 125 μg of zirconium. About 700 mg of ammonium thiocyanate (as measured by a Coors micro crucible, size 5/0, filled to the top) is added to the acidic solution and the resulting solution extracted for 10 minutes with 5 ml of 0.01*M* TOPO in *cyclo*hexane.

A one- to three-ml aliquot of the organic phase is then transferred to a 25-ml volumetric flask, and in succession are added 10 ml of absolute ethanol, one ml of 0.05% pyrocatechol violet, and 5 ml of pyridine. The resulting solution is diluted to the mark with absolute ethanol and the absorbance measured immediately against ethanol in Corex 1-cm cells at 655 mμ with a Beckman spectrophotometer, Model DU or B.

Extraction from nitric acid solution

The solution to be extracted is first made approximately 7*M* with respect to nitric acid; at this point the volume of the aqueous phase should be no greater than 25 ml and should preferably contain less than 125 μg. of zirconium. The resulting solution is extracted for 10 minutes with 5 ml of 0.02*M* TOPO in *cyclo*hexane. A one- or two-ml aliquot of the organic phase is then transferred to a 25-ml volumetric flask and the colour is developed as described for the hydrochloric acid solution. The absorbance is then measured against ethanol in Corex 1-cm cells at 655 mμ with a Beckman spectrophotometer, Model DU or B.

Work carried out under contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Zusammenfassung—Eine empfindliche colorimetrische Methode zür Bestimmung von Zirkon in organischen Extrakten, welche Tri-*n*-octylphosphinoxyd (TOPO.) in Cyclohexan enthalten, wurde entwickelt. Die Methode beruht auf der Absorption des violetten Komplexes von Zirkon-Pyrokatechin in TOPO.-Cyclohexan-Äthyl Alkohol bei 655 mμ. Die molare Absorption dieses Komplexes beträgt bei 655 mμ ungefähr 40,000. Der Komplex folgt dem Beer'schen Gesetz bis zu einer Konzentration von 1,0 μg Zirkon pro ml.

Wenn Zirkon aus einem Chloridmedium extrahiert wird, so ist diese Methode zür Bestimmung von Zirkon in Anwesenheit grosse Mengen von Al, U, V, Fe und Cr nützlich. Mässige Mengen von Th stören nicht, Mo, Ti und Hf hingegen stören.

Das Verfahren ist anwendbar bei Anwesenheit von Milligramm-Mengen Phosphat- und Sulfat-Ionen. Wenn Zirkon aus einem Nitratmedium extrahiert wird, so ist die Methode zür Bestimmung von Zirkon bei Gegenwart von Al, Ti, Mo, V, Fe und Cr gut verwendbar. Mikrogramm-Mengen von Phosphat- und Sulfat-Ionen stören nicht.

Diese Methode besitzt den allgemeinen Vorteil, dass Zirkon aus wässerigem Proben in ein kleines Volumen des organischen Lösungsmittels extrahiert werden kann. Die Varianz für die Bestimmung von Zirkon nach dieser Methode liegt unter 3%.

Résumé—Les auteurs ont mis au point une méthode sensible pour le dosage colorimétrique du zirconium qu'on peut utiliser dans des extraits organiques contenant l'oxide tri-*n*-octylphosphine (TOPO) dans le cyclohexane. Cette méthode est basée sur l'absorption du complexe violet zirconium-pyrocatéchine en milieu TOPO—cyclohexane—alcool éthylique à une longueur d'onde de 655 mμ. L'absorption molaire pour ce complexe à 655 mμ est d'environ 40,000. Le complexe suit la loi de Beer jusqu'à une concentration de 1,0 μg de zirconium par ml. Lorsqu'on extrait le zirconium d'un milieu chlorhydrique, cette méthode permet le dosage du zirconium en présence de grandes quantités d'aluminium, d'uranium, de vanadium, de fer et de chrome; des quantités moyennes de thorium ne gênent pas. Le molybdène, le titane et le hafnium gênent avec cette méthode. Le procédé est applicable en présence de quantités de PO_4^{3-} ou de SO_4^{2-} de l'ordre du milligramme. Lorsqu'on extrait le zirconium d'un milieu nitrique, la méthode permet le dosage du zirconium en présence d'aluminium, de titane, de molybdène, de vanadium, de fer et de chrome; cependant l'uranium, le thorium et le hafnium gênent. On peut tolérer des quantités de PO_4^{3-} ou de SO_4^{2-} de l'ordre du microgramme. Cette méthode a l'avantage commun à la plupart des méthodes d'extraction: c'est-à-dire que le zirconium qui est présent dans un échantillon aqueux peut être extrait dans un volume organique plus petit. Le coefficient de variation pour le dosage du zirconium par cette méthode est inférieur à 3 pour cent.

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AMPEROMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF SULPHIDE SULPHUR*

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(*Received* 7 *June* 1958)

Summary—The limiting sensitivity of the starch end-point in the iodimetric titration of microgram quantities of sulphide sulphur has been improved by an amperometric technique. The titration can be performed with a standard amperometric assembly fitted with a twin platinum electrode. As little as 10 to 30 micrograms of sulphur can be determined with a standard deviation of 1.4 microgram. The method has been applied to the determination of sulphides in solids and of hydrogen sulphide in air.

THE analysis of sulphide sulphur in solid materials usually involves acid treatment of the sample, whereby hydrogen sulphide is evolved and absorbed in a cadmium or zinc salt solution. Hydrogen sulphide in air is collected by passing a metered volume through the absorbing solution. The sulphide precipitate that is formed is then estimated by iodimetric titration with starch indicator.[4,6]

One source of error in the analysis of minute amounts of sulphur by this method is the variation of the starch end-point. The amount of iodine necessary to produce a permanent blue colour, under favourable conditions, is of the order of 0.001 to 0.002 milliequivalent. The precision of the blank becomes critical when the amount of sulphur being titrated is equal to or less than this amount. This difficulty precludes the use of the starch end-point for determining microgram amounts of sulphur.

Foulk and Bawden[2] first suggested an amperometric technique, which they termed a "dead-stop" end-point, for applications in iodimetry. Subsequent workers, notably Delahay[1] and Stone and Sholten,[8] investigated the reaction at the electrodes and postulated mechanisms.

Despite the encouraging theoretical investigations, few analytical applications of this amperometric method have been reported. Therefore, the authors investigated the conditions for iodimetric analysis of sulphide sulphur employing an amperometric technique to determine accurately microgram quantities of sulphide sulphur in solids and of hydrogen sulphide in air. In the method presented, the sulphide precipitate reacts in a closed system with excess iodine (added as iodate–iodide solution), and the unreacted iodine is back-titrated amperometrically. By graphing the titration, the end-point is more sharply defined than with the dead-stop technique.

APPARATUS AND REAGENTS

Amperometric assembly: Titrations were performed with a Fisher Elecdropode fitted with a twin platinum electrode and a magnetic stirrer.

Distillation apparatus: The apparatus used to evolve and collect hydrogen sulphide from solid samples consists of a 250-ml Erlenmeyer flask fitted with a ground-glass inlet for introducing purge gas, an exit tube leading into the absorbing solution, and a side-arm for introducing acid.

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* Presented at Second Delaware Valley Regional Meeting, ACS, Philadelphia, Penna., U.S.A., February 5, 1958.

Standard potassium iodate solution, 0.001N: Dissolve 0.0713 gram of recrystallised potassium iodate in water. Add 2 grams of sodium hydroxide and 140 grams of potassium iodide, and dissolve in a total volume of 2 litres.

Alkaline cadmium hydroxide suspension: Dissolve 3.85 grams of cadmium chloride dihydrate in water. Add 0.3 gram of sodium hydroxide dissolved in water and make up to 1 litre.

Standard sodium thiosulphate solution: Prepare an approximately 0.002*N* solution with freshly boiled and cooled distilled water. Add about 0.2 ml of chloroform per litre and let stand for several days. Standardise against the standard potassium iodate solution, using the amperometric titration described below. Standardise daily until successive values agree within ±1%. Weekly standardisation thereafter is sufficient.

EXPERIMENTAL

Applied potential

The results of current-voltage measurements of an iodine solution with the twin platinum electrodes are shown in Figure 1 (Curve A). The current-voltage plot shows a plateau between 90 and 130 millivolts. Similar measurements for sodium thiosulphate solution (Curve B) show low and essentially constant current in this range, with a corresponding sharp rise at an applied potential of about 200 millivolts because of dissolved oxygen. An applied potential of 110 millivolts was selected for the titration.

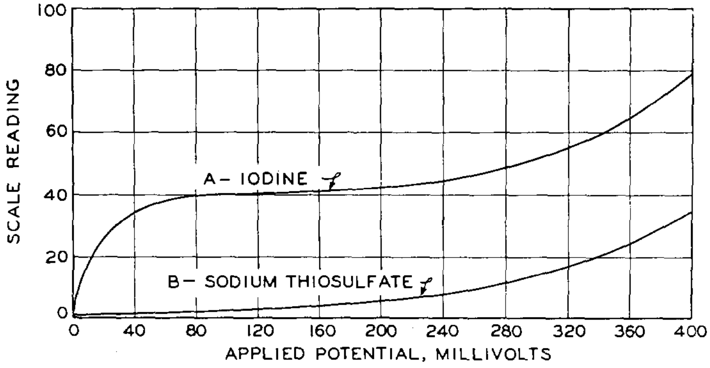

FIG. 1.

Potassium iodide–iodate ratio

The volatility of iodine is sharply reduced by the formation of tri-iodide ion with excess potassium iodide. Usually a ten- or twenty-fold weight ratio of potassium iodide to potassium iodate is added. Therefore, in a 0.001*N* potassium iodate solution, the absolute amount of potassium iodide normally present is small. At these low concentrations, considerable galvanometer drifting was noticed when the potassium iodide–iodate weight ratio was approximately twenty. However, when the weight ratio was increased to approximately two thousand, this instrument drift was effectively eliminated. In the sample analysed in the work on which this report is based, the amount of potassium iodate required per sample was low, and approximately one gram of potassium iodide gave the required iodide–iodate ratio.

Acidification

The collected sulphide precipitate is acidified in the presence of a known excess of potassium iodate solution. The reaction is carried out in a closed system so that hydrogen sulphide and iodine are simultaneously evolved without loss of gaseous hydrogen sulphide, as is possible in direct titration procedures.

High acidity favours air-oxidation of iodide. By adding only a slight excess of acid beyond that required to complete the reaction, this difficulty is avoided. As much as 60 milliequivalents of excess hydrochloric acid may be tolerated in a volume of about 125 ml.

Absorbing solutions

An ammoniacal solution of a zinc or cadmium salt is usually employed to precipitate sulphide. However, the amperometric titration of an ammoniacal blank solution containing a known amount of standard iodate solution gave a value less than the equivalent iodate. The difference varied with the ammonia concentration. Because the ammonia content of sample and blank could not be equated —due to variable purging volumes—other absorbing solutions with constant blank values were sought. Low and essentially constant blanks were obtained with 2% aqueous solutions of cadmium chloride, or cadmium acetate and an alkaline cadmium hydroxide suspension. The cadmium acetate solution was selected for the determination of hydrogen sulphide in air. For sulphide in solids, alkaline cadmium hydroxide suspension was used so as to neutralise any acid that might distil over with the hydrogen sulphide.

TABLE I.—DETERMINATION OF SULPHUR IN NBS INGOT IRON (55 b)

Sample weight *mg*	S present, *micrograms**	S found *micrograms*	S found %
53.8	10.0	10.4	0.0194
102.2	18.9	19.3	0.0189
117.8	21.8	21.7	0.0184
132.0	24.4	21.9	0.0166
154.0	28.4	26.7	0.0173

* Based on 0.0185% sulphur.

Average 0.0181
Standard deviation −0.0010%

Cadmium sulphide stability

Direct sunlight decomposes cadmium sulphide.[3] Even diffused sunlight can cause appreciable error over an extended period of time. For example, a 1-mg sample of reagent grade cadmium sulphide in 30 ml cadmium acetate solution was allowed to stand several hours exposed to diffused natural light. Amperometric analysis of the exposed sample gave a titre 11% lower than that given by an identical sample that was titrated immediately.

In the authors' work, sulphide was absorbed in flasks protected from light by a rubber cover.

SULPHIDE SULPHUR IN SOLIDS

The determination of sulphur in solids by evolution is based on the assumption that the sulphur is present in a form convertible to hydrogen sulphide. In metal alloys, incomplete dissolution and high carbon content contribute to low recovery.[7] National Bureau of Standards Ingot Iron (55 b) was chosen for evaluation of the method since the carbon content is very low and the metal is readily dissolved by dilute mineral acids.

Samples containing between 10 and 30 micrograms of sulphur were analysed by the amperometric method. The results are shown in Table I.

Procedure

Transfer a sample estimated to contain at least 10 micrograms of sulphur to the distillation flask. Connect a small piece of glass tubing to the exit tube and extend it into a 50-ml mixing cylinder containing 30 ml of alkaline cadmium hydroxide. Shake the cadmium suspension well before adding. Introduce about 30 ml of dilute hydrochloric acid (1 : 1) into the flask and heat the mixture moderately. Purge the system with nitrogen until the sulphide evolution is complete.

Disconnect and leave the delivery tube in the mixing cylinder, and add a known excess of standard potassium iodate. Introduce about 5 ml of concentrated hydrochloric acid, stopper quickly, and mix well. Cool the cylinder to approximately room temperature and transfer the solution to the titration beaker.

Apply a potential of 110 millivolts across the platinum–platinum electrodes. Add the thiosulphate titrant until the iodine colour is pale yellow and adjust the sensitivity dial to bring the galvanometer indicator on scale. Add small increments of titrant and plot the respective scale reading against the total volume. Because the resultant curve is essentially a straight line with a negative slope, it is convenient to plot just four or five well-distributed points. As the end-point is approached, the curve becomes assymptotic with the limiting current value. This limiting current value or baseline is defined as the value at which no appreciable change in current results when excess titrant is added. The intersection of the straight line and the baseline is the end-point. A typical graph is shown in Fig. 2.

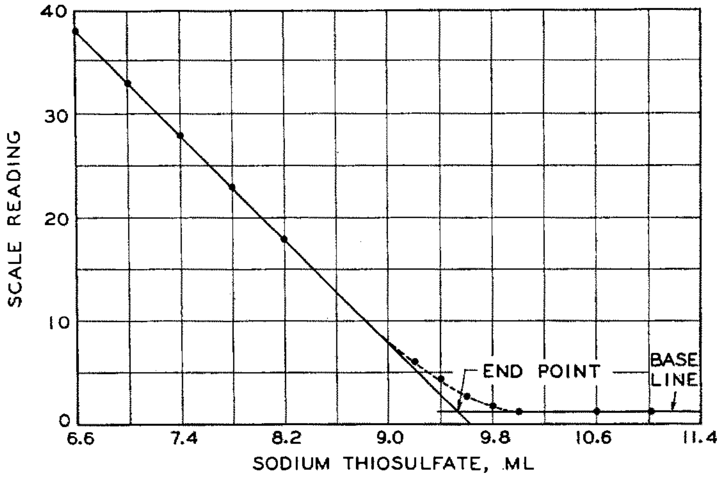

FIG. 2.

A blank titration on the absorbing solution and the same amount of iodate solution is also run. With experience the titration and graphing can be performed in 15 minutes.

HYDROGEN SULPHIDE IN AIR

In blending mixtures of hydrogen sulphide and air, considerable difficulty was encountered with plugging of the capillary flow-meter by mercuric sulphide. Therefore, a metered amount of sulphur dioxide was quantitatively reduced to hydrogen sulphide by passing the gas through a strong stannous chloride solution.[5]

TABLE II.—DETERMINATION OF HYDROGEN SULPHIDE IN AIR

Volume sampled, *litres*	Hydrogen sulphide present, *ppm*	Hydrogen sulphide found, *ppm*
10.13	10.4	10.3
10.06	15.9	15.7
7.11	67.6	68.6
5.02	202	197
1.05	611	640
0.53	1200	1230

The test mixtures were sampled with a covered midget impinger-flask containing 15 ml of 2% cadmium acetate solution. A wet-test meter was used to measure the sample volume. The results of analyses of hydrogen sulphide–air mixtures are presented in Table II.

Procedure

Pass a metered volume of air through a covered absorbing flask containing 2% cadmium acetate solution. Add a known excess of standard potassium iodate, acidify with a few millilitres of hydrochloric acid, stopper the outlets, and mix well. Transfer the solution to a titration beaker and titrate as previously described.

DISCUSSION

The blank correction with the starch end-point involves a variation equivalent to 16 to 32 micrograms of sulphur; thus, the determination of microgram quantities of sulphur is subject to considerable error. With the amperometric method, samples containing 10 to 30 micrograms of sulphur can be analysed with a standard deviation of only 1.4 microgram (Table I). This is particularly valuable for the analysis of microsamples. For example, at the authors' laboratory, the method is used for the determination of sulphide sulphur in de-oiled engine deposits, where in many cases only milligram amounts of sample are available.

The method has also been used for hydrogen sulphide in air. A maximum error of 5% is indicated for the range of 10 to 1200 parts per million (Table II).

Acknowledgement—The authors wish to express their thanks to William A. Tettemer, who assisted with the experimental work and to Oscar I. Milner and Richard J. Zahner for helpful suggestions with the manuscript.

Zusammenfassung—Die Nachweisgrenze des Stärke-Endpunktes in der jodometrischen Titration bei Mikrogramm-Mengen von Sulphid-Schwefel wird durch eine amperometrische Methode verbessert. Man kann die Titration mit einem gewöhnlichen amperometrischen Apparat mit doppel Platin-Elektroden versehen, ausführen. Es wird so eine kleine Menge wie 10 bis 30 Mikrogramm Schwefel mit einer Standard-Abweichung von 1,4 Mikrogramm bestimmt. Die Methode wird zur Bestimmung von Sulphiden in festen Körpern und Schwefelwasserstoff in Luft verwendet.

Résumé—On a pu par une technique amperometrique abaisser d'avantage la limite de sensibilité du point équivalent mis en évidence par l'amidon dans le titrage iodometrique de quantities de sulfure a l'echelle du microgramme. Pour effectuer le titrage on utilisé un montage amperometrique classique pourvu d'une double electrode du platine. On peut doser jusqu'à 10 a 30 microgrammes de sulfure, l'écart-type étant de 1,4 microgramme. On a appliqué cette méthode au dosage des sulfures dans des solides et de H_2S dans l'air.

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Talanta, 1958, Vol. 1, pp. 281–282. Pergamon Press Ltd., London.

SHORT COMMUNICATION

The use of fluorescein complexone

(*Received* 3 *June* 1958)

For the complexometric titrations of calcium, strontium, and barium with the indicator fluorescein complexone [Calcein, Fluorexone] Diehl and Ellingboe[1] and others[2,3] use sodium hydroxide solutions of the samples. The alkalinity of such solutions should be about $0{\cdot}1N$ NaOH. No systematic study of the most suitable medium for these titrations has been published so far. We have studied the fluorescence and colour properties of fluorescein complexone[4,5] and also the reactions with cations of metals other than those mentioned above.[6] Continuing our research we have now found that fluorescein complexone also gives fluorescence reactions with cations of some alkali metals, the reaction with sodium being particularly pronounced. This may be seen from Fig. 1, where the fluorescence intensities of the alkaline solutions of the fluorescein complexone (in % as compared with a standard) are plotted against NaOH, LiOH and KOH concentrations respectively. The lowest tendency to form a fluorescent complex with fluorescein complexone is shown by the potassium ion.* On adding sodium chloride to the potassium hydroxide solution of fluorescein complexone the fluorescence increases. This is not the case with an equivalent amount of potassium chloride instead of sodium chloride.

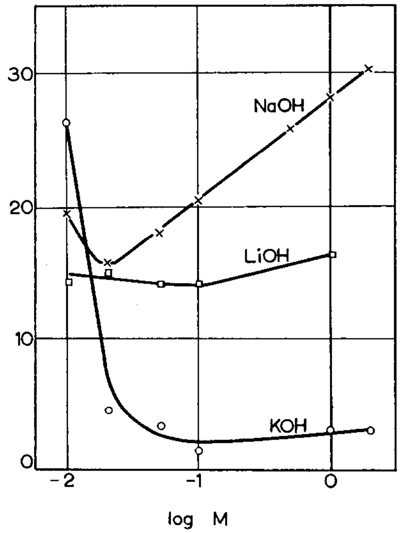

Fig. 1. Dependence of the fluorescence intensities of a $1{\cdot}2 \times 10^{-5}M$ fluorescein complexone on alkali hydroxide concentrations. [Standard: $0{\cdot}6 \times 10^{-5}M$ fluorescein complexone in $0{\cdot}1N$ KOH with excess of Ca^{2+}.]

Although in respect of sensitivity the fluorescence reaction of the sodium ion with fluorescein complexone cannot be compared with the analogous reactions of the alkaline earths cations, it is not negligible in the complexometric titrations of these latter metals. There is a great difference in the end-point quality when using sodium or potassium hydroxide for adjusting the samples to be titrated to the required alkalinity. Only potassium hydroxide is satisfactory for this purpose. This applies particularly to barium determination and to indirect sulphate determination.[7]

On the basis of our experiments the avoidance not only of sodium hydroxide but also of other sodium salts in procedures with fluorescein complexone is strongly recommended.

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* Rubidium and caesium ions were not tried.

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Talanta, 1958, Vol. 1, pp. 283-284. Pergamon Press Ltd., London.

PRELIMINARY COMMUNICATION

Elimination of errors in uronic acid determinations

(*Received* 29 *August* 1958)

DURING the past two years a systematic study of the Lefèvre and Tollens[1] decarboxylation method has been made. The form of apparatus described by McCready, Swenson and Maclay[2] has been extensively modified for use on the semi-micro scale. All unnecessary traps and joints have been eliminated; there is no apparatus or reagent "blank", and reproducible results are obtained using 10–15 mg samples of a pure uronic acid, or 20–30 mg of heterogeneous carbohydrate fractions containing 10–50% uronic acid. The CO_2 liberated in the decarboxylation reaction is determined titrimetrically in an absorption trap of special design. The entire apparatus was designed for ease of use in routine analyses, and has been widely used for analysis of carbohydrate fractions isolated by several workers in this department.[3] The apparatus, together with some of the results obtained, will be described fully in a forthcoming issue of this journal.

Using 19% (w/v) aqueous HCl, kinetic studies have shown that, under the experimental contions used, quantitative decarboxylation is not complete in less than 2½ hours. Deviation from the kinetic values of Huber[4] have been found, and decarboxylation using metal ions[5] was not successful. It has been found, however, that traces of metals[6] do have a catalytic effect on decomposition of the non-acidic carbohydrates generally present in a complex uronic acid containing polysaccharide.

It has been reported[7] that amino-sugars and proteins interfere in uronic acid estimations, and also that, in acidic hydrolysis of protein/carbohydrate materials, by-product 5-hydroxymethylfurfural reacts with the protein present.[8] This may be important in analysis of mucopolysaccharides. To date, no interference in uronic acid estimations caused by presence of protein or amino-sugars has been found.

The nature of (*a*) volatile decomposition products from the reaction and (*b*) the solid polymeric materials which form in the reaction flask have been investigated by infra-red spectroscopy and gas chromatography. Contrary to the findings of Bowman and McKinnis,[9] small quantities of carbon monoxide have been found, and the decarboxylation reaction shown to be oxygen-sensitive; further work on this aspect is in progress.

Under the analytical conditions used, the volatile decomposition products from *non-methylated* acidic and non-acidic carbohydrates, either simple sugars or polymers, have been shown to be furan (*not* furfural) and CO_2; the molar ratio of CO_2 to furan produced is dependent on internal configuration. The quantities of CO_2 reported in earlier investigations[10] to be evolved from simple sugars have been generally confirmed. It has been found possible, however, to decrease in some instances the amount of CO_2 evolved by non-acidic substances, by the addition of complex-forming reagents. It is hoped that further work will lead to the general suppression of evolution of CO_2 from undesirable side-reactions to some extent, so making the analytical reaction more specific.

The volatile decomposition products from methyl sugars and from acidic and non-acidic methylated polysaccharides have been shown to include CO_2, methyl chloride, methyl formate, 2-methylfuran and dimethylformal. In analysis of pectins, etc., precautions are therefore necessary to ensure that such substances capable of acidic reaction are not determined together with CO_2. It is hoped that further investigations into these volatile decomposition products will provide some evidence regarding the decarboxylation mechanism.

Full details of the investigations outlined here will be published elsewhere in due course.

The author thanks Professor E. L. Hirst, C.B.E., F.R.S., for his encouragement and interest in this work.

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Talanta, 1958, Vol. 1, pp. 285-289. Pergamon Press Ltd., London.

BOOK REVIEWS

Qualitative Inorganic Analysis. G. Charlot, translated by R. C. Murray. Methuen, London, 1954. Pp. xi + 354. 42s.

Quantitative Inorganic Analysis. G. Charlot and D. Bézier, translated by R. C. Murray. Methuen, London, 1957. Pp. xi + 691. 84s.

Professor Charlot has had an excellent idea in bringing together the principles of inorganic and physical chemistry and showing their application to the understanding and development of qualitative analysis. Most practising analysts and teachers of analytical chemistry are aware of these principles, but it is convenient to have them assembled into a text-book. Part I of the text of his qualitative book deals with the theory of the subject, and unfortunately shows signs of careless writing. For example, on p. 5 hydrogen sulphide is said to be a stronger acid than water because sulphur is more electronegative than oxygen (!) whereas on p. 128 the reason given is that the sulphide ion is bigger than the oxide ion. The S^{2-} ion is called the hydrosulphide ion. The definition on p. 45 of condensed ions as "compounds with the ions of water, $Cr_2O_7^{2-}$ for example" is meaningless, and the section on valency theory seems rather inadequate in a modern text. There is a fair amount of repetition in Part I, and quite often ideas are applied in a manner at variance with their initial description. On p. 46, for instance, it is assumed that an increase in ionic strength necessarily implies an increase in activity coefficients. On p. 48 there is confusion between pH and hydrogen ion activities (*e.g.* "Right up to a pH of 9·1, the concentration of Hg ions is independent of pH . . . . Even at pH of 1, approximately 90% of the $Hg(CN)_2$ remains undissociated."). There are a number of typographical errors in this section, some of which may be confusing to the student. On p. 22 V(II +) is said to be reduced to V(IV), and on p. 57 log H^+ is equated with log pH.

Part II deals with the detailed chemistry of most of the elements and has a most useful compilation of equilibrium constants and oxidation potentials. The diagrams showing how solubilities and potentials change with pH are particularly useful. A few minor points should be mentioned however. It is implied on p. 150 that the oxinates of calcium, strontium, and barium do not precipitate in alkaline solution (they come down at pH 9, but dissolve in hot ammoniacal ammonium chloride solution). The statement on p. 137 about the stability of the argentocyanide ion in acid solution seems at variance with that given on p. 88. Perchromates should not be represented by the CrO^{4+} ion (p. 169) and it is at least debatable whether AlO_2^- ions and ZnO_2^{2-} ions exist in solution. The potential of −1·6 volts for the PrO_2/Pr^{3+} couple, and the description of sodium peroxide as a complex of the O_2^- ion are probably printer's errors. Part III gives a brief account of the practical application of the first two parts.

On the whole, this is a useful book which should prove helpful to students of analytical chemistry. The translation seems remarkably free from infelicities, although a few sentences are somewhat vague, notably that on p. 22 referring to equal proportions of oxidant and reductant.

The companion volume on quantitative analysis falls into two parts—one on general principles and methods of analysis, and the other on a systematic description of the determination of the principal elements. Much of the first part of the book on qualitative analysis is repeated in Part I, and in addition there are chapters on sampling, statistics, physical methods, etc. In general, the treatment of the various topics is rather uneven, and sometimes barely adequate. Thus sampling is dealt with in just over a page, emission spectroscopy in five, and radioactivation methods in five and a half, whereas twenty-eight pages are devoted to a very detailed account of electrolysis and another thirty-one to its application.

Part II is a rather uncritical compilation of methods of determination. Many are indicated by a reference and a brief mention of the principle involved; in others an outline of the method is given, but often too sketchily to be of great use. In general the descriptions given are so condensed as to preclude mention of what may be small but important details of technique (such as the importance of stirring in the determination of aluminium as the oxinate). It is rather surprising to find ferrous ammonium sulphate and ferric alum quoted as primary standards (of guaranteed purity). The error in calcium titrations with EDTA can be reduced from 1–2% (p. 369) to about 0·2% by spectrophotometric detection of the end-point. There are relatively few typographical errors, though +0·1% for +1% on p. 51, and "$n = 1$ measurement" on p. 7 may be confusing.

The translation is, if anything, even more felicitous than that of the companion volume. One feels that at the price the book is more likely to be found in the library than as a personal possession, but in the library it should undoubtedly be.

R. A. CHALMERS

Das Dithizon und seine Anwendung in der Mikro– und Spurenanalyse. GEORG IWANTSCHEFF. Verlag Chemie, Weinheim, 1958. Pp. 272. DM 29.80.

IT is possible that the initial reaction by some to the suggestion of a book on dithizone may be doubt if the reagent has sufficiently wide applicability and interest to merit the writing of a book about its capabilities. It is probably true that such a person will recall that the reagent is excellent for the determination of traces of lead but may be hard pressed to recall many other applications. For such, this book has been written; because it is not a collection of procedures culled from the literature. Indeed, if the claim is correct that all the procedures recommended have been tested and proved in the author's laboratory, the book must be nearly unique among current analytical text-books.

The author is an analytical chemist in the research laboratory of the Siemens-Schuckertwerke AG., Erlangen and has managed to indicate in this publication his obviously very wide knowledge of the subject.

The book consists of five main parts. The first is introductory and deals with dithizone and its inner-complex salts. In the following part, general analytical techniques are considered. Here the basis of methods of determination and separation are discussed, including direct and indirect extractive titrations, single-colour and mixed-colour colorimetric methods and the various techniques which can be used to assist separations.

The "bread and butter" of the book, so to speak, is, however, the section which follows, dealing with the use of dithizone in quantitative analysis. Procedures for eighteen metals are presented, including less familiar metals such as polonium, indium, palladium, platinium, and thallium. So much information is given under each metal that it appears impossible that anything has been missed, and yet the presentation is such that one does not get the feeling of being overwhelmed.

After dealing with the quantitative applications of the reagent, the author illustrates its use in qualitative analysis; and in the final part of the book special applications are discussed, including those in emission spectrographic and polarographic analysis, in adsorption chromatography, and as an indicator in titrimetric analysis.

An appendix contains details of the preparation of dithizone. The bibliography contains hundreds of references, some as recent as 1956. One may feel however after reading this book, if he has an interest in dithizone, that they are superfluous.

This book is recommended to the attention of analytical chemists.

R. J. MAGEE

Gas Chromatography. A. I. M. KEULEMANS. Edited by C. G. VERVER. Reinhold Publishing Corporation, New York: Chapman and Hall, Ltd., London, 1957. Pp. xix + 217. 60s.

THE potentialities of chromatographic separations based on the partition of the components of a volatile mixture between a stationary liquid phase and a moving gas phase were first indicated by Martin and Synge in 1941. It was not, however, until ten years later, when Martin and James demonstrated the feasibility of such separations, that general interest in this technique was aroused.

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The subsequent phenomenal rate of growth of that interest has led to a rapidly expanding body of knowledge relating to the technique. Any author attempting to cover a developing field is of necessity at a disadvantage and, in the present instance, the very high rate of development makes the disadvantage a serious one. The author and editor state in their preface to this book that use is made of work published only up to 1st January. 1956. Even work presented at the Dallas and the London Symposia in 1956 had in the main to be omitted, being covered in the more important cases merely by footnotes; and, of course, much has appeared since then. However, the main features of the technique had been delineated by 1956 and it is on these that the author concentrates.

The various types of chromatography are briefly described with a view to systematising nomenclature and defining terms. The main subject matter of the book, namely gas-liquid chromatography, is embarked upon with a brief survey of some typical separations and the effect of the operating conditions thereon. This is followed by a very useful chapter on apparatus. The treatment then becomes theoretical in emphasis and for three chapters (75 pp.) this aspect is explored in relation to the factors which influence resolution; in a further chapter, this treatment is related to the evaluation of thermodynamic parameters. A short chapter on gas-solid chromatography concludes the book. All this is very well done. The style is easy and lucid, and the discussion often revealing. The presentation, including the clarity and helpfulness of the many diagrams, is pleasing. And yet one feels that perhaps this book does not achieve all that one had hoped it might. Having in mind the book's interim nature and the purpose for which it will most often be read, it must be said that the balance of subject matter leaves something to be desired.

In spite of its powers in other directions, gas chromatography has been developed first and foremost as an analytical tool and a book on this subject will be most used by people wanting to solve an analytical problem. Such people would like to find systematised information relating to (*a*) separations already achieved; (*b*) the characteristics of the various stationary liquids, supports and adsorbents available; (*c*) details of apparatus; and (*d*) theoretical treatments to use as a guide in the choice of operating conditions. This book makes no attempt at (*a*); there is not even an alphabetical subject index. Appendix I deals in some measure with (*b*) and will prove very useful. Chapter 3 and Appendix II cover (*c*), but could well have been extended at the expense of some of the following chapters. Great weight has been given to the katharometer for detection, and the author has placed the experience gained in his own laboratory at the disposal of his readers, but a more detailed and critical account of the other methods of detection would have been welcome. As already indicated, a great deal of the book has been devoted to (*d*) and very instructive this section is. Unfortunately, a quantitative theory of gas chromatography is not available. All we have are some semi-quantitative, but mostly qualitative notions of the factors of importance to this technique. These could have been more simply and more forcefully stated in a shorter treatment than given in this book and the analytical chemist will wish that the author had restrained his enthusiasm for and insight into this aspect of his subject. None the less, anybody interested in the difficulties to be surmounted before theoretical treatments become of practical value will find much of interest in this survey.

The book is creditably free from errors, except for some of a trivial character. For example equation (7a), p. 80, should be $\Delta t = -\epsilon(t_w - t_e)$ and the equations derived therefrom adjusted accordingly; equation (10), p. 81, has an "I" too many; p° is the vapour pressure of the solute and not of the solvent as stated on p. 161. It is a pity that the abbreviation "R.V." is used for retention volume after a carefully chosen symbolism has been defined.

To summarize, this is a stylish book which anybody using or thinking of using gas chromatography would do well to read (or even buy, if he can afford it!); it has limitations arising from the distribution of emphasis, but it will do much to enhance the already considerable reputation of gas chromatography as an analytical method.

DESMOND BRENNAN

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HERMANN SPECKER

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pH Measurements. VICTOR GOLD. Methuen and Co., Ltd., London, 1956. Pp. x + 320. 9s. 6d.
The Book of pH. R. B. WEBBER. George Newnes, Ltd., London, 1957. Pp. 111. 30s.

CHEMISTS are indeed few who have not at some time required to make use of pH measurements. Surprisingly, many scientists still remain vague as to the true chemical concept of pH and its measurement. A thorough discussion of pH, its meaning, physicochemical measurement and application, is attempted in the first of these volumes, which is one of Methuen's Monographs on Chemical Topics. The treatment is, as intended, rigorous.

The book contains nine chapters. The first, introductory in nature, defines pH; and suitable appendices are listed at the conclusion of the book.

Chapter II related the theory of proton transfer with reference to activity coefficient, ionic strength, acidic and basic dissociation constants, and the ionic product of water. This is followed in Chapter III by a study of the principles of galvanic cells using a thermodynamic approach.

Chapters IV and V deal respectively with the interpretation of the pH scale and the techniques used in pH measurement, mainly by e.m.f. methods. The former chapter discusses well the problem of standardising the pH scale, explaining how the practical scale results from a compromise between theory and measurement procedure. The latter chapter describes the practical methods involved in determining pH, tracing the development of various circuits and electrode systems. Three measuring electrodes discussed are the hydrogen electrode, the glass electrode and the quinhydrone electrode.

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Talanta, 1958, Vol. 1, p. 290. Pergamon Press Ltd., London.

NOTICES

The Society for Analytical Chemistry

A Report on *The Use of Radiochemical Methods to Investigate the Recovery of Trace Elements from Organic Materials* will be given by T. T. GORSUCH, B.Sc., A.R.I.C. in the Lecture Theatre of The Royal Institution, 21, Albemarle Street, London, W.1. at 6.30 p.m. on Wednesday 1 October 1958. There will be an introduction by R. SPENCE, C.B., Ph.D., D.Sc. on *Radiochemical Methods.*

Visitors will be welcome. No tickets will be needed.

An Ordinary Meeting of the North of England Section of the Society will be held at 2.15 p.m. on Saturday, 4 October 1958, at the City Laboratories, Mount Pleasant, Liverpool, 3. This will take the form of a discussion on *Laboratory Balances*, to be opened by J. G. LUNT, B.Sc., F.R.I.C. and G. F. HODSMAN, B.Sc., Ph.D. Visitors will be welcome.

An Ordinary Meeting of the Midlands Section of the Society will be held on Wednesday, 8 October 1958, at the Technical College, The Butts, Coventry. A discussion on *The Determination of Trace Impurities in Metals* will be opened by B. BAGSHAWE, A. Met. (*Ferrous Metals*) and W. T. ELWELL, F.R.I.C. (*Non-ferrous Metals*). Visitors will be welcome.

A Discussion Meeting of the Biological Methods Group of the Society will be held at 6.30 p.m. on Thursday, 9 October 1958, in "The Feathers", Tudor Street, (off Bouverie Street, Fleet Street,) London, E.C.4. The subject for discussion will be *Strategy in the Assessment of Disinfectants*, and it will be introduced by G. SYKES, M.Sc., F.R.I.C. Visitors will be welcome.

An Ordinary Meeting of the Midlands Section of the Society will be held at 7.00 p.m. on Tuesday, 14 October 1958, in the Gas Showrooms, Nottingham. A discussion on *The Identification of the New Permitted Food Colours* will be opened by P. S. HALL, F.R.I.C. Visitors will be welcome.

A Joint Meeting of the Physical Methods Group and the North of England Section of the Society with the Modern Methods Analysis Group of the Sheffield Metallurgical Association will be held at 7.00 p.m. on Tuesday, 21 October 1958, in the Conference Room of the British Iron and Steel Research Association, Hoyle Street, Sheffield, 3. Two papers will be presented and discussed: *The Determination of Gases in Metals by the Microvacuum Fusion Method*, by E. BOOTH, B.Sc., and *The Determination of Oxygen and Hydrogen in Steel*, by C. E. A. SHANAHAN, B.Sc., F.R.I.C., F.I.M. Visitors will be welcome.

Talanta, 1958, Vol. 1, pp. 291–292. Pergamon Press Ltd., London.

BOOKS RECEIVED

Methods of Analysis for Petrochemicals. E. R. LITTMANN. Chemical Publishing Co., Inc., New York, 1958. pp. 384. $12.00.

Modern Manufacturing Formulary. EMIL J. BELANGER. Chemical Publishing Co., Inc., New York, 1958. pp. 399. $10.00.

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Talanta, 1958, Vol. 1, pp. 293–304. Pergamon Press Ltd., London.

PHOTOMETRIC TITRATIONS

JAMES B. HEADRIDGE
Chemistry Department, Sheffield University, England

(*Received* 6 *June* 1958)

Summary—Within the last few years, photometric titration has become an increasingly important analytical method. The principles of the method are discussed and sources of error briefly mentioned. A comprehensive review of recent applications of the technique is given.

IN this paper, an outline is given of the analytical application of photometric titrations, and material published in the period 1954 to mid-1957 is reviewed. Reference is also made to papers appearing up to the end of 1957 in the more readily available analytical journals. Papers published before the beginning of 1954 have been adequately reviewed by Osburn, Elliott and Martin,[1] and by Goddu and Hume.[2]

In photometric titrations the property studied, in order to obtain the titration equivalence point, is the optical density of the solution. For monochromatic light passing through a solution, the Lambert-Beer Law states that

$$\text{Optical density} = \log \frac{I_0}{I} = kcd$$

where I_0 is the intensity of the incident light, I that of the transmitted light, k is a constant (the absorption coefficient), c is the concentration of the absorbing species and d is the length of the light path. Since photometric titrations are carried out in a vessel for which the length of the light path is constant, the method is based on the simple relationship that the optical density is directly proportional to the concentration of the absorbing species. Changes occur in the concentration of the absorbing species, and hence in the optical density of the solution, during the course of a titration and by interpreting these changes the end-point is obtained.

In most photometric titrations, a plot is drawn of optical density against volume of titrant added, and a study of such a plot gives the end-point. Since the Lambert-Beer Law is only rigidly adhered to for monochromatic light, the most accurate photometric titrations are performed using a spectrophotometer; but many useful titrations may be carried out with a filter photometer. A few titrations have been described where unfiltered light is used but these are the least satisfactory.

The first photometric titrations using a conventional-type photometer were performed by Müller and Partridge[3] in 1928. The potentialities of the method have been greatly increased since use was first made of a spectrophotometer by Goddu and Hume[4] in 1950.

Most photometric titrations fall into one of three classes.

I. *Self-indicator systems*, i.e. *titrations of solutions without the use of an added indicator*

An example of a titration in this class is that of ferrous ions with cobaltic ions[5] (Fig. 1).

Visual titration on solutions in this class can only be performed when either the species being titrated or the titrating substance absorbs very strongly in the visible region of the spectrum, *e.g.* the titration of iodine solutions with thiosulphate ion without the use of starch as an indicator, and the titration of ferrous ions with permanganate ions. In photometric titrations neither reagent need absorb strongly provided that a change in optical density occurs during the course of the titration. Titrations can equally well be made in the ultra-violet and very near infra-red regions of the spectrum. Titrations to maximum turbidity, named heterometric titrations by Bobtelsky,[6] also come into this class.

II. *Titrations in solutions containing more than enough of an indicator to complex, either the substance being titrated, or post-end-point additions of titrant.*

An example is the titration of bismuth with ethylenediaminetetra-acetate in the presence of thiourea as indicator[7] (Fig. 2). The different types of photometric plots for substances in classes I and II are discussed by Goddu and Hume.[2]

III. *Titrations of solutions containing sufficient indicator to complex only a fraction of the substance being titrated, or of the post-end-point additions of titrant. (pH and pM indicators)*

Many recent photometric titrations are in this class. When microgram quantities of a substance are being titrated visually with the use of an indicator it is often observed that sharp end-points are not obtained because the indicator changes colour over a considerable portion of the whole titre. Using a photometric titration excellent results are obtained in these cases.

An example of a titration in this class is that of zinc with ethylenediaminetetra-acetate in the presence of Eriochrome Black T as indicator[8] (Fig. 3).

From what has already been mentioned, it is obvious that photometric titrations have a wide field of application. The method is particularly useful for the titration of coloured solutions since slight changes in optical density, not easily assessed in visual titrations, are readily detected on a photometer. Substances in class I whose reactions are incomplete at the end-point, but complete in the presence of excess of the titrant, can be satisfactorily titrated since the straight portions of the plot well before and well after the end-point may be extrapolated to intersect at the end-point.

Sources of error in photometric titrations

In these titrations, corrections of the optical density readings to constant volume should be made, if the increase in volume of the solution during the titration exceeds 1 %. Otherwise errors in end-point detection will result.

It is also essential to make sure that the titration cell is light-proof with respect to extraneous light. Goddu and Hume[2] have discussed the errors that arise from stray light. In certain cases, the heat of the reaction will increase appreciably the temperature of the solution being titrated and, at times, this may lead to an error in the titration since many absorbing systems are sensitive to temperature changes. In such cases, thermostatically-controlled titration cells may be employed, but for most titrations such a refinement is unnecessary.

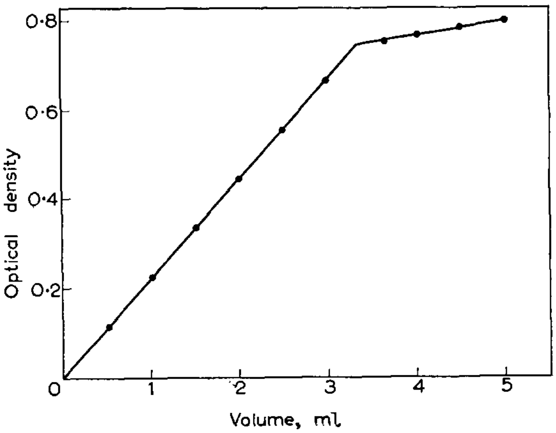

FIG. 1.—Titration of about 1·8 mg of iron^{II} with approx. 0·01M cobalt^{III} sulphate at 360 mμ.

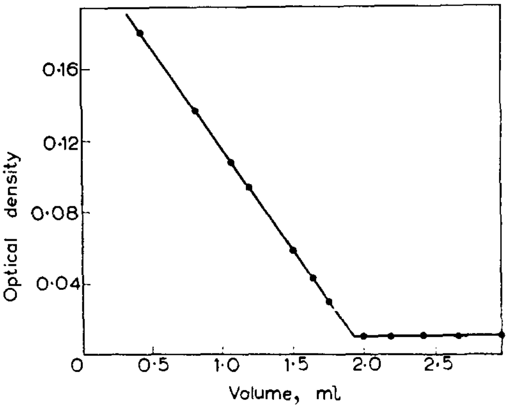

FIG. 2.—Titration of 4·18 mg of bismuth with 0·01M ethylenediaminetetra-acetic acid at 400 mμ (indicator: thiourea).

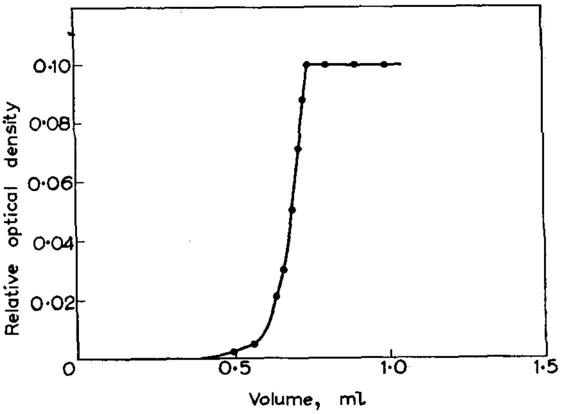

FIG. 3.—Titration of about 100 μg of zinc with 0·0025M ethylenediaminetetra-acetate at 665 mμ (indicator: Eriochrome Black T).

Apparatus

A commercial spectrophotometer is quickly adapted for photometric titrations. For example, Hunter and Miller[8] have modified the Unicam SP 500 and Bricker and Sweetser[9] have converted the Beckman DU for titrations.

REVIEW OF RECENT WORK

Apparatus

Maher[10] has discussed the development of automatic photometric titrimeters. The Beckman Model B spectrophotometer has been modified for automatic titrations.[11] An instrument for automatic derivative spectrophotometric titrations has been described,[12] and Chalmers and Walley[13] have constructed a recording titrimeter.

Stolyarov[14] has described an apparatus for titrations in ultra-violet light where a filter with maximum transmission at 365 mμ is used. Details have been given for the modification of the Beckman DU spectrophotometer for titrations.[15] Wallraf[16] has constructed a filter photometer for the titration of calcium and magnesium with ethylenediaminetetra-acetate.

Review articles and theoretical considerations

Goddu and Hume[2] have discussed the principles of the photometric titration method and have reviewed previous work in the field up to the end of 1953. Underwood[17] has described the advantages of photometric titrations and the application of the method to acid-base, oxidation-reduction, turbidimetric and complexometric reactions.

Grunwald[18] has reported a method for accurate end-point determination in photometric titrations where the titration curves are rounded in the vicinity of the end-point.

Class I *titrations*

Acid-base: Goddu and Hume[19] have studied the photometric titration of a weak acid (or base) with a strong base (or acid) and have shown that a sharp inflexion of the graph of optical density plotted against volume of titrant is obtained only when the product of ionization constant and molarity of the weak component, is $\geqslant 10^{-12}$ at concentrations of $10^{-5}M$ and above.

Telluric acid has been satisfactorily titrated with aqueous ammonia at 240–280 mμ.[20]

In glacial acetic acid, quinoline, *o*-chloroaniline, *m*-chloraniline and sodium acetate have been titrated photometrically with acetous perchloric acid.[21] Photometric titrations in non-aqueous solvents have so far received little attention. Further investigations in this field could be profitably undertaken.

Oxidation-reduction: Cerous ions in the presence of large amounts of ceric ions in neutral pyrophosphate medium have been determined with permanganate.[22] Cerium, in bismuth-base alloys, can be determined by the titration of the cerium$^{\text{III}}$ in pyrophosphate medium with permanganate in the E.E.L. absorptiometer.[23]

Deshmukh and Bapat[24] have titrated thiourea quantitatively in hydrochloric acid-bromide solutions with potassium iodate solution, using a Hilger Spekker absorptiometer for photometric end-point detection.

Sweetser[25] has titrated arsenic$^{\text{III}}$ with cerium$^{\text{IV}}$ at 320 mμ and, iron$^{\text{II}}$ and uranium$^{\text{IV}}$

with cerium^{IV} at 340–360 mμ. The end-point in bromate-bromide titrations has been determined by the absorption of the tribromide ion at 270–360 mμ.[25] Stolyarov[26] has detected the end-point in many titrations by the use of cerium^{IV} and radiation in the region of 365 mμ passing through the solution on to a fluorescent screen. The screen goes dark with one drop of cerium^{IV} in excess.

Iron^{II} has been titrated spectrophotometrically with dichromate at 350 mμ.[27] Bricker and Loeffler[5] have titrated iron^{II}, cerium^{III} and ferrocyanide with cobalt^{III} Selenite has been determined by reduction with ascorbic acid and photometric titration of excess ascorbic acid with iodine.[28] Dichromate has been titrated with iron^{II} or arsenic^{III}, and vanadate with iron^{II} at 350 mμ.[29]

Complexometric: Magnesium, calcium, zinc and cadmium have been determined by titrating with ethylenediaminetetra-acetate at 222 or 228 mμ.[30] Procedures have been described for the ultra-violet spectrophotometric titration of iron^{III}, copper, nickel and cobalt.[31] Wilhite and Underwood[32] have determined bismuth and lead simultaneously in perchlorate solution by titrating with ethylenediaminetetra-acetate at 240 mμ.

Bertschinger[33] reports that calcium can be determined spectrophotometrically by titration with ethylenediaminetetra-acetate without the use of an indicator. A titration of nickel in the presence of cobalt with ethylenediaminetetra-acetate at 1000 mμ has been described.[34]

Precipitation: In the period 1954–1957, Bobtelsky and co-workers have published a series of papers[6,36–67] on heterometric titrations, *i.e.* titrations to maximum turbidity The first paper by Bobtelsky on such titrations was published in 1953,[35] and he has discussed the fundamental principles of the method.[6]

Magnesium has been determined by titration with 8-hydroxyquinoline in 50% ethanol.[36] Calcium, in the presence of a large excess of magnesium ions and in a strongly ethanolic solution, has been titrated with sulphuric acid.[37] 8-hydroxyquinoline in ethanol or acetic acid solution has been employed to titrate aluminium ions.[38]

A titration of lead with sodium diethyldithiocarbamate has been reported.[39] Bismuth may also be determined with sodium diethyldithiocarbamate.[40] Molybdate in acid solution has been titrated with alcoholic α-benzoinoxime solution.[41]

Iron^{III} has been titrated turbidimetrically with an ethanolic solution of 1-nitroso-2-naphthol[42] and with aluminon (ammonium aurintricarboxylate.[43,44] Cobalt may be determined with an ethanolic solution of 1-nitroso-2-naphthol).[45,46] Palladium^{II} was titrated with 1-nitroso-2-naphthol in ethanol,[47] dimethylglyoxime in ethanol,[48] sodium diethyldithiocarbamate[49] and rubeanic acid (dithio-oxamide).[50]

Copper has been titrated turbidimetrically with 8-hydroxyquinoline in 50% ethanol[51,52] sodium quinaldinate (sodium quinoline-α-carboxylate),[53] salicylaldoxime,[54] sodium diethyldithiocarbamate,[55] and rubeanic acid in ethanol.[56] A solution of *p*-dimethylaminobenzylidinerhodanine has been used to titrate silver ions.[57] Gold may be determined by a turbidimetric titration with sodium diethyldithiocarbamate[49] or rubeanic acid.[50]

Zinc can be titrated with sodium quinaldinate[58] or sodium diethyldithiocarbamate.[59] Cadmium was determined in a titration with sodium diethyldithiocarbamate.[60] Mercury^{II} was titrated heterometrically with mercaptobenzothiazole in ethanol[61,62] and with sodium diethyldithiocarbamate.[63,64] Uranium^{VI} has been titrated turbidimetrically with potassium ferrocyanide solution[65] and with disodium hydrogen phosphate.[66]

Sulphate in an acid solution containing ethanol may be determined by titrating with barium nitrate in 50% ethanol.[67]

Turbidimetric titrations have been used to study the systems, barium sulphate-barium chloride-ethanol-water, barium sulphate-hydrogen chloride-ethanol-water, and barium sulphate-barium chloride-hydrogen chloride-ethanol-water.[68]

Blood-serum proteins have been studied by turbidimetric titration of the serum in a buffer solution with copper and zinc sulphates.[69]

Class II *titrations*

Titanium^{IV} in the presence of hydrogen peroxide has been titrated spectrophotometrically with ethylenediaminetetra-acetate at 450 mμ. The titanium-peroxide complex is converted to a titanium-peroxide-ethylenediaminetetra-acetate complex with a different absorption spectrum, but the method is stated to have few advantages over other existing titrimetric and photometric procedures for titanium.[25,30]

Zirconium has been determined by titration of an added excess of ethylenediaminetetra-acetate with standard iron^{III} in the presence of salicylic acid at 520 mμ.[30] Milner and Edwards[70] have determined zirconium by photometric titration of an excess of ethylenediaminetetra-acetate with iron^{III} using sodium salicylate as indicator in the pH range 3 to 7, and potassium benzohydroxamate in the range 1·8 to 3·3. A similar method has been employed with potassium benzohydroxamate as indicator, to the determination of zirconium in zirconium-uranium alloys[70] and zirconium-cerium alloys.[71] Milner and Barnett[72] also applied the method of back-titrating with iron^{III} to the determination of zirconium in certain ternary alloys.

Thorium has been titrated automatically at 290 mμ with ethylenediaminetetra-acetate in the presence of copper^{II} as indicator.[73] Naphthopurpurin has been employed as an indicator in the photometric titration of thorium with ethylenediaminetetra-acetate.[74] Milner and Sheddon[75] determined thorium by adding an excess of ethylenediaminetetra-acetate and titrating photometrically with thorium perchlorate, eriochrome cyanide being used as indicator. Thorium has also been determined by adding excess ethylenediaminetetra-acetate and back-titrating photometrically with thorium nitrate solution, and with alizarin red S (sodium alizarin sulphonate) as indicator.[76] Banks and Edwards[77] have determined thorium by a procedure based on an initial spectrophotometric titration of a standard ethylenediaminetetra-acetate solution with standard thorium nitrate solution in the presence of Chrome Azurol S as indicator, for the construction of a calibration curve of optical density against volume of thorium nitrate solution added. A solution containing an unknown quantity of thorium is added to the same amount of ethylenediaminetetra-acetate and indicator, as is used for the calibration curve, and the solution is titrated with the standard thorium nitrate solution until the end-point has been passed. The optical density of the solution is then measured, and from the calibration curve, the total quantity of thorium in the solution is found. The unknown quantity of thorium, initially added, is obtained by subtraction.

Bismuth has been titrated with ethylenediaminetetra-acetate at 745 mμ with copper^{II} as indicator. Bismuth is complexed primarily, and, after the end-point, the optical density readings increase as the copper^{II} is complexed.[7] Bismuth may also be titrated spectrophotometrically with ethylenediaminetetra-acetate, in the presence of an excess of thiourea, whose complex with bismuth absorbs strongly at 400 mμ and is broken down in preference to the more stable bismuth ethylenediaminetetra-acetate complex.[7]

Copper^{II} in the presence of ammonia as indicator may be titrated at 630 mμ with ethylenediaminetetra-acetate. The cuprammonium ions, which absorb strongly at 630 mμ are broken down by the ethylenediaminetetra-acetate with the formation of the copper^{II}-ethylenediaminetetra-acetate complex.[78]

Calcium, in strongly ammoniacal solution, has been titrated with ethylenediaminetetra-acetate at 630 mμ, with cuprammonium ions as indicator. Under these conditions, the calcium is first titrated and, only after the end-point of the calcium titration, do the cuprammonium ions react with the ethylenediaminetetra-acetate.[79]

Cyanide, in ammoniacal solution, may be titrated photometrically with silver nitrate in the presence of potassium iodide as indicator.[80]

Fluoride has been titrated photometrically in the presence of sodium alizarin sulphonate, with thorium nitrate solution.[81,82] Hollingworth[83] has determined fluoride by titrating a solution at 580 mμ with thorium nitrate in the presence of sodium 2-(*p*-sulphophenylazo)-1:8-dihydroxy-naphthalene-3:6 disulphonate, which forms a blue-violet lake with excess thorium ions. Dean and co-workers[84] have compared photometric and visual titration techniques for the determination of fluoride using thorium nitrate and alizarin red S indicator.

Class III *titrations*

Acid-Base: A spectrophotometric titration has been employed to determine a mixture of hydrobromic and boric acids with sodium hydroxide as titrant. Methyl red and methyl red-methylene blue indicators were used for the hydrobromic acid and phenolphthalein for the boric acid.[85]

Huguchi, Rehm and Barnstein[86] have shown that endpoints in spectrophotometric titrations can be readily determined by plotting the relative concentration of the acid and basic forms of the indicator in solution against the volume of standard acid or base added or its reciprocal. For systems where $pK_1 \gg pK$ (K is the dissociation constant for the acid or base, and K_1 that of the indicator) the indicator colour-ratio is plotted directly against the volume. For systems where $pK_1 \triangleq pK$, linear plots are only possible if the plots are made against the reciprocal of the volume. The relative concentration of the acid and basic forms of the indicator is found from optical density readings.

A method has been described for the titration of basic substances using weak basic indicators whose colour change occurs primarily after the basic sample has been titrated with an acid. Linear extrapolation of information obtained beyond the end-point gives the stoichiometric value. The method can be applied to the titration of very weak bases, such as aniline, in water, and to the titration of practically non-basic compounds, such as urea, in glacial acetic acid.[87]

Complexometric: Fortuin, Karsten and Kies[88] have evaluated theoretically the conditions for sharp end-points in the titration of bivalent metal ions with ethylenediaminetetra-acetate using murexide as indicator. They are, that the complex-forming capacity of the titrant should be at least 10^4 times greater than that of the indicator, that the complex-forming capacity of the indicator should be large, about 10^4 to 10^5, that the concentration of the indicator should be as low as possible, and that of the substance being titrated as high as possible.

Ringbom and Vanninen[89] have also derived theoretical conditions for the photometric determination of exact equivalence point in the titration of metals with ethylenediaminetetra-acetate using single-colour or two-colour indicators. The principles are illustrated and confirmed experimentally by the titration of copper^{II} with murexide as indicator and the titration of magnesium with Eriochrome Black T as indicator.

Chalmers[90] has determined calcium by spectrophotometric titration at 610 mμ, with ethylenediaminetetra-acetate using murexide as indicator. Calcium in serum and urine has been titrated with ethylenediaminetetra-acetate at 600 mμ with murexide as indicator.[91] Calcium in phosphate solutions has been titrated spectrophotometrically with ethylenediaminetetra-acetate and murexide indicator.[92]

Hoffman and Shapiro[93] have titrated photometrically, calcium and magnesium from agricultural liming materials, using murexide and Eriochrome Black T as indicators, respectively. Ethylenediaminetetra-acetate was the titrant. The theoretical principles for sharp end-points derived by Fortuin and co-workers[88] have been applied to the titration with ethylenediaminetetra-acetate of calcium using murexide or *o*-cresolphthalein complexone as indicator, and of magnesium with Eriochrome Black T or *o*-cresolphthalein complexone.[94]

A circulatory system for the photometric titration of calcium, in the presence of murexide, with ethylenediaminetetra-acetate has been described. The titrant is added to the solution in an external titration cell and a circulatory pump maintains a continuous flow of solution from the titration cell to the flow-through cell of the photometer and back again.[95] Eldjarn *et al.*[96] have titrated serum calcium spectrophotometrically with ethylenediaminetetra-acetate. Calcium and magnesium in carbonate rocks have been determined by automatic titration of calcium with ethylenediaminetetra-acetate and murexide as indicator, and of magnesium with the same titrant and Eriochrome Black T, after the removal of calcium as tungstate.[97]

Horner[98] has determined calcium in biological materials by titration with ethylenediaminetetra-acetate at 620 mμ, murexide being employed as indicator. Calcium in water was determined by spectrophotometric titration with ethylenediaminetetra-acetate, with murexide as indicator.[99] Bertschinger[33] has determined calcium by spectrophotometric titration with ethylenediaminetetra-acetate and an indicator. Campen *et al.*[100] have determined water-soluble calcium in gypsum by titrating the solution photometrically with ethylenediaminetetra-acetate using unfiltered light and murexide as indicator.

Lheureux *et al.*[101] determined calcium and magnesium in rocks and waters by photometric titration with ethylenediaminetetra-acetate using murexide and Eriochrome Black T as indicators. Zak *et al.*[102] have determined calcium and magnesium in spinal fluid by spectrophotometric titration. Calcium is determined in the precipitated oxalate and magnesium in the supernatant liquid by titration at 660 mμ with ethylenediaminetetra-acetate using Eriochrome Black T as indicator.

Serum has been analysed for calcium and magnesium by means of a spectrophotometric titration with ethylenediaminetetra-acetate. Total calcium and magnesium are determined with Eriochrome Black T as indicator and calcium alone with murexide.[103,104]

Rowley *et al.*[105] have titrated barium with ethylenediaminetetra-acetate at 650 mμ

using Eriochrome Black T as the indicator. Barium in the presence of *o*-cresolphthalein complexone, has been determined by photometric titration with ethylenediaminetetra-acetate.[106] Vrestal and Kotrly[107] have studied the possibility of determining lead by photometric titration with ethylenediaminetetra-acetate using Brilliant Congo Blue as indicator. Zinc has been determined by a spectrophotometric titration with ethylenediaminetetra-acetate, Eriochrome Black T being the indicator.[8]

Silver may be determined by adding an excess of potassium tetracyanonickelate^{II} and titrating the liberated nickel, at 440 mμ in the presence of murexide, with ethylenediaminetetra-acetate.[108]

Nitrilotriacetic acid has been determined by photometric titration with copper sulphate solution, either catechol violet or murexide being used as indicator. Large amounts of acid may be titrated without the use of an indicator.[109]

Precipitation: Photometric titrations have been carried out to study the colour change at the end-point of the titration of sulphate with barium chloride using tetrahydroxyquinone indicator. It has been shown that the visual end-point is detected more readily when light, transmitted by a blue filter, illuminates the solution.[110]

Coulometric titrations with spectrophotometric end-points

Wise *et al.*[111] have constructed a ratio-detecting photometer for use in the coulometric titration of acids and bases with photometric detection of the end-point. Photometric end-point detection has been used for the titration of arsenic^{III} with electrically generated iodine.[112] Arsenic^{III} has also been titrated coulometrically with cerium^{IV} in the presence of osmium tetroxide catalyst. The end-point was determined by the absorption of excess cerium^{IV} at 320, 360 or 375 mμ[113]

Malmstadt and Roberts[114] determined vanadium in titanium tetrachloride by hydrolysing the tetrachloride, removing oxygen and chlorine, and titrating the vanadium coulometrically with electrically generated titanium^{III}. The end-point was detected automatically by optical density changes at 490 or 760 mμ. Iron^{III} from titanium sponge has been titrated coulometrically with titanium^{III} generated from the titanium^{IV} in the solution. The end-point is detected spectrophotometrically at 665 mμ by the use of leuco methylene blue indicator. An automatic derivative titrimeter is used.[115]

Titanium in a solution from titanium ores and metal has been determined by passing the solution through a cadmium reductor and collecting the effluent containing titanium^{III} in iron^{III} solution. The excess iron^{III} was titrated coulometrically as in the previous paper.[116] Chromium and iron in titanium can be determined in one titration after oxidation to chromium^{VI} and iron^{III}. Chromium^{VI} is first reduced to chromium^{III} by electrolytically generated titanium^{III}, with diphenylamine sulphonate as indicator for automatic derivative spectrophotometric end-point detection. Iron^{III} is then reduced to iron^{II}, the end-point being detected by means of leuco methylene blue.[117]

Miller and De Ford[118] have determined olefins in glacial acetic-methanol solvent by coulometric titration with bromine generated from potassium bromide and using mercuric chloride as a catalyst. A spectrophotometric end-point was used.

Miscellaneous titrations

Principles, apparatus and procedure have been described for photometric titrations in the ultra-violet region of the spectrum, based on the addition of pure solvent to a concentrated solution until the optical density is exactly equal to that of a known solution. Anthracene is determined in a crude sample by using radiation of 375 mμ and methanol as solvent.[119]

CONCLUSION

The principles of the analytical method of photometric titration have been given. Photometric titrations were classified into three groups, namely (I) titrations in self-indicator systems, (II) titrations in solutions containing more than enough of an indicator to complex, either the substance being titrated, or post-end-point additions of titrant, and (III) titrations in solutions containing sufficient indicator to complex only a fraction of the substance being titrated, or of the post-end-point additions of titrant. An example of the plot of optical density against volume of titrant added, was given for each class of titration. Sources of error in photometric titration and the apparatus used have been discussed. Recent work in the field has been reviewed under the following headings—apparatus, review articles and theoretical considerations, Class I, Class II and Class III titrations, coulometric titrations with spectrophotometric end-points and miscellaneous titrations.

Zusammenfassung—Innerhalb der letzten Jahre wird die photometrische Titration zu einer zunehmend wichtigen Methode. Die Grundsätze der Methode werden besprochen, und die Fehlerquellen kurz erwähnt. Es wird eine umfassende Übersicht der neuen Anwendungen der Technik gebracht.

Résumé—Le titrage photométrique est devenu depuis ces dernières années une méthode analytique d'importance croissante. On discute les principes de la méthode et mentionne brièvement les sources d'erreur. On passe en revue les récentes applications de cette technique.

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Talanta, 1958, Vol. 1, pp. 305–309. Pergamon Press Ltd., London.

A NEW METHOD FOR THE TITRIMETRIC DETERMINATION OF THE FERRICYANIDE ION

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(*Received* 28 *March* 1958)

Summary—The direct titration of ferricyanide ions with the mercurous-thiocyanate system is studied, the influence of pH, thiocyanate concentration, time and temperature being considered. The standard deviation of the proposed method is 0·26 per cent.

THE general use of $Hg_2(NO_3)_2$ as a reagent in redox titrations is a relatively recent accomplishment. Bradbury and Edwards, in 1940, proved that in the presence of a great excess of thiocyanate ion, Fe^{3+} can be reduced to Fe^{2+}, and thus mercurous nitrate may be utilised as a reagent for the direct titration of this ion. Later the titration of copper, dichromate, permanganate, cerium, vanadate and other oxidising and reducing agents was proposed.[2]

The mercurous-thiocyanate system has not been applied to the titration of the ferricyanide ion. There is only one determination by the mercurous-iodide system.[3] The present work relates to a study of the direct titration of ferricyanide, utilising mercurous perchlorate as a reagent in the presence of thiocyanate, according to the reaction.

$$2Fe(CN)_6^{3-} + Hg_2^{2+} + 8SCN^- \rightarrow 2Fe(CN)_6^{4-} + 2Hg(SCN)_4^{2-}$$

The main inconvenience of this titration is the interferences which can be produced as a result of the reduction of the ferricyanide by the thiocyanate and of the precipitation of mercury ferrocyanide.

In this work the influence of pH, of temperature, of time and of the concentration of thiocyanate are studied, and finally the conditions under which the titration is possible have been determined. The end-point was detected potentiometrically.

EXPERIMENTAL

Apparatus

A Beckman pH-meter, Model G, with a platinum or glass electrode as indicator and a calomel electrode for reference.

Solutions

(1) *Mercurous perchlorate:* 0·1*N*. This salt is used instead of the nitrate because, as indicated by Pugh,[4] of the greater stability of its solutions, which are also almost neutral, and therefore permit a study under better conditions of the influence exercised by acidity. These solutions were prepared in accordance with the method cited by Pugh and modified by S. Arribas.[5]

(2) *Potassium ferricyanide:* 0·1*N*.

(3) *Potassium thiocyanate:* 5*N*.

(4) *Acetic acid:* 5*N*.

THE INFLUENCE OF pH

Titrations were made in the following conditions: (*a*) Sulphuric acid, 0·5*N*; (*b*) Acetic acid, 0·25*N*, pH = 3·0; (*c*) pH = 6·5 (no buffer added), (*d*) Saturated sodium bicarbonate, pH = 8·0; (*e*) Ammonium nitrate–Ammonium hydroxide buffer, pH = 9·2; (*f*) Sodium carbonate, 1%, pH = 10·9; (*g*) Sodium hydroxide, 0·5*N*.

In each case the pH value of the solution to be tested was first measured electrometrically by a glass electrode.

PROCEDURE

Different volumes of ferricyanide solution were taken, the calculated quantity of the substance for regulating the pH value of the solution was added, and the solution was then diluted to 100 ml. Finally, 20 ml of 5*N* KSCN were added and the solution was titrated with mercurous perchlorate solution. During titration, the solution was stirred mechanically. The results obtained are shown in Table I.

TABLE I

pH conditions	Ferricyanide taken, *meq*	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
a	2·355	20·75	2·318	−0·037	−1·5
b	2·372	21·20	2·368	−0·004	−0·2
c	2·385	21·35	2·385	—	—
d	2·372	21·05	2·351	−0·021	−0·9
e	2·372	20·90	2·335	−0·037	−1·8
f	2·385	21·05	2·351	−0·034	−1·4
g	2·385	—	—	—	—

Remarks

When titration in acid medium is halfway completed, a green intermediate compound is formed which later disappears and has no influence on the final result. This compound, whose nature has not been defined, is more easily formed, the greater the ferricyanide concentration of the solution to be tested.

In alkaline medium, the precipitate formed at the beginning of the titration is of a slightly reddish-brown colour, probably due to the transitory formation of some HgO, or of mercury ferrocyanide or ferricyanide, together with metallic Hg. There is no formation of an intermediate green compound.

Potentiometric measurement indicates at the end-point, on the addition of a single drop of mercurous reagent, a jump in the potential that varies between 100 mV and 60 mV. This potential jump decreases with increasing concentration of the solution: for which reason the quantity of ferricyanide present should therefore not exceed 2·3 meq for each 100 ml of solution. The potential is rapidly stabilised, except near the end-point, where the reaction is rather slow, so that one minute is required after each addition of perchlorate. The potential change, even in the most unfavourable cases, is quite perceptible.

At the beginning of a titration in 0·5*N* NaOH, a drabbish-black precipitate is obtained, which does not disappear despite violent stirring. The reduction which occurs, although only slight, decreases the potential of the system in a variable manner, so that titration of ferricyanide under such conditions is not possible.

By a study of the Table I, it appears that the pH value at which the titration should be carried out must not be less than 3 or greater than 7. Tests were made varying the quantity of acetic acid from 1 to 20 ml, and similar results were obtained in all cases.

THE INFLUENCE OF THIOCYANATE CONCENTRATION

Procedure

At a fixed pH (acetic acid medium) the amount of thiocyanate was varied, operating as described above. The results obtained are shown in Table II.

Remarks

Where the thiocyanate concentration is less than or equal to 0·5*N*, and the amount of ferricyanide is more than 2 meq, an early appearance of a precipitate will cloud the solution. This first is dark green, becoming darker and changing to navy blue. The solution at the end-point is decolorised and has a yellow-greenish tint.

The potential jump is more clearly defined, the greater the thiocyanate concentration. From these results, the concentration used in subsequent work was 20 ml of 5*N* KSCN for each 100 ml of solution, representing a 1*N* concentration of SCN^-.

TABLE II

KSCN concentration	Ferricyanide taken, *meq*	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
0·25*N*	2·385	21·00	2·346	−0·039	−1·6
—	0·949	8·50	0·949	—	—
0·50*N*	2·385	21·15	2·362	−0·023	−1·0
—	0·949	8·45	0·943	−0·006	−0·6
0·75*N*	2·385	21·25	2·373	−0·012	−0·5
—	0·949	8·50	0·949	—	—
1·0*N*	2·372	21·15	2·362	−0·010	−0·4
—	0·949	8·50	0·949	—	—

INFLUENCE OF TIME

In the earlier experiments titration was carried out immediately after adding the KSCN to the mixture of ferricyanide and acetic acid. In order to check on a possible secondary reaction between the ferricyanide and the thiocyanate, variable lengths of time were allowed to pass between the addition of KSCN and titration.

TABLE III

Time interval	$Hg_2(ClO_4)_2$ 0·1117*N* *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
0	16·85	1·882	−0·002	−0·1
5 min	16·75	1·871	−0·013	−0·6
10 min	16·70	1·865	−0·019	−1·0
15 min	16·75	1·871	−0·013	−0·6
30 min	16·70	1·865	−0·019	−1·0
60 min	16·65	1·860	−0·024	−1·3
2 hr	16·65	1·860	−0·024	−1·3
4 hr	16·60	1·854	−0·030	−1·6
6 hr	16·55	1·849	−0·035	−1·9
12 hr	16·50	1·843	−0·041	−2·2
24 hr	16·35	1·826	−0·058	−3·1
48 hr	16·10	1·798	−0·086	−4·5

Procedure

In all cases 20 ml of 0·0942*N* ferricyanide, 5 ml of 5*N* acetic acid and 20 ml of 5*N* KSCN were used. The lapse of time between the addition of the thiocyanate and the beginning of the titration was measured. The results are shown in Table III.

Remarks

With passage of time a gradual reduction of ferricyanide takes place; acetic acid or neutral solutions change their yellow colour, and within two hours acquire a slight olive tint which, after six hours changes to green and within twenty-four hours to very dark green.

On the other hand, alkaline solutions allowed to stand for the same length of time do not change in appearance, although when titrated they also show a decrease in ferricyanide concentration.

The reduction to which the solutions are subject after a certain length of time offers no great inconvenience, as it can be overcome by adding the thiocyanate immediately before the beginning of the titration.

TABLE IV

Temperature °C	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
15°	16·85	1·882	−0·002	−0·1
20°	16·75	1·871	−0·013	−0·6
25°	16·65	1·860	−0·024	−1·3
30°	16·40	1·832	−0·052	−2·7
45°	16·00	1·787	−0·097	−5·2

INFLUENCE OF TEMPERATURE

In order to determine whether an increase of temperature favours the reaction between the ferricyanide and the thiocyanate, tests were made at various temperatures.

Procedure

The solutions were independently heated before being mixed. On mixing the solutions at temperatures over 25°, they became dark green in colour. The amount of ferricyanide used was 1·884 meq. The results are shown in Table IV.

Remarks

At temperatures over 20° there is an appreciable reduction of ferricyanide.

Other experiments in the present work were carried out at a temperature of 14° ± 1°.

RECOMMENDED METHOD

The solution, containing 0·4 to 3 meq. of ferricyanide is treated with 5 ml of acetic acid, diluted to 100 ml and treated with 5 ml of 5*N* acetic acid and 20 ml of 5*N* KSCN. It is immediately titrated at ordinary temperature (less than 20°) with mercurous perchlorate, the end-point being detected potentiometrically.

Specimen results are shown in Table V.

CONCLUSIONS

In the direct titration of ferricyanide with mercurous perchlorate in the presence of thiocyanate ion, it is found that:

1. The satisfactory pH range is from 3 to 7. Outside this range lower results are obtained, probably because part of the ferricyanide is reduced by the thiocyanate ion.

2. The lowest optimum concentration of thiocyanate ion is 1*M*, at which concentration the potential jump at the end-point is large and correct results are obtained. On decreasing the SCN^- concentration, the potential jump gradually becomes smaller.

3. A secondary reaction occurs between ferricyanide and thiocyanate. If the ferricyanide and the thiocyanate solutions are mixed immediately before the beginning of the titration this does not affect the results.

4. At temperatures over 20° there is an appreciable and immediate reduction of ferricyanide.

5. Direct mercurometric titration of ferricyanide in the presence of thiocyanate ion is possible in conditions which have been established. The standard deviation of the method is 0·26%.

TABLE V

Ferricyanide taken, *meq*	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
2·847	25·50	2·848	+0·001	+0·04
2·372	21·15	2·362	−0·010	−0·4
1·898	16·95	1·893	−0·005	−0·3
1·423	12·75	1·424	+0·001	+0·1
0·949	8·50	0·949	—	—
0·474	4·25	0·475	+0·001	+0·2

Zusammenfassung—Die direkte Titration von Ferricyanid-Ionen mit dem Merkurothiocyanat-System wird studiert und der Einfluss von pH, Thiocyanat-Konzentration, Zeit und Temperatur untersucht. Die Standard-Abweichung der vorgeschlagenen Methode beträgt 0,26%.

Résumé—On étudie le titrage direct des ions ferricyanhydriques par le système du thiocyanate-mercureux, compte tenu de l'influence du pH, de la concentration du thiocyanate, du temps, de la température. L'écart-type de la méthode proposée est 0,26 pour cent.

Resumen—Se estudia la volumetria directa del ion ferricianuro con el sistema mercurioso-sulfocianuro, viendose la influencia del pH, concentración de sulfocianuro, tiempo y temperatura. La desviación típica del método propuesto es 0,26%.

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Talanta, 1958, Vol. 1, pp. 310–313. Pergamon Press Ltd., London.

TITRIMETRIC DETERMINATION OF SMALL AMOUNTS OF COBALT WITH AN EQUIVALENT RATIO OF 1 : 37

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Summary—The nitrite content of the $KPb[Co(NO_2)_6]$ precipitate has been determined by reducing nitrite with excess of Fe^{II} salt. The excess of Fe^{II} or the Fe^{III} formed was then determined. With an equivalent ratio of 1 : 37 an exact method could thus be obtained for the titrimetric determination of small amounts of cobalt.

THE cobaltinitrite method is suitable for the titrimetric determination of both potassium and cobalt. The first requirement for the determination of cobalt is a well defined *ratio* of Co^{III} and NO_2^-. On the other hand for the determination of potassium a definite *composition* of precipitate is necessary. In the determination of cobalt where potassium is in great excess, the composition of precipitate is exactly $K_3[Co(NO_2)_6]$. In the determination of potassium the composition of precipitate varies with the conditions of precipitation, the ratio K : Na deviating more or less from the value of 2 : 1. Nevertheless, numerous methods have been elaborated for the determination of potassium but there are only a few procedures for cobalt. A plausible reason for this is that the analytical chemistry of potassium is not so extensive as that of cobalt. Among cobaltinitrite methods for the determination of cobalt, only one is generally applied, viz. permanganometric titration of nitrite content of the precipitate. In this method the equivalent weight of cobalt is 1/11 of the atomic weight, a ratio rendering possible the determination of small amounts of cobalt.

The present work aims to develop this method, but the nitrite content of the precipitate was determined by a method with an equivalent ratio of 1 : 37 which is very advantageous for the determination of small amounts of cobalt.

Recently, a procedure for the titrimetric determination of nitrate ions was reported.[1] In this procedure ferrous hydroxide reduces nitrate to ammonia in a slightly alkaline medium, in the presence of silver catalyst:

$$KNO_3 + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + KOH$$

The excess of the reducing agent is back-titrated.

The reduction of nitrite also takes place rapidly without a catalyst:

$$KNO_2 + 6Fe(OH)_2 + 5H_2O \rightarrow NH_3 + KOH + 6Fe(OH)_3$$

From these equations the equivalent ratios of nitrate and nitrite are 1/8 and 1/6 of the ionic weight, respectively.

Consequently, the determination of the nitrite content of the potassium cobaltinitrite precipitate by the above method, gives an unusually low equivalent weight of cobalt: for the reduction of six nitrites 36 equivalents, and for the reduction of Co^{III} 1 equivalent of Fe^{II} is consumed; thus the equivalent weight of cobalt is 1/37 of the atomic weight.

The precipitate $2K_3[Co(NO_2)_6]\cdot 3H_2O$ is slightly soluble in water; the solubility decreases in alcoholic or dilute acetic acid medium. The solubility of the precipitate can be further decreased if potassium is partly substituted by heavy metals.

Precipitates of $K_2Ag[Co(NO_2)_6]$ and $KPb[Co(NO_2)_6]$ have the lowest solubility, the latter being more soluble.[2] The ratio of K : heavy metal is in neither case stoichiometric,[3] but this is not important since the cobalt : nitrite ratio is constant. According to the view of a number of authors the most suitable reagent for potassium is silver cobaltinitrite. However, the $K_2Ag[Co(NO_2)_6]$ precipitate cannot be used for the determination of cobalt because silver ion also forms a precipitate with nitrite ion. Conversely, the great solubility of lead nitrite renders the precipitation of potassium lead cobaltinitrite possible.

The precipitation was therefore carried out in the presence of lead salt. This has also the advantage that the analysis of the precipitate can be performed after one hour, since the quantitative precipitation takes place much more rapidly than in the absence of lead.

The determinations were carried out on a $Co(NH_4)_2(SO_4)_2\cdot 6H_2O$ solution. Because of the large excess of lead, lead sulphate also precipitates. According to our observations, the co-precipitated lead sulphate influences the form of $KPb[Co(NO_2)_6]$ favourably and consequently the sedimentation and washability of the precipitate. Therefore, if none be originally present it is useful to add a small amount of sulphate ions. The presence of larger amounts of lead sulphate is, however, disadvantageous, because the precipitate becomes rather flocculent and its washing is difficult.

To separate the precipitate the solution was centrifuged. The precipitation was consequently carried out in centrifuge tubes. The precipitate was washed with saturated potassium sulphate solution in which the solubility of the precipitate is very low; in addition, the sulphate ions displace adsorbed nitrite ions.

After washing, the precipitate was treated with sodium hydroxide, which decomposes the complex:

$$KPb[Co(NO_2)_6] + 7NaOH \rightarrow KNO_2 + 5NaNO_2 + Co(OH)_3 + Na_2PbO_2 + 2H_2O$$

EXPERIMENTAL

Depending on the quantity of cobalt the determination was carried out in one of two ways. In the case of 0·3–3 mg of Co the excess of ferrous salt was back-titrated by 0·1*N* potassium permanganate. When the amount of cobalt is less than 0·3 mg, and using 0·01*N* potassium permanganate for the titration, the accuracy is not satisfactory. Therefore in such cases iodometric titration was used. The reduction was carried out by ferrous salt, and the Fe^{III} formed was determined iodometrically. 0·01*N* sodium thiosulphate was used as standard solution.

Solutions

Acetic acid: 96%
Lead acetate: 180 g $Pb(CH_3COO)_2\cdot 3H_2O$ per litre.
Potassium nitrite: 1000 g KNO_2 per litre.
Potassium sulphate: saturated solution.
Sodium hydroxide: 30% solution.
Ferrous sulphate: 135 g $FeSO_4\cdot 7H_2O$ and 30 ml conc. sulphuric acid per litre.*
Sulphuric acid: 30% solution.
Hydrochloric acid: 4*N*

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* In the case of a micro method it is essential that the Fe^{III} content of Fe^{II} is kept small, because in this case the Fe^{III} is measured. The presence of small amounts of Fe^{III} does not interfere, and the amount of Fe^{III} must be determined as a blank.

Potassium permanganate: 0·1N
Sodium thiosulphate: 0·01N

Procedure for determination of 0·3–3 mg Co

5 Ml of a neutral solution of cobalt salt are introduced into a centrifuge tube. If the solution does not originally contain sulphate ions, potassium sulphate should be added in a quantity such that the equivalent ratio of the sulphate ions to Co expected is about 1 : 4. To this solution 0·3 ml of acetic acid, 1 ml of lead acetate solution and finally 1 ml of potassium nitrite solution are added. After standing for an hour the mixture is centrifuged for 20 minutes at 3000 rpm. The precipitate is washed three times by 3 ml of saturated potassium sulphate solution. For each portion of the wash solution 10 minutes centrifugation is carried out. After washing, the precipitate is transferred with 90 ml of water into a 250-ml flask. After the addition of 10 ml of 30% NaOH the mixture is boiled for 10 minutes to remove air and to decompose the complex. Thereafter, keeping the mixture boiling, 10 ml of ferrous sulphate solution are added. A mouthpiece is then adjusted in the neck of the flask[1] to avoid air passing easily into the flask, and to inhibit too rapid evaporation of the solution.

TABLE I.

Co taken *mg*	Consumption of 0·1N $KMnO_4$ *ml*	Co found *mg*	Error %
2·872	17·99	2·866	−0·2
	17·92	2·855	−0·6
	17·84	2·842	−1·0
1·436	8·99	1·432	−0·3
	9·04	1·440	+0·3
0·574	3·60	0·573	−0·2
	3·58	0·570	−0·7
Co taken *μg*	**Consumption of 0·01N $Na_2S_2O_3$** *ml*	**Co found** *μg*	**Error** %
295·3	18·75	298·8	+1·2
	17·77	283·1	−4·1
	17·80	283·6	−4·0
147·6	8·90	141·8	−3·9
	9·07	144·4	−2·2
	8·88	141·5	−4·1
103·3	6·14	97·8	−5·3
	6·63	108·1	+4·6
44·3	2·65	42·2	−4·7
	2·80	44·6	+0·7
	2·70	43·1	−2·7

The time for complete reduction is 3–6 minutes. (The odour of ammonia vanishes.) Then 40 ml of sulphuric acid are carefully added to the flask through the mouthpiece. When the precipitate has completely dissolved the boiling should be stopped, and after cooling, the unoxidized ferrous salt is titrated by 0·1*N* $KMnO_4$.

A blank determination must also be carried out. The difference between the blank and the sample gives the volume of 0·1*N* $KMnO_4$ actually used. 1 ml 0·1*N* $KMnO_4$ ≡ 0·1593 mg cobalt.

Procedure for determination of 30–300 μg Co

To 2 ml of neutralized test solution 0·2 ml of acetic acid, 0·5 ml of lead acetate solution and 0·5 ml of potassium nitrite solution are added. If the solution does not contain sulphate, potassium sulphate must also be added as before. The contents of the centrifuge tube are stirred and after standing for an hour, are centrifuged for 10 minutes. The precipitate is washed three times by 3 ml of potassium sulphate solution, and each portion is centrifuged for 5 minutes. The precipitate is transferred to a 100-ml flask with 25 ml water followed by 5 ml of 30% sodium hydroxide; after 5 minutes boiling, 5 ml of ferrous sulphate solution are added. After 5 minutes further boiling, 20 ml of 4*N* hydrochloric acid are added to the flask. A few pieces of marble are then placed in the solution. After cooling the solution to 40–50°, and addition of 5 g* potassium iodide, the iodine formed is titrated by 0·01*N* thiosulphate.

In this method a blank is also required. 1 ml 0·01*N* $Na_2S_2O_3$ ≡ 15·93 μg cobalt.

The results of some titrations are summarized in Table I.

As Table I shows the error of the determination by the macro method is about ±1%, and that of the micro method about ±5%. The micro method makes the determination of less then 40 μg Co possible, but in this case the error increases with decreasing amount of Co.

Acknowledgement—The authors wish to express their gratitude to Prof. Dr. Z. G. Szabó for his kindly interest and valuable discussion.

Zusammenfassung—Der Nitritgehalt des $KPb[Co(NO_2)_6]$-Niederschlages wird über die Reduktion des Nitrits mit einem Uberschuss von Fe(II)-Salz bestimmt, wobei der Uberschuss von Fe(II) oder das gebildete Fe(III) erfasst wird. So konnte bei einem Aquivalent-Verhältnis von 1 : 37 eine genaue Methode für die volumetrische Bestimmung kleiner Mengen von Kobalt erhalten werden.

Résumé—La teneur en nitrite du précipité $KPb[Co(NO_2)_6]$ a été déterminée par la réduction du nitrate par un excès de Fe(II). On a effectué ensuite le dosage de l'excès de Fe(II) ou du Fe(III) formé. Le rapport équivalent 1 : 37 a permis d'obtenir une méthode exacte pour le dosage volumétrique de petites quantités de cobalt.

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* The completion of the reaction: $Fe^{3+} + I^- \rightleftharpoons Fe^{2+} + 1/2\ I_2$ in the forward direction requires a large amount of KI because of the large excess of Fe^{II}.

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TITRIMETRIC DETERMINATION OF ALUMINIUM WITH ETHYLENEDIAMINETETRA-ACETIC ACID IN THE PRESENCE OF IRON, COPPER, TITANIUM, MANGANESE, CALCIUM, MAGNESIUM AND PHOSPHATE

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(*Received* 2 *April* 1958)

Summary—The authors have developed a rapid and accurate titrimetric method for the determination of 5–15 mg of aluminium with Complexone-III in the presence of iron, copper, titanium, manganese, calcium, magnesium and phosphate.

INTRODUCTION

IN THE research undertaken for the enrichment of certain raw materials such as manganese ores, clays and feldspars in Israel Mining Industries Laboratories, a rapid method was needed for the determination of aluminium in the above mentioned materials.

In the literature some complexometric methods were found for the determination of aluminium when present alone,[1–12] and also for a few cases when it is present together with other ions[13–16] but here either the analytical results were insufficiently accurate or the methods were complicated. It was therefore decided to essay to develop a complexometric method for the determination of aluminium in the presence of iron, copper, titanium, manganese, calcium, magnesium and phosphate.

The research was done in several steps: in the first one, the optimum conditions for the determination of aluminium, when present alone, were determined, taking into account the methods found in the literature and their experimental verification; in the next step, a method for the determination of aluminium in the presence of iron, copper and phosphate was elaborated; in the third step, a cation-exchange method was established for the separation of aluminium from titanium, manganese, calcium and magnesium; a general procedure was then developed for the determination of aluminium in the presence of all the above mentioned ions, considering the minimum time requirement; finally the maximum allowable quantity of the above mentioned ions that can be present, without impairing the accuracy of the aluminium determination, was determined. The results of this research are given below.

PART I: THE DETERMINATION OF ALUMINIUM WHEN PRESENT ALONE

Reagents and standard solutions

1. *Aluminium sulphate solutions:* Aluminium sulphate was dissolved in distilled water and the solution was then made distinctly acidic with hydrochloric acid (around $3N$) to prevent hydrolysis on long standing. From this rather concentrated solution (about 10 mg aluminium per ml) lower concentrations were prepared by dilution after standardisation.

The standardisation was done by two methods: (*a*) Gravimetrically by ammonia precipitation and ignition to the oxide[17] and (*b*) Gravimetrically with 8-hydroxyquinoline.[18] The mean value was 9·026 mg Al/ml.

2. 0·01*M* *solution of Complexone-III*: (the disodium salt of ethylenediaminetetra-acetic acid, dihydrate, abbreviated as EDTA): prepared by dissolving 3·722 g of Complexone-III in twice-distilled water and making the total volume up to one litre. The solution can be standardised against either 0·01*M* solution of magnesium chloride or 0·01*M* solution of zinc chloride, using Eriochrome Black T as indicator. Accurate concentrations of either may be prepared from magnesium and zinc metal respectively, as primary standards.

3. 0·01*M* *solution of zinc chloride:* prepared by dissolving 1·363 g of anhydrous zinc chloride in twice distilled water and making the total volume up to one litre.

Using the above 0·01*M* solution of EDTA, we standardised the 0·01*M* solution of zinc chloride at pH 6·7–7·3 as follows:—Into an Erlenmeyer flask of 250-ml capacity 25 ml of 0·01*M* solution of EDTA, 10 ml of ammonium acetate solution 10%, a little Eriochrome Black T indicator and 80–100 ml of distilled water were introduced. The solution was then titrated with the 0·01*M* zinc chloride solution till the colour of the indicator changed from blue to bluish-violet. The colour change is sharp and easily seen on addition of one drop of the titrant.

The factor for the same zinc chloride solution is different when the titration is done at pH 6·7–7·3 and at pH 10. Since the aluminium will be determined by the back-titration of the excess EDTA at pH 6·7–7·3, the standardisation of the zinc chloride solution must also be done at pH 6·7–7·3.

4. *Eriochrome Black T indicator:* 0·1 g triturated with 10 g of sodium chloride.
5. *Methyl red indicator:* 0·1 g dissolved in 100 ml of ethanol 50%.
6. *Ammonium acetate solution:* 10%.
7. *Ammonia solution:* 5%.

Procedure "A" for the determination of aluminium

The slightly acidic solution of the sample, containing 5–10 mg of aluminium in a volume of 5–10 ml, is introduced into a Pyrex 250-ml Erlenmeyer flask. A known excess of 0·01*M* solution of EDTA is added, followed by one drop of methyl red indicator. Ammonia solution 5% is then added with shaking, till the solution turns from red to yellow. The solution is then boiled for three minutes, cooled to below 10°, and 10 ml of ammonium acetate solution 10% are added, followed by a little Eriochrome Black T. The excess of EDTA is now back titrated with 0·01*M* solution of zinc chloride till the colour of the indicator turns from blue to bluish-violet.

Calculation of the results

$$A = (BC - DE)(0{\cdot}2697)$$

where: A = mg Al found.
B = ml 0·01*M* solution of EDTA added.
C = the factor of the EDTA solution.
D = 0·01*M* solution of $ZnCl_2$ required for the back-titration.
E = the factor of the $ZnCl_2$ solution.
0·2697 = the factor for aluminium.

Table I shows some typical results obtained according to the above mentioned method.

Conclusion

As indicated by Table I, the results are accurate.

Discussion

1. In the light of the literature data and the experimental checks which we have made on few complexometric methods for the determination of aluminium, using various indicators such as Eriochrome Black T,[1,7] Chromazurol S,[6] dithizone,[10] ferro-ferricyanide + benzidine,[14] 1-(2-pyridylazo)-2-naphthol (PAN),[15] salicylic acid,[4] to mention but a few, we chose Eriochrome Black T as the indicator in our research. Schwarzenbach and Biedermann[19] were the first to suggest the use of this indicator for complexometric titrations. In spite of the interference of aluminium when using Eriochrome Black T,[20] we concluded, nevertheless, that it is the most suitable for our purpose.

2. Boiling the solution with excess EDTA is necessary if we have to chelate the aluminium quantitatively.

3. It is necessary to cool below 10° when titrating the excess EDTA in order that the end-point be reversible. (Table I, Exp. 5–7).

4. Aluminium chelate is unstable at pH 10 in the absence of excess free EDTA (as it is the case at the end-point), so that during the back-titration of the excess EDTA the aluminium chelate decomposes to yield free EDTA, causing the red colour to turn to blue. Although Amin[7] suggests that the back-titration should be done very quickly, nevertheless, a large error was obtained, even through a quick titration, since the colour returned after a few seconds. We decided, therefore, to titrate the excess of EDTA at pH 6·7–7·3 instead of at pH 10, since at the former pH value the aluminium chelate is more stable.

TABLE I. DETERMINATION OF ALUMINIUM WITH EDTA ACCORDING TO PROCEDURE "A", UNDER VARIOUS CONDITIONS

Exp. no.	Time of boiling with excess of EDTA *minutes*	Temperature during the back-titration of EDTA °C	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %	Notes
1	3	25	4·513	4·526	+0·013	+0·3	*
2	5	25	4·513	4·520	+0·007	+0·2	*
3	15	25	4·513	4·509	−0·004	−0·1	*
4	15	25	4·513	4·522	+0·009	+0·2	*
5	15	0	4·513	4·520	+0·007	+0·2	†
6	3	0	4·513	4·525	+0·012	+0·3	†
7	3	10	4·513	4·522	+0·009	+0·2	†

* Irreversible end-point.
† Reversible end-point.

Although accurate results were obtained according to procedure "A", the method is a back-titration one and any metal ion chelated by EDTA at pH 6·7–7·3, such as ferric or cupric ion, would give a high result for aluminium. In other words this procedure is applicable only for pure aluminium compounds.

It was thought therefore, that if a reagent were found that could liberate, under our conditions, free EDTA from its chelate with aluminium but had no effect on the chelates of other metals, then this liberated free EDTA, which is proportional to the quantity of aluminium in the sample, might be estimated through simple titration with a standard solution of zinc. The applications of the method would thus be more general.

Triethanolamine, a known masking agent for aluminium in complexometric titrations,[21,22] was tried. We also tested oxalate, tartrate and citrate. It was found that none of these compounds liberate EDTA from the aluminium chelate at pH 6·7–7·3. Sodium fluoride was then examined for this purpose.

Sajo[14] determines aluminium, after the addition of excess EDTA and back-titration of the excess, by the addition of sodium fluoride and the titration of the EDTA, liberated from the aluminium chelate, at pH 5–6·7 with a standard solution of zinc, using ferro-ferricyanide + benzidine as indicator.

In order to examine the use of sodium fluoride under our conditions, procedure "A" was modified into procedure "B".

Procedure "B" for the determination of aluminium

To the bluish-violet solution, obtained after back-titration of the excess EDTA, 1·5 g of sodium fluoride is added, the solution is kept at 90° for 20 minutes, cooled to below 10°, and the liberated EDTA is titrated with 0·01M standard solution of zinc to the same end-point of Eriochrome Black T.

If this liberation of EDTA is quantitative, then the quantity of the zinc solution used will be a measure of the quantity of aluminium in the sample. Table II shows some of the results obtained according to this procedure.

Conclusion

As indicated by Table II, the results are accurate. At pH 6·7–7·3 the liberation of EDTA from the aluminium chelate by sodium fluoride is quantitative. This offers an indirect method for the determination of aluminium.

Note: It should be noted that the addition of sodium fluoride does not alter the pH of the solution (pH 6·7–7·3). This is important, since any change in the pH of the solution after the back-titration of the excess EDTA affects the accuracy of the method.

TABLE II. DETERMINATION OF ALUMINIUM WITH EDTA ACCORDING TO PROCEDURE "B"

Exp. No.	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	4·513	4·509	−0·004	−0·1
2	4·513	4·524	+0·011	+0·2
3	4·513	4·501	−0·012	−0·3
4	9·026	9·048	+0·022	+0·2
5	9·026	9·007	−0·019	−0·2

The next step was to investigate the behaviour of iron in the determination of aluminium, according to procedure "B".

The behaviour of iron in the determination of aluminium, according to procedure "B"

Early experiments showed that even less than 0·2 mg of ferric iron interferes, since it forms a very stable chelate (brownish-black precipitate) with Eriochrome Black T. This interference could not be prevented by adding fluoride, oxalate, tartrate, citrate, etc., as masking agents. It was thought possible to get rid of the interference of ferric iron by reducing the former to the bivalent state. Various reducing agents, such as ascorbic acid, hydrazine sulphate, hydroxylamine hydrochloride and sulphite were tried at pH 6·7–7·3. But, when excess EDTA was added, the solution slowly turned yellow, indicating air oxidation and formation of ferric chelate, even in the presence of a large excess of the reducing agent. Finally it was thought that an alcoholic medium might alter the formation constant of ferric iron with Eriochrome Black T. It was found that this chelate is so weak in the presence of alcohol that the interference of iron is eliminated. By conducting the titration in alcoholic medium, the optimum condition for a sharp colour change was found to correspond to about 40% of alcohol in water. No difference was found by using *iso*propyl alcohol instead of ethyl alcohol. The back-titration method according to procedure "A" was now applied to a pure standard solution of iron. (Table III, Exp. 1). The determination was then repeated adding 1·5 g of sodium fluoride to the solution after boiling with excess EDTA, *i.e.* before proceeding to determine aluminium according to procedure "B" (Table III, Exp. 2). The results obtained are shown in Table III.

Conclusions

1. Ferric iron behaves like aluminium in that it is quantitatively chelated by EDTA and therefore aluminium cannot be determined according to procedure "A" in presence of iron, in which case procedure "B" should be followed.
2. Ferric-EDTA chelate, unlike the aluminium chelate, is not affected by fluoride, since it is more stable than the ferric fluoride complex; thus ferric iron does not interfere in the determination of aluminium according to procedure "B".

TABLE III. DETERMINATION OF FERRIC IRON ACCORDING TO PROCEDURES "A" AND "B" FOR DETERMINATION OF ALUMINIUM

Proc.	Exp. No.	Conc. of alcohol used %	Temp. at which the titration was done °C	Fe^{3+} present *mg*	Fe^{3+} found *mg*	Diff. *mg*	Rel. error %	Notes
A	1	40	8–10	5·819	5·807	−0·012	−0·2	reversible end-point
B	2	40	8–10	5·819	5·830	+0·011	+0·2	

PART II: DETERMINATION OF ALUMINIUM IN THE PRESENCE OF IRON, COPPER AND PHOSPHATE

Reagents and standard solutions

1. *0·05M solution of Complexone-III (EDTA)*: prepared by dissolving 18·610 g of Complexone-III in twice distilled water and making the total volume up to one litre.
2. *0·01M solution of Complexone-III (EDTA):* (See Part I, reagent no. 2).
3. *0·05M solution of zinc chloride:* prepared by dissolving 6·815 g of anhydrous zinc chloride in distilled water and making the total volume up to one litre.
4. *0·01M solution of zinc chloride*: (See Part I, reagent no. 3).
5. *Ammonia solution:* 5%.
6. *Ammonium acetate solution:* 10%.
7. *Sodium fluoride.*
8. *Methyl red indicator.* (See Part I, reagent no. 5).
9. *Eriochrome Black T indicator.* (See Part I, reagent no. 4).

Procedure for the determination of aluminium in the presence of iron, copper and phosphate

The solution of the sample, in a volume of around 5 ml and containing not more than 15 mg of aluminium, is introduced into a Pyrex 250-ml Erlenmeyer flask. From a burette 0·05*M* solution of EDTA is introduced in such an amount as to be in excess to that required to chelate the aluminium, iron and copper in the sample. A very large excess should be avoided. 1–2 Drops of methyl red indicator are added. With distilled water the total volume is then brought to about 20 ml, followed by the dropwise addition of ammonia solution 5%, with constant shaking, until the colour of the indicator turns from red to yellow. The solution is then boiled for three minutes, cooled, 10 ml of ammonium acetate 10% are added, followed by 25 ml of *iso*propyl alcohol, and distilled water to make the total volume up to approximately 60–65 ml. The solution is then cooled in ice-water to below 10° and Eriochrome Black T is added in such an amount as to impart on shaking the first perceptible blue colour to the solution. The flask is removed from ice-water and titrated from a burette with 0·05*M* solution of zinc chloride until the colour turns red. Now 1 or 2 drops of 0·05*M* solution of EDTA are added just to get back the blue colour and then the solution is titrated with 0·01*M* solution of zinc chloride until a bluish-violet end-point is obtained. The colour should persist for one minute while the solution is cooled in ice-water during standing. 1·5 g of sodium fluoride are now added, the solution is heated to near boiling (the boiling temperature of the solution is around 80°) and let stand on the hot plate for 20 minutes so as to keep it near the boiling point. The solution is then cooled to below 10° and titrated with 0·01*M* solution of zinc chloride to a persistent bluish-violet colour. The time required for one determination is 60 minutes approximately.

Calculation of the results

$$A = n \times f \times 0{\cdot}2697$$

where: A = mg Al found.
n = ml 0·01*M* solution of zinc chloride.
f = the factor of the zinc chloride solution.
0·2697 = the factor for aluminium.

Tables IV, V and VI show some typical results obtained, according to this method, for aluminium alone and for aluminium in the presence of iron, copper and phosphate.

Table IV. Determination of aluminium with EDTA, when present alone

Exp. No.	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	0·4513	0·4540	+0·0027	+0·6
2	0·9026	0·8990	−0·0036	−0·4
3	2·256	2·255	−0·001	—
4	4·513	4·525	+0·012	+0·3
5	9·026	9·048	+0·022	+0·2

Conclusion

The results for aluminium alone are accurate, especially in the determination of more than one mg of aluminium. (Table IV.)

Table V. Determination of aluminium with EDTA, in the presence of iron

Exp. No.	Fe^{3+} present *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	0·582	0·4513	0·4500	−0·0013	−0·3
2	4·656	0·4513	0·4550	+0·0037	+0·8
3	4·656	2·256	2·267	+0·011	+0·5
4	5·820	2·256	2·265	+0·009	+0·4
5	4·656	4·513	4·527	+0·014	+0·3
6	5·820	4·513	4·501	−0·012	−0·3
7	4·656	9·026	9·048	+0·022	+0·2
8	5·820	9·026	9·024	−0·002	—

The determination of aluminium in the presence of iron is accurate. (Table V.)

Notes: 1. More than 5 mg of iron make the titration difficult due to the yellow colour of iron chelate and also to the effect of iron on the indicator. For example, various shades of olive-green to green were obtained which made the titration of EDTA with the zinc chloride solution difficult.

Table VI. Determination of aluminium with EDTA in the presence of copper

Exp. No.	Cu^{2+} present *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	0·500	0·4513	0·4527	+0·0014	+0·3
2	4·000	0·4513	0·4555	+0·0042	+0·9
3	3·000	2·256	2·242	−0·014	−0·6
4	4·000	2·256	2·270	+0·014	+0·6
5	3·000	4·513	4·526	+0·013	+0·3
6	4·000	4·513	4·527	+0·014	+0·3
7	3·000	9·026	9·007	−0·019	−0·2
8	4·000	9·026	9·053	+0·027	+0·3

2. Iron was added as a solution of ferric chloride acidified with hydrochloric acid 5 %.

The determination of aluminium in the presence of copper is accurate. (Table VI).

Notes: 1. More than 4 mg of copper make the titration difficult due to the blue colour of copper chelate and also to the effect of copper on the indicator.

2. Copper was added as a solution of copper nitrate acidified with nitric acid 1 %.

TABLE VII. DETERMINATION OF ALUMINIUM WITH EDTA IN THE PRESENCE OF PHOSPHATE

Exp. No.	P_2O_5 present *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	20	0·4513	0·4540	+0·0027	+0·6
2	50	0·4513	0·4558	+0·0045	+1·0
3	20	2·256	2·249	−0·007	−0·3
4	50	2·256	2·265	+0·009	+0·4
5	20	4·513	4·525	+0·012	+0·3
6	50	4·513	4·527	+0·014	+0·3
7	20	9·026	9·048	+0·022	+0·2
8	50	9·026	9·007	−0·019	−0·2

The determination of aluminium in the presence of phosphate is accurate. (Table VII.)

Notes: 1. Phosphate does not interfere in the determination of aluminium, provided only 1–2 drops of 0·05*M* solution of zinc chloride are added in excess during the titration of the excess EDTA. When more than a few drops of the zinc chloride solution are added, zinc phosphate may precipitate, which impairs the sharpness of the end-point.

2. Phosphate was added in the form of potassium dihydrogen phosphate and calculated as P_2O_5.

Discussion

(1) *Acidity of sample:* The solution of the sample should not contain excessive amounts of free acids (*e.g.* not more than 5 ml conc. HCl). Free acids give rise to an equivalent amount of ammonium salts during the ammonia-neutralisation step. These salts, being a buffer on the acidic side of the pH scale, counteract the buffer action of ammonium acetate and impair the sharpness of the Eriochrome end-point. Table VIII shows the effect of the pH on the accuracy of the aluminium determination and the sharpness of the end-point.

TABLE VIII. EFFECT OF pH ON THE ACCURACY OF THE ALUMINIUM DETERMINATION AND ON THE SHARPNESS OF THE END-POINT

Exp. No.	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %	pH	Notes
1	4·513	4·500	−0·013	−0·3	6·0	end-point not sharp
2	4·513	4·519	+0·006	+0·1	6·7	end-point sharp
3	4·513	4·524	+0·011	+0·2	7·0	end-point sharp
4	4·513	4·527	+0·014	+0·3	7·3	end-point sharp
5	4·513	4·420	−0·093	−2	8·0	end-point sharp

Conclusion: The pH has no effect on the accuracy of the aluminium determination within the range 6·7–7·3.

(2) *Heating period with sodium fluoride:* The solution should be heated with 1·5 g of sodium fluoride for 20 minutes in order to liberate the EDTA quantitatively from the aluminium chelate at

pH 6·7–7·3. Table IX indicates the effect of the heating period and of the amount of sodium fluoride on the accuracy of the determination.

TABLE IX. EFFECT OF HEATING PERIOD AND AMOUNT OF SODIUM FLUORIDE ON THE ACCURACY OF THE ALUMINIUM DETERMINATION

Exp. No.	Heating period *minutes*	Sodium fluoride added *g*	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %
1	5	1·5	4·513	4·462	−0·051	−1·1
2	10	1·5	4·513	4·490	−0·023	−0·5
3	20	0·5	4·513	4·422	−0·091	−2·0
4	20	1·0	4·513	4·494	−0·019	−0·4
5	20	1·5	4·513	4·522	+0·009	+0·2
6	10	1·5	9·026	8·986	−0·040	−0·4
7	20	0·5	9·026	8·901	−0·125	−1·4
8	20	1·5	9·026	9·032	+0·006	+0·1

In the Schwarzenbach table for the log of the formation constants of chelates of metals with EDTA,[23] ferric and cupric ions precede aluminium. This indicates that the two former ions are chelated before aluminium when excess EDTA is introduced into a solution of these three ions. Therefore, the back-titration method for the determination of aluminium—according to procedure "A"—is not applicable in the presence of iron and copper. In such a case the fluoride method, *i.e.* procedure "B" for the determination of aluminium by an indirect method, is applicable.

PART III: THE DEVELOPMENT OF A CATION-EXCHANGE METHOD FOR THE DETERMINATION OF ALUMINIUM IN THE PRESENCE OF TITANIUM, MANGANESE, CALCIUM AND MAGNESIUM

The interference of titanium, manganese, calcium and magnesium in the determination of aluminium

We found that titanium, manganese, calcium and magnesium seriously interfere with the determination of aluminium, according to the procedure given in Part II. This interference is due to the fact that at pH 6·7–7·3 these cations are partially chelated by EDTA giving rise to an equilibrium condition:

$$\text{metal ion} + \text{free EDTA} \rightleftharpoons \text{metal chelate}$$

This equilibrium condition exists when the excess of EDTA is titrated with zinc chloride solution, whereas the metal chelate does not dissociate completely, and hence the indistinct end-point. At the stage where sodium fluoride is added and the solution is heated to liberate EDTA from the aluminium chelate, metal fluorides are obtained and free EDTA is liberated giving rise to high results for aluminium:

$$\text{EDTA-chelate} + \text{NaF} \rightarrow \text{cation fluoride} + \text{EDTA-Na}$$

The interference of manganese, titanium, calcium and magnesium was observed when the excess EDTA, added to the solution containing aluminium plus one of these cations, was titrated with zinc solution. The end-point was not sharp and the bluish-violet colour turned blue within a few seconds. The return of the colour was due to the dissociation of the metal chelate when nearing the end-point, as the excess of free EDTA was removed during the titration with zinc chloride solution.

Several known complexing agents were tried in order to mask these interfering cations, but without success. An attempt was made to eliminate these cations with the aid of a cation-exchange resin, and three resins were systematically studied for this purpose: Amberlite IR-100, Amberlite IR-120 and Dowex-50. Their behaviour towards free EDTA and aluminium chelate was investigated. The results are given in tables X, XI and XII.

TABLE X. THE BEHAVIOUR OF FREE EDTA TOWARDS SOME CATION-EXCHANGE RESINS

Exp. No.	Type of resin	Cycle form	0·01*M* EDTA passed through the resin *ml*	0·01*M* EDTA found in the effluent *ml*	pH of the effluent
1	Amberlite IR-100	H	25	0·5	2·2
2	Amberlite IR-120	H	25	2·1	2·5
3	Dowex-50	H	25	0·7	2·3
4	Amberlite IR-100	Na	25	24·5	7·4
5	Amberlite IR-120	Na	25	24·6	7·5
6	Dowex-50	Na	25	24·6	7·5
7	Amberlite-IR-100	NH_4	25	24·6	5·7
8	Amberlite IR-120	NH_4	25	24·6	5·5
9	Dowex-50	NH_4	25	24·2	5·6

CONCLUSIONS

1. The resins in the hydrogen cycle cannot be used for two reasons: (*a*) They retain free EDTA (Exp. 1, 2, 3), (*b*) Free acids are liberated during the ion exchange and the consequent lowering of pH interferes with the determination of aluminium. (Table X.)

2. In comparison with the acid cycle, the retention of EDTA by the resins in the sodium or ammonium cycle is very low. (Table X.)

TABLE XI. THE BEHAVIOUR OF Al-EDTA TOWARDS CATION-EXCHANGE RESINS

Exp. No.	Type of resin	Cycle form	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %	pH of the effluent
1	Amberlite IR-100	H	4·513	2·360	2·153	−47	less than 1
2	Amberlite IR-120	H	4·513	2·200	2·313	−51	less than 1
3	Dowex-50	H	4·513	2·592	1·921	−43	less than 1

The resins in the hydrogen cycle retain Al-EDTA. (Table XI.)

Note: The aluminium was determined in the effluent according to the procedure given in Part II.

Since free EDTA is not retained by the resins in the sodium or ammonium cycle, our next step was to find out the behaviour of Al-EDTA towards these resins. This was tried as follows: known amounts of aluminium were treated with excess EDTA. After adjusting the pH with ammonia to the yellow colour of methyl orange, the solution was boiled for three minutes, cooled and passed through the resin. Aluminium was determined in the effluent after concentration to about 20–30 ml, following the procedure given in Part II. The results are given in Table XII.

Conclusion

Al-EDTA passes quantitatively through the cation-exchange resins in the cycle-form sodium or ammonium (Table XII).

Taking into account the presence of manganese, titanium, calcium and magnesium in the sample to be analysed, the procedure to be followed for the determination of aluminium in the presence of these cations should be to add EDTA in slight excess to that required for aluminium only and to pass the solution through resin. These interfering cations are retained, while Al-EDTA passes through into the effluent.

TABLE XII. THE BEHAVIOUR OF Al-EDTA TOWARDS CATION-EXCHANGE RESINS IN THE CYCLE FORM SODIUM OR AMMONIUM

Exp. No.	Type of resin	Cycle form	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	Amberlite IR-100	Na	0·4513	0·4527	+0·0014	+0·3
2	Amberlite IR-100	Na	2·256	2·265	+0·009	+0·4
3	Amberlite IR-100	Na	4·513	4·526	+0·013	+0·3
4	Amberlite IR-100	NH_4	2·256	2·249	−0·007	−0·3
5	Amberlite IR-100	NH_4	4·513	4·526	+0·013	+0·3
6	Amberlite IR-120	Na	2·256	2·242	−0·014	−0·6
7	Amberlite IR-120	Na	4·513	4·526	+0·013	+0·3
8	Amberlite IR-120	NH_4	2·256	2·270	+0·014	+0·6
9	Amberlite IR-120	NH_4	4·513	4·526	+0·013	+0·3
10	Dowex-50	Na	2·256	2·267	+0·011	+0·5
11	Dowex-50	Na	4·513	4·526	+0·013	+0·3
12	Dowex-50	NH_4	2·256	2·267	+0·011	+0·5
13	Dowex-50	NH_4	4·513	4·501	−0·012	−0·3

It was found essential not to add a large excess of EDTA over that required to chelate aluminium; otherwise the interfering cations—manganese, calcium, titanium and magnesium—will pass through into the effluent. This is due to the fact that the degree of dissociation of the chelates of these metals is higher in the absence of a large excess of free EDTA and as a result, the cations of the interfering metals are exchanged by the sodium or ammonium ions from the resin.

A spot test was then devised for the detection of a slight excess of free EDTA, which is a modification of the spot test described by Feigl[24] for the detection of zinc with dithizone.

Spot test for free EDTA

This test must indicate the presence of free EDTA at the point where enough has been added to chelate only aluminium, copper and iron in the presence of the above mentioned cations. The pH at which this test should be performed must not exceed 4, since manganese, calcium, magnesium and titanium are appreciably chelated above this pH value.

According to Feigl,[24] the spot test for the detection of zinc is performed by mixing in a small test tube a drop of the solution to be tested with a drop of dithizone solution in carbon tetrachloride. In the presence of zinc the green colour of dithizone turns red due to the formation of zinc dithizonate chelate.

The mechanism of our spot test reaction for EDTA is as follows: a drop of the solution to be tested is mixed on a spot plate with zinc dithizonate solution (red) at pH 3·4–4·0. If free EDTA is present, the colour turns green owing to the dithizone liberated from the zinc dithizonate. The zinc dithizonate solution is composed of a buffer of pH 2·6 (HCl plus potassium biphthalate)—according to Tomiček[25]—to which traces of zinc and a certain amount of acetone and carbon tetrachloride are added. The use of carbon tetrachloride only as a solvent for dithizone does not permit enough contact between the aqueous solution to be tested and the carbon tetrachloride solution of dithizone, thus the addition of acetone is necessary. The pH of the buffer is raised to 3·8 after the addition of the organic solvents. It was found that dithizone functions well at this pH and 0·5 μg of free EDTA can be detected in one drop of the solution to be tested. It was also found that the presence of carbon tetrachloride increases the sensitivity of the test. Since solutions of dithizone are unstable at room temperature, dithizone can be added to the buffer when the spot test is to be performed. As its concentration in the buffer is low (0·005%) dithizone is added to the buffer after being mixed with solid sodium chloride (1% mixture).

Copper interferes with the spot test for EDTA. Since copper dithizonate is more stable than copper-EDTA, dithizone will chelate copper and thus free EDTA cannot be indicated in the presence of copper; colour change to green could not be observed. It was observed, however, that the incorporation of a little sodium diethyldithiocarbamate in the dithizone-sodium chloride mixture, which is added to the buffer solution, will obviate this difficulty. Copper will form a chelate with the carbamate which is more stable than the copper dithizonate. Thus the interference of copper in the spot test for free EDTA is eliminated.

The cation-exchange resin used

Since the pH of the effluent for the resin in the ammonium form is lower than that in the sodium form (Table X, Exps. 4–9) the former is more suitable. This is because the dissociation of manganese-, titanium-, calcium- or magnesium-EDTA is higher at lower pH values and these cations are more completely eliminated by the resin. Amberlite IR-120 was used in all subsequent experiments.

PART IV: THE DETERMINATION OF ALUMINIUM IN THE PRESENCE OF IRON, COPPER, MANGANESE, TITANIUM, CALCIUM, MAGNESIUM AND PHOSPHATE

Reagents and standard solutions

1. *0·05M solution of Complexone-III (EDTA):* prepared by dissolving 18·610 g of Complexone-III in 0·1N solution of NaOH and making the total volume up to one litre with 0·1N NaOH.
2. *0·01M solution of Complexone-III (EDTA):* (See Part I, reagent No. 2).
3. *Spot test buffer solution:* prepared by mixing 33 ml of 0·2M HCl with 50 ml of 0·2M potassium biphthalate followed by the addition of 100 ml of acetone, 3 ml of carbon tetrachloride and 0·5 ml of 0·01M solution of zinc chloride.
4. *Dithizone indicator:* 0·1 g dithizone and 0·1 g sodium diethyldithiocarbamate are intimately ground together in a mortar with 10 g of sodium chloride.
5. *Ammonium chloride solution:* 15%.
6. *Cation-exchange resin:* Amberlite IR-120 was used in a column 30 cm long and 2 cm in diameter. The resin was regenerated by passing through about 300 ml of ammonium chloride solution 15% at a flow rate of 10 ml per minute, followed by washing with equal volume of water at a flow rate of 40 ml per minute. The regeneration is done after passing through solutions of samples ten times.
7. *Ammonia solution:* 1%.
8. *Ammonia solution:* 5%.
9. *Methyl orange indicator:* 0·05% solution in water.
10. *Isopropanol:* The reagent should be tested before use as follows: 100 ml of water, 35 ml of the *iso*propanol, 10 ml ammonium acetate 10%, 1 ml triethanolamine 10% and Eriochrome Black T indicator are introduced into a 250-ml Erlenmeyer flask. The solution is titrated with 0·01M solution of EDTA to a blue end-point and then titrated with 0·01M solution of zinc sulphate to a bluish-violet colour. The colour change in these two titrations should be sharp and easily seen with one drop of titrant.
11. *Ammonium acetate solution:* 10%.
12. *Eriochrome Black T indicator:* (See Part I, reagent No. 4).
13. *Sodium fluoride.*
14. *Triethanolamine:* 10%.
15. *0·01M solution of zinc sulphate:* prepared by dissolving 2·875 g of zinc sulphate ($ZnSO_4 . 7H_2O$) in distilled water, and making up the total volume to one litre after the addition of one drop of concentrated HCl. The solution is standardised as follows: 25 ml of 0·01M solution of EDTA are introduced into a Pyrex 250-ml Erlenmeyer flask, 80–100 ml of distilled water are added, followed by 10 ml ammonium acetate solution 10%, 25 ml *iso*propanol, 1 ml triethanolamine 10% and Eriochrome Black T indicator. The solution is now titrated from a burette with the zinc sulphate solution till the colour turns bluish-violet.
16. *Hydrochloric acid:* 0·1N.

Procedure for the determination of aluminium in the presence of iron, copper, titanium, manganese calcium, magnesium and phosphate

The solution of the sample, containing 5–15 mg of aluminium, is introduced into a Pyrex 150-ml beaker. Water is added to a total volume of about 15 ml, followed by one drop of methyl orange indicator. The solution is neutralised with ammonia 5% till it turns yellow. 4 Ml of 0·1*N* HCl are then added, the solution is heated to near boiling, and 0·4 ml portions of 0·05*M* EDTA are introduced until enough has been added to chelate the aluminium, iron and copper in the sample.* When approaching approximately the point of chelating Al, Fe, Cu in the sample with EDTA, the solution is tested for the presence of free EDTA as follows: 5 ml of the spot test buffer solution (Reagent No. 3) are introduced into a test tube and about 15 mg of the dithizone-carbamate-NaCl indicator mixture (Reagent No. 4) are added and dissolved. The solution thus obtained is stable for about one hour. 5–6 Drops of the spot solution are introduced into a spot plate and the tip of a glass rod moistened with the solution of the analysed sample is brought in contact with the spot solution and stirred. If the red colour does not turn green, the addition of 0·4 ml portions of 0·05*M* EDTA to the solution of the sample is continued with the application of the spot test till the colour of the spot solution turns green, indicating excess free EDTA. A large excess of the latter should be avoided. It was found essential to apply the spot test while the solution of the analysed sample is kept nearly boiling. The beaker is now covered with a watch-glass and the solution is boiled gently for three minutes. It is then left to cool to room temperature and ammonia solution 1% is added dropwise until the colour of the solution turns yellow. The addition of excess ammonia should be avoided. 2 Ml of 0·01*M* solution of zinc sulphate are now added, followed by 0·1*N* HCl, until the colour of the solution turns orange, but not red. The solution is then passed through a column containing Amberlite IR-120 in the ammonium cycle at a flow rate of about 8 ml per minute. The resin is washed with distilled water until the total volume of the effluent amounts to 200–230 ml. The effluent is received into a Pyrex 500-ml Erlenmeyer flask and to it are then added 75 ml *iso*propanol, 10 ml ammonium acetate solution 10% and 1 ml triethanolamine 10%. After cooling below 10°, a little Eriochrome Black T indicator is added and the excess of EDTA is titrated with 0·01*M* solution of zinc sulphate to a permanent bluish-violet end-point. 1·5 G of sodium fluoride are now added, the solution is heated to near boiling and then kept at this temperature for 20 minutes. After cooling again to below 10°, the solution is titrated with 0·01*M* solution of zinc sulphate to a persistent bluish-violet end-point.

Calculation of the results

$$A = n \times f \times 0{\cdot}2697$$

where A = mg Al found
n = ml 0·01*M* solution of zinc sulphate
f = factor of the zinc sulphate solution
0·2697 = the factor for aluminium

The time required for a single determination is 1½–1¾ hours approximately, whereas much less time is required when determinations are carried out in series.

The accuracy of the determination of aluminium in the presence of various anions

A series of determinations was done according to the procedure described above in order to test the accuracy of the method in the presence of various quantities of anions (NO_3^-, CH_3COO^-, SO_4^{2-}, Cl^-). Some of the typical results obtained are shown in Table XIII.

Conclusion

The determination of aluminium in the presence of chloride, sulphate, acetate and nitrate ions is accurate.

Table XIV shows some typical results obtained for aluminium in the presence of iron, copper, titanium, manganese, calcium, magnesium and phosphate.

Conclusions

(1) The method described for the determination of aluminium is accurate.

TABLE XIII. DETERMINATION OF ALUMINIUM WITH EDTA IN THE PRESENCE OF CHLORIDE, SULPHATE, ACETATE AND NITRATE

Exp. No.	Anion added	Compound form of anion added	Anion added *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	Chloride	NH_4Cl	1100	9·026	9·053	+0·027	+0·3
2	Chloride	NH_4Cl	1100	13·539	13·550	+0·011	+0·1
3	Sulphate	$(NH_4)_2SO_4$	500	9·026	9·007	−0·019	−0·2
4	Acetate	CH_3COONa	800	9·026	9·007	−0·019	−0·2
5	Nitrate	NH_4NO_3	1000	9·026	9·007	−0·019	−0·2
6	Nitrate	NH_4NO_3	1100	13·539	13·536	−0·003	—

* In order to determine the approximate volume of 0·05*M* EDTA solution necessary and also to avoid random trials, a preliminary test with the same aliquot of the solution of the sample is done, adding larger portions (2 ml) of 0·05*M* EDTA solution.

(2) The maximum limit allowable for other cations that may be present without affecting the accuracy of the determination of aluminium is as follows :

Iron	8 mg
Copper	3 mg
Titanium	1 mg
Manganese	20 mg
Calcium	20 mg
Magnesium	20 mg
Phosphate (as P_2O_5)	40 mg

Note: Since the titration is performed in a relatively large volume, the tolerance for iron is increased above the 5-mg limit mentioned in Part II of this paper.

DISCUSSION

1. As previously pointed out, the solution of the sample should be weakly acidic. The analysed solution is, therefore, neutralised with ammonia and re-acidified with a limited amount of hydrochloric acid to a pH below 2. Excessive amounts of free acids interfere, for example more than 5 ml of concentrated hydrochloric acid in the sample taken. In such cases the solution should be concentrated to a total volume of about 0·5 ml before analysis.

2. Reducing agents interfere, if the sample contains iron or copper, and should be previously oxidised with an excess of bromine water. The excess of the latter should be expelled by boiling for several minutes; thus iron and copper exist in their higher valency states.

3. Oxalates, tartrates, citrates, pyrophosphates and fluorides interfere, and they should be previously eliminated by evaporation with 0·2 ml of concentrated sulphuric acid.

4. As already pointed out, it is necessary to boil the solution with the excess of EDTA in order to stabilise the aluminium chelate. It was found that the aluminium can be also stabilised by boiling the weakly acid solution with excess of EDTA instead of doing so after neutralisation with ammonia, *i.e.* instead of boiling the neutral solution.

TABLE XIV. DETERMINATION OF ALUMINIUM IN THE PRESENCE OF IRON, COPPER, TITANIUM, CALCIUM, MAGNESIUM AND PHOSPHATE

Exp. No.	Compound form of cation added *mg*	Cation added *mg*	Al present *mg*	Al found *mg*	Diff. *mg*	Rel. error %
1	$FeCl_3$	Fe 8	4·513	4·526	+0·013	+0·3
2	$FeCl_3$	Fe 8	13·539	13·511	−0·028	−0·2
3	$Cu(NO_3)_2$	Cu 3	9·026	9·075	+0·049	+0·5
4	$Cu(NO_3)_2$	Cu 3	13·539	13·500	−0·039	−0·3
5	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4	Fe 8, Cu 3, P_2O_5 40	4·513	4·490	−0·023	−0·5
6	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4	Fe 8, Cu 3, P_2O_5 40	13·539	13·580	+0·041	+0·3
7	$Ti(SO_4)_2$	Ti 1	9·026	9·075	+0·049	+0·5
8	$Ti(SO_4)_2$	Ti 1	13·539	13·550	+0·011	+0·1
9	$Ti(SO_4)_2$, $FeCl_3$, KH_2PO_4	Ti 1, Fe 8, P_2O_5 40	4·513	4·553	+0·040	+0·9
10	$Ti(SO_4)_2$, $FeCl_3$, KH_2PO_4	Ti 1, Fe 8, P_2O_5 40	9·026	9·048	+0·022	+0·2
11	$MnSO_4$	Mn 20	4·513	4·526	+0·013	+0·3
12	$MnSO_4$	Mn 20	13·539	13·536	−0·003	—
13	$MnSO_4$, $FeCl_3$, KH_2PO_4	Mn 20, Fe 8, P_2O_5 40	4·513	4·494	−0·019	−0·4
14	$MnSO_4$, $FeCl_3$, KH_2PO_4	Mn 20, Fe 8, P_2O_5 40	13·539	13·587	+0·048	+0·4
15	$CaCl_2$	Ca 20	4·513	4·526	+0·013	+0·3
16	$CaCl_2$	Ca 20	13·539	13·500	−0·039	−0·3
17	$MgSO_4$	Mg 20	4·513	4·490	−0·023	−0·5
18	$MgSO_4$	Mg 20	13·539	13·587	+0·048	+0·4
19	$CaCl_2$, $MgCl_2$	Ca 20, Mg 20	4·513	4·494	−0·019	−0·4
20	$CaCl_2$, $MgCl_2$	Ca 20, Mg 20	13·539	13·550	+0·011	+0·1
21	$CaCl_2$, $MgCl_2$, KH_2PO_4	Ca 20, Mg 20, P_2O_5 40	4·513	4·526	+0·013	+0·3
22	$CaCl_2$, $MgCl_2$, KH_2PO_4	Ca 20, Mg 20, P_2O_5 40	13·539	13·580	+0·041	+0·3
23	$CaCl_2$, $MgCl_2$, $FeCl_3$	Ca 20, Mg 20, Fe 8	4·513	4·494	−0·019	−0·4
24	$CaCl_2$, $MgCl_2$, $FeCl_3$	Ca 20, Mg 20, Fe 8	13·539	13·500	−0·039	−0·3
25	$CaCl_2$, $MgCl_2$, $Cu(NO_3)_2$	Ca 20, Mg 20, Cu 2	9·026	9·007	−0·019	−0·2
26	$CaCl_2$, $MgCl_2$, $Cu(NO_3)_2$	Ca 20, Mg 20, Cu 2	13·539	13·538	−0·001	—
27	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4, $Ti(SO_4)_2$, $CaCl_2$, $MgCl_2$, $MnSO_4$	Fe 8, Cu 3, P_2O_5 40, Ti 1, Mn 20, Ca 20, Mg 20	4·513	4·494	−0·019	−0·4
28	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4, $Ti(SO_4)_2$, $CaCl_2$, $MgCl_2$, $MnSO_4$	Fe 8, Cu 3, P_2O_5 40, Ti 1, Mn 20, Ca 20, Mg 20	13·539	13·587	+0·048	+0·4

5. It was found, at this stage, that by adding triethanolamine to the solution before the titration of the excess EDTA, it was no longer necessary to evaporate the solution to a small volume in order to maintain a 40% concentration of *iso*propanol and prevent the partial interference of iron and copper with the colour change of the indicator.

6. Through the addition of a small fixed amount of 0·01*M* solution of zinc (2 ml) the quantity of excess EDTA present can be reduced to the minimum since it is chelated by zinc. Thus larger amounts of foreign cations can be tolerated, because the dissociation of the chelates of these cations is more complete owing to the reduction of the quantity of excess EDTA.

7. Instead of zinc chloride solution as titrant, 0·01*M* solution of zinc sulphate can be used.

Acknowledgement—The authors are indebted to Dr. A. Baniel, chief chemist of Israel Mining Industries Laboratories, for his personal interest in the progress of work and for permission to publish this paper.

Zusammenfassung—Die Verfasser haben eine schnelle und exakte volumetrische Methode zur Bestimmung des Aluminiums (5–15 mg) mit Komplexon-III in Anwesenheit von Eisen, Kupfer, Titan, Mangan, Calcium, Magnesium und Phosphat ausgearbeitet.

Résumé—Les auteurs ont élaboré une méthode volumétrique rapide et exacte pour la détermination de l'aluminium (5–15 mg) au moyen de Complexone-III en présence de Fer, Cuivre, Titane, Manganèse, Calcium, Magnésium et Phosphate.

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THE SEPARATION AND DETERMINATION OF NIOBIUM AND TANTALUM BY PARTITION CHROMATOGRAPHY

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(*Received* 5 *May* 1958)

Summary—A procedure is outlined for the separation and determination of niobium and tantalum by paper chromatography. A mixture of methyl *iso*butyl ketone and hydrofluoric acid was used as solvent and the metals were detected by means of 8-hydroxyquinoline. The minimum amount of each element detectable is 20 μg.

The procedure was applied successfully to the quantitative determination of small amounts of niobium and tantalum in a steel.

BECAUSE of the lanthanide contraction the atomic volumes of niobium and tantalum are almost identical, and the chemical resemblance between them is very close. Both elements are invariably associated together in minerals, and are occasionally encountered in steels and other alloys. The great difficulties in the analysis of these metals are stressed by at least two authors.[1,2] Discussing the importance of niobium as a metal in nuclear technology, Colter[3] states that, although there are a number of methods used for the extraction of niobium from columbite, the major difficulty in all of them is separation from the accompanying tantalum.

It is not surprising that, because of the difficulty in separating these elements, many attempts have been made to determine one element in the presence of the other.[4–6] An extensive review of recent works on the separation of these two elements by means of organic solvents has been prepared by West.[7] A feature of many of these separations based on liquid-liquid extraction processes is, however, that while they are successful for microgram amounts of the elements, they are not at all efficient when the quantities are increased.

Few chromatographic methods have been developed for the separation of the elements. Cabell and Milner[8] achieved a separation using anion-exchange resin De-Acidite FF. The separation is claimed to be quantitative, less than 0·01% of tantalum being present in the niobium fraction. Bruninx *et al.*, report the separation of these elements on paper by electrophoresis.[9] The largest quantities separated are 50 μg. The same authors also[10] report a separation by paper chromatography using the oxalates of the metals and a solvent-mixture composed of ethyl methyl ketone and 10*N* hydrochloric acid. Microgram amounts are separated.

This paper describes the separation and determination of the elements niobium and tantalum by means of partition chromatography.

EXPERIMENTAL

Preliminary investigations

Little information is available to indicate the effect of simple alcohols or mixtures of alcohols on niobium and tantalum. A number of experiments were therefore carried out on Whatman No. 1 filter paper using methanol, ethanol and butanol. These alcohols or mixtures of alcohols gave no separation. Ketones were next used and they showed some separation. With methyl propyl ketone, niobium remained at the top of the paper and tantalum moved with the solvent-front but showed considerable "tailing". Methyl *iso*butyl ketone gave a similar result to methyl propyl ketone while mesityl oxide, *iso*phorone and diacetyl alcohol showed little improvement.

Admixture of alcohols with the ketones only succeeded in destroying the partial separation achieved by ketones alone.

Simple acids were now tried and it was found that hydrofluoric acid effected a separation. The positions of the niobium and tantalum on the paper were, however, reversed.

The behaviour of acid-ketone mixtures was now examined. Since the metals were present as their fluorides, hydrofluoric acid was used. This showed a marked improvement on the ketone separation in all cases. It therefore appeared necessary to examine the composition of the acid-ketone mixtures thoroughly in order to find that best suited to the separation. Two solvent-mixtures showed promise, methyl propyl ketone and methyl *iso*butyl ketone, each with hydrofluoric acid. These were examined in detail, and some of the results are shown in Table I.

TABLE I

No.	Solvent mixture	R_f values	
		Nb	Ta
1*	MPK 48 ml : HF 2 ml 2%	0–0·20	0·83–0·95
2*	MPK 46 ml : HF 2 ml 2%	0·40	0·90
3	M*iso*BK 50 ml : HF 2½ ml 4%	0·60	0·89
4*	M*iso*BK 50 ml : HF 1½ ml 40%	0·1	0·87
5*	M*iso*BK 50 ml : HF 3 ml 4%	0·70	0·80
6	M*iso*BK 50 ml : HF 2 ml 4%	0·53	0·63
7	M*iso*BK 50 ml : HF 2½ ml 2%	0·23	0·72
8	M*iso*BK 50 ml : HF 2 ml 40%	0·80	0·91
9*	M*iso*BK 50 ml : HF 2 ml 20%	0·15–0·40	0·84
10*	M*iso*BK 50 ml : HF 4 ml 4%	0·43	0·81

*Indicates "bearding" and/or "tailing" with the solvent mixture.

Mixtures of methyl propyl ketone and acid were not entirely satisfactory because of the "tailing" which occurred. Of the methyl *iso*butyl ketone-hydrofluoric acid mixtures, the best separation and banding were obtained with solvent-mixture No. 3, containing 2·5 ml of 4% hydrofluoric acid in 50 ml of ketone. This is a two-phase system, and is used directly on preparation. The niobium in this two-phase solvent mixture moves with the acid front, and the tantalum with the ketone front. In approximately three hours the acid front travels 10 cm, and the ketone front 3 cm further. This gives an excellent separation of the two elements.

Spraying reagents

Most workers who have carried out investigations on niobium and tantalum have precipitated them by forming the thiocyanate complex,[11] the cupferron complex[12] or by the addition of pyrogallol.[13] Niobium has also been detected by tannic acid.[14]

All of these reagents were found to be unsatisfactory for development of the elements on a paper chromatogram, with the exception of tannic acid which, however, could only be used for niobium. It was considered, therefore, that it would be a great advantage if a single reagent could be found which would detect both elements on the chromatogram.

Various reagents were investigated but that which fulfilled requirements most satisfactorily was 8-hydroxyquinoline. A 5% (w/v) solution of the reagent in methanol–chloroform–water (48 : 48 : 4) was used.

Development of the bands may be carried out in two ways. Firstly, the paper may be sprayed with a $5N$ ammonium hydroxide solution and then with the 8-hydroxyquinoline solution. It is then dried in an oven at 120° and, as the strip dries, both metals develop as bright yellow bands. On the other hand, if the strip is not so sprayed with ammonium hydroxide solution, niobium may be detected as a bright orange and tantalum as a pale orange band. Under ultra-violet light niobium fluoresces bright yellow but tantalum, although visible, fluoresces only slightly. Although both methods are quite satisfactory, the limit of detection being the same in each case, the first procedure was used in all succeeding work.

DETAILED PROCEDURE

1. Place the solvent-mixture (methyl *iso*butyl ketone–4% HF) in the solvent trough of a Chromatank at least one hour before starting the experiment.
2. Cut sheets of Whatman No. 1 paper into strips 16 cm wide.
3. At distances of 2·5, 4 and 6 cm from the top, rule lines across the paper and bend along the first of these lines.
4. Along the 6-cm line place 0·01 ml of the metal fluorides. The spots should not be allowed to dry before inserting into the Chromatank.
5. Allow the solvent-mixture to run down the paper—the acid front to the 10-cm mark and the ketone to about the 15-cm mark. This development takes about three hours.
6. Remove the strips from the tank and allow to dry in air. The paper is now ready for spraying.
7. Attach the strip to the strip-holder and spray with 5*N* ammonium hydroxide solution and then with a 5% solution of 8-hydroxyquinoline in methanol-chloroform–water (48 : 48 : 4).
8. Dry the strip in an oven at 120° for 30 minutes.
9. Wash with hot water to remove excess 8-hydroxyquinoline.
10. Dry in an oven for about 1 hour.
11. Examine the strip in ultra-violet light when niobium will be observed as a brilliant yellow band (R_f 0·60). Tantalum, detected by the naked eye, has an R_f value of 0·90.

Standards, limits of detection, synthetic mixtures.

Standards of 20, 100, 250, 350, and 500 μg amounts were prepared for each element. For both elements the limit of detection is 20 μg and an upper limit of at least 1 mg may be used. These standards were very satisfactory.

Synthetic mixtures of "unknown" composition were analysed by one of us (I.A.P.S.). Estimations were carried out by comparison of band intensities and areas with the set of standards. The results are shown in Table II. Where the actual amount present differs from that found, the former is written in parentheses.

TABLE II

No.	Nb, μg	Ta, μg
1	400 (500)	20 (25)
2	300 (350)	350
3	50 (25)	30 (25)
4	—	200 (250)
5	230 (250)	—
6	220 (200)	250
7	25	425 (400)
8	20	—
9	400 (425)	20 (25)
10	—	25 (20)

Application of the method to quantitative determinations.

The success achieved in the semi-quantitative analysis of these elements suggested that the separation might be applied quantitatively. Since the elements exist on the chromatograms as their oxinates, investigations were centred on the removal of these from the paper and their determination spectrophotometrically. Each element was investigated separately.

(*a*) *Niobium.* Using the procedure outlined for the detection of this element, it was found that precipitation of niobium oxinate on the paper was complete. After detection the square of paper containing the developed band was cut out. To remove the complex from the paper it was shaken in a separatory funnel with 10 ml of hot 2*N* hydrochloric acid. To extract niobium oxinate from the acid solution chloroform was used. pH conditions for the extraction were found to be critical. On the acid side, extraction is small but, as the pH is increased, extraction increases to a maximum in the range pH 8–9. Above this range it again decreases. pH 8·5 was used in all subsequent investigations.

After adjustment of the pH with ammonia, using indicator paper, the niobium oxinate solution was shaken with three 3-ml portions of chloroform; the combined extracts were dried over sodium sulphate and make up to the 10-ml mark in a calibrated flask. This solution, when examined spectrophotometrically, showed a strong maximum at 385 mμ.

(*b*) *Tantalum.* As was the case for niobium, the procedure used for the detection of the element ensured complete precipitation of tantalum oxinate on the paper. Hot 2*N* hydrochloric acid was again very suitable for removal of all the complex from the paper and extraction of this complex by chloroform was greatest in the range pH 9–11. A pH of 10·0 was used in all subsequent investigations.

Extraction was carried out in exactly the same manner as described for niobium oxinate and the extracts, when examined spectrophotometrically, showed strong maxima at 310 mμ and 390 mμ.

Since at wave lengths 385 mμ (niobium) and 390 mμ (tantalum) there is no interference from 8-hydroxyquinoline, these values were chosen respectively for spectrophotometric determination of the elements.

Solutions of both metal oxinates showed adherence to Beer' laws.

Alloy analysis

The analysis of a "straight N6 18/12" Stainless Steel, with certificate figures by the Bureau of Analysed Samples, Ltd., was carried out using this procedure.

The bulk components of the steel were removed as soluble perchlorates, the niobium and tantalum perchlorates were ignited to the oxides and were treated with hydrofluoric acid to give the fluorides.

Procedure

Place 1 g of the steel in a beaker and dissolve in 100 ml of a 1 : 1 (v/v) mixture of 37%hydrochloric acid and 70% nitric acid.

Treat the solution with 100 ml of 71% perchloric acid, heat to boiling, and reflux for 30 minutes. Cool. Treat with 100 ml of water and 100 ml of saturated sulphurous acid. Heat to boiling and digest for two hours. After cooling, filter and wash the residue with 2% hydrochloric acid. Ignite at dull red heat for about one hour. Convert the oxides to the fluorides with 40 per cent hydrofluoric acid and a few drops of concentrated nitric acid. Dissolve the fluorides in 1 ml of hydrofluoric acid.

Results

The solution obtained using the above procedure was applied in 0·05-ml amounts to the paper and chromatograms were prepared using the methyl *iso*butyl ketone-hydrofluoric acid solvent-mixture. Development of the niobium and tantalum positions was carried out with 8-hydroxyquinoline and the oxinates of the elements were extracted into chloroform in the manner already described.

From prepared calibration curves, in the range 0–500 μg of metal the amounts of niobium and tantalum in steel were found to be: Nb 0·69% (present 0·67%); Ta 0·05% (present 0·04%).

It is interesting to note that a semi-quantitative analysis carried out independently, in which the developed oxinates on the paper were compared directly with the sets of standards, gave values of 0·65% and 0·04% for niobium and tantalum respectively.

Zusammenfassung—Es wird ein Verfahren für die Trennung und Bestimmung von Niob und Tantal mittels Papierchromatographie angegeben. Als Lösungsmittel dient eine Mischung von Methyl*iso*butylketon und Fluorwasserstoffsäure. Die Identifizierung der Metalle erfolgt mit 8-Oxychinolin und besitzt eine Nachweisgrenze von 20 μg. Das Verfahren wurde mit Erfolg für die quantitative Bestimmung kleiner Mengen von Niob und Tantal in nichtrostendem Stahl angewandt.

Résumé—Description d'un procédé de séparation et de dosage du niobium et du tantale par chromatographie sur papier. Utilisant comme solvant une mélange: méthyl*iso*butylcetone-acids fluorhydrique, on a identifié les métaux à l'aide de la 8-hydroxyquinoleine. La quantité minimum décelable de chaque élément est 20 μg.

On a pu appliquer avec succès cette méthode à la détermination quantitative du niobium et du tantale dans un acier.

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NUCLEATION IN ANALYTICAL CHEMISTRY

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(*Received* 16 *June* 1958)

Summary—Precipitation involves two processes, nucleation and subsequent crystal growth. The nucleation process is of extreme importance in determining the number and size of the final crystalline particles. The significance of experimental studies of nucleation is discussed and the need for further research indicated.

IN analytical chemistry it is often desirable that a precipitate be produced in the form of relatively large crystals. Such a precipitate is not only more easily handled during subsequent operations but is less subject to contamination, because its surface area is smaller than that of a micro-crystalline or gelatinous precipitate. Empirical rules for the formation of macro-crystalline precipitates were formulated by von Weimarn.[22] Subsequent studies of the kinetics of precipitation and of crystal growth have generally confirmed and elucidated these rules.

Two distinct steps are involved in precipitation. The first, nucleation, is the formation within a supersaturated solution of the first particles of precipitate capable of spontaneous growth. In the second step these first particles, not observable by the naked eye, grow as ions are deposited on them from the solution. The number of particles is determined by the number of nuclei formed in the initial step, and hence so are both the rate of precipitation and the particle size of the precipitate.

In a solution, ions interact with each other to form relatively short-lived clusters. Nucleation is generally considered to occur by this mechanism, with ions or molecules associating in a series of step-wise equilibria to form clusters of various sizes, as follows:

$$\begin{gathered} X + X \rightleftharpoons X_2 \\ X_2 + X \rightleftharpoons X_3 \\ \vdots \\ X_{n-1} + X \rightleftharpoons X_n \\ X_n + X \rightarrow X_{n+1} \end{gathered}$$

All the clusters smaller than X_n are a part of the mother phase. The nucleus is X_n, and is the smallest cluster which can be considered to be solid phase. Clusters in general tend to dissociate rather than to grow because growth requires work to extend the interface between the cluster and the solution. Dissociation is opposed by the tendency of the supersaturated solution to deplete itself by deposition of ions onto the clusters. The nucleus, X_n, is in metastable equilibrium with the solution so that either dissociation or growth can proceed with a decrease in free energy. At a given supersaturation there is one particle size which is in metastable equilibrium; particles smaller than this disperse whereas larger particles grow. This is expressed in the Kelvin-Gibbs equation derived for the case of a spherical droplet of liquid in contact with its supersaturated vapour:

$$RT \ln P_r/P_0 = 2\sigma V/r,$$

where

P_r = the vapour pressure of a drop of radius r,
P_0 = the vapour pressure of the plane liquid surface,
σ = surface tension of the droplet,
V = molal volume of the liquid.

CURRENT THEORIES

Two theoretical approaches to nucleation have been proposed. The classical theory, as given by Volmer,[21] Becker and Doering,[1] and Frenkel,[9] uses the work of formation of the nucleus, obtained from the surface tension, as the activation energy in a kinetic expression for the nucleation rate. The size of the nucleus is obtained from the Kelvin equation or a modification of it, and consequently is a function of supersaturation. The rate of nucleation is found to increase very rapidly with increasing supersaturation, so that the formation of nuclei appears to be a critical function of the degree of supersaturation. The theory, derived for condensation of a vapour, has been modified for nucleation in condensed systems by Turnbull and Fisher.[20] Turnbull[19] gives the following, for nucleation of $BaSO_4$:

$$I \approx K_V \exp\left[-a\sigma^3 v^2/k^3T^3(\ln S)^2\right],$$

where

I = rate of nucleation,
$K_V \approx n\nu \exp\left[-\Delta G_A/kT\right]$,
a is a geometrical factor,
σ = interfacial energy per area between nucleus and solution,
v = volume per "molecule" of $BaSO_4$ crystal,
S = critical supersaturation = $(K_{\mathrm{I.P.}}/K_{\mathrm{S.P.}})^{1/2}$, where $K_{\mathrm{I.P.}}$ is the ion-product,
n = number of Ba^{2+} and SO_4^{2-} ions per volume,
ν = jump frequency,
ΔG_A = free energy of activation for growth of crystals.

This equation is difficult to apply because the energy terms are not well defined. For example, there are little available data on the surface energy of solids; further, the surface energy varies from plane to plane. The structure of a small nucleus is not yet known, but if it is a polyhedron, the contribution of its edges and corners to the interfacial energy is significant. The term, ΔG_A, is also complex, because crystal growth involves both diffusion and a variety of surface processes, each of which has a characteristic activation energy.

A more empirical approach has been developed by Christiansen and Nielsen.[4] Their theory concerns itself with the nature of the induction period, which is the interval between the time of mixing two solutions to form a supersaturated solution and the time when precipitation is first observed. The following equation describes the relationship between the induction period and the concentration of the supersaturated solution of many slightly soluble salts:

$$k = C_0^p T,$$

where

C_0 = initial concentration of the supersaturated solution,
T = induction period,
k and p are constants.

Christiansen and Nielsen consider that the induction period represents the time required to build up clusters of size X_n, according to the mechanism previously outlined. They treat all reactions leading to X_n as steady-state processes; by assuming that X_n is different from smaller clusters in that it is more likely to gain another ion than to lose one, and that precipitation is observed when a constant fraction of the solute has deposited, they were able to derive the above equation, and to identify p as $n - 1$, where n is the total number of ions in the nucleus.

The above two theories are apparently in opposition, inasmuch as the classical theory predicts that, (*a*) the size of the nucleus varies with supersaturation, and (*b*) the rate of nucleation depends very drastically upon supersaturation, which signifies a large nucleus. The Christiansen–Nielsen theory predicts a constant nucleus size and a much less drastic dependence of nucleation rate on supersaturation, thus indicating a relatively small nucleus. Supportof one or the other of these viewpoints by comparison of experimental results has not yet been possible, both because of theoretical and operational uncertainties, and because the theories have been derived to fit essentially different cases. The classical theory assumes that supersaturation is built up homogeneously and extremely slowly until a critical supersaturation is reached; that is, steady-state concentrations of clusters of various sizes are always present in the solution, and precipitation is observed when the supersaturation is increased enough to shift the concentrations so that there is an appreciable concentration of clusters X_n. The Christiansen–Nielsen theory assumes that the supersaturated solution initially contains no clusters of any size, and that some finite time interval is required to form the nuclei *via* a steady-state process, with precipitation again occuring when there is an appreciable concentration of clusters X_n. Thus, the two theories may not be actually contradictory. Progress toward harmonizing them has been made by Collins,[6] who introduces the induction period into the classical theory.

EXPERIMENTAL ASPECTS AND DISCUSSION

The greatest conflict between the two theories lies in the often contradictory experimental results which are obtained, depending on the approach used. When two solutions are mixed to form a supersaturated solution, an induction period is usually observed, and a small nucleus size is calculated.[4] If the supersaturation is built up slowly, a critical supersaturation below which precipitation will not occur is observed, and a large nucleus size is calculated.[14]

The results of induction period measurements for a number of slightly soluble salts have been summarized by Nielsen.[16] They indicate that nuclei of these salts are small; examples are $(Ag_2CrO_4)_2$, $(CaF_2)_3$, and $(AgCl)_3$. In Christiansen and Nielsen's work,[4] rapid-flow kinetic methods were used to study a wide range of induction periods, the time scales extending over an interval of from four to six powers of ten; straight line plots of the log of salt concentration vs. the log of the induction period were obtained. Other investigators (*cf.* reference 16), working in more limited concentration ranges, also obtained straight line plots.

Because it affords a means for slowly and homogeneously increasing the concentration of a salt from virtually zero to the critical value, the technique of precipitation from homogeneous solution has been used with success in studies of nucleation. LaMer and Dinegar[14] have used this method of precipitation, as well as direct mixing techniques, as outlined previously, in their studies of the precipitation of barium sulphate.

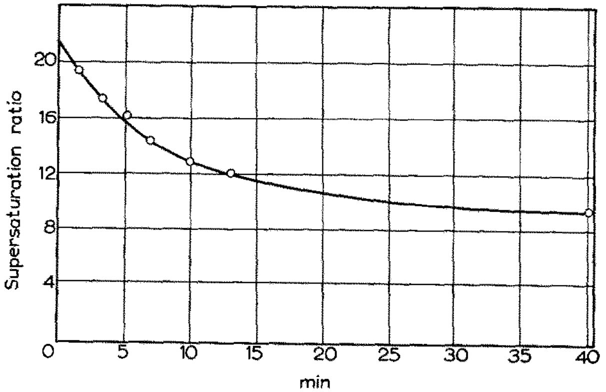

FIG. 1.—Time of appearance of crystalline phase ($BaSO_4$) as a function of supersaturation ratio, by direct mixture of solutions.[14]

In the latter experiments, these investigators rapidly mixed dilute solutions of varying concentrations of barium nitrate and sodium sulphate, and examined the resulting solutions for the time of appearance of barium sulphate crystals. The results are shown in Fig. 1. The supersaturation ratio, S, is again defined as

$$(K_{\mathrm{I.P.}}/K_{\mathrm{S.P.}})^{1/2}.$$

For supersaturation ratios above 12, the time of appearance of crystals was sharp and well defined. For ratios below 12, there was no sharp transition point. Their data, combined with those of Christiansen and Nielsen,[4] give a nucleus consisting of seven ions, either $[Ba_4(SO_4)_3]^{2+}$ or $[Ba_3(SO_4)_4]^{2-}$.

When barium was precipitated from homogeneous solution, by generating sulphate by the reaction,

$$S_2O_8^{2-} + 2S_2O_3^{2-} = 2SO_4^{2-} + S_4O_6^{2-},$$

precipitation became apparent at a constant supersaturation ratio. This "critical" supersaturation ratio, S_c, was found to be 21·5 ± 0·4 over the range of $(Ba^{2+}) = 5$ to $20 \times 10^{-4}M$. This compares favourably with the value of 21·2 obtained from Fig. 1 by extrapolation to zero time. LaMer and Dinegar modify the Kelvin equation as follows, for the nucleation of a salt from solution:

$$iRT/M \ln S_c = 2\sigma/\rho r,$$

where

i = van't Hoff factor,
M = molecular weight,
S_c = critical supersaturation,
σ = interfacial tension,
ρ = density,
r = radius of nucleus.

Using the values 21·5 for S_c, and 1500 dynes/cm for σ, they calculate that $r = 0{\cdot}01\mu$ for $BaSO_4$.

Although the values of the critical supersaturation ratio found by LaMer and Dinegar are remarkably constant, it appears that the nucleation which occurs is heterogeneous rather than homogeneous, *i.e.*, it involves foreign bodies. Collins and Leineweber[7] have repeated the experiments of LaMer and Dinegar and have found that the observed supersaturation ratio, although again remarkably constant for a given set of experiments, is nevertheless strongly dependent upon the purity of the reagents. Impurities present in the sodium thiosulphate obtained from commercial sources proved very effective in lowering the critical supersaturation ratio. Upon purification of the reagents by recrystallizations and successive filtrations, a maximum supersaturation ratio of about 32 was obtained; when no attempts were made to remove impurities, the value was 19. "Critical" supersaturations between these two values were also obtained, depending on the rigour of the purification. Collins and Leineweber conclude that the nucleation process in their experiments is probably heterogeneous but that further purification of the materials used would be required for a firm conclusion with regard to this point.

In precipitation by direct mixing, several investigators have observed effects which can be explained by assuming that heterogeneous nucleation is involved. Bogan and Moyer[3] find that the final size of particles of precipitated barium sulphate depends on the age of the barium chloride solution used in the precipitation. Aged solutions, or solutions filtered through a 2 to 5 micron Selas crucible, produced crystals seven to ten times as large as those from fresh, unfiltered barium chloride. They attribute this to fragments of the barium chloride lattice which remain undissolved and act as nuclei for the precipitation. Benedetti-Pichler[2] has observed a similar effect. He attributes nucleation to impurities in the barium chloride; these impurities, during ageing, are removed by adsorption on the walls of the storage vessel. Nielsen[17] has studied the relationship between the number of particles of barium sulphate precipitate and the rigour of cleaning of the reaction vessels. With ordinary methods of cleaning he obtains about 2000 particles/mm^3; when his vessels are cleaned by steaming, this decreases to about 100/mm^3, and in some cases to as low as 25/mm^3. Nielsen believes that the most reasonable explanation for these observations is that suitable nuclei exist in the system before the solutions are mixed, although this explanation makes the significance of the nucleus sizes obtained by his theory rather questionable. This effect of impurities on the critical supersaturation may explain some of the conflicting results obtained by various investigators. Cobbett and French[5] found that $BaSO_4$ would not precipitate below a $K_{\mathrm{I.P.}}$ of $1{\cdot}59 \times 10^{-8}$; LaMer and Dinegar[14] measured an induction period of about 12 minutes for this concentration. For AgCl of $K_{\mathrm{I.P.}}$ below $3{\cdot}14 \times 10^{-10}$, Davies and Jones[8] found that no precipitation took place even after 18 hours, while Kobayashi[12] obtained an induction period of about 25 minutes for this concentration. It is also interesting to note from the data of LaMer and Dinegar that the crystalline phase appears in 10 minutes (*cf.* Fig. 1) for an initial supersaturation ratio of 13 in a direct-mixing experiment, whereas calculation shows that 60 minutes (*cf.* run No. 9 of Table I of reference 14) are required to proceed from a supersaturation ratio of 13 to the value of about 21 required for nucleation in the case where sulphate is slowly generated by the chemical method.

Turnbull[19] has investigated the kinetics of precipitation of barium sulphate using direct-mixing experiments and finds that the rate of precipitation of the salt is dependent, for a given initial supersaturation ratio, upon the relative concentrations of the solutions being mixed and on the method of mixing. For example, when equal amounts of barium hydroxide of concentration $2m_0$ and sulphuric acid of concentration $2m_0$ are mixed to produce a solution of barium sulphate of initial concentration m_0, the fraction of barium sulphate precipitated in 20 minutes is about 0·48, whereas the fraction precipitated in the same time is about 0·05 when barium hydroxide of concentration $215m_0$ and sulphuric acid of concentration m_0 are rapidly mixed to produce barium sulphate of initial concentration m_0.

Turnbull's data are presented as curves showing the relation between X, the fraction of barium sulphate precipitated, and t, the time. By multiplying the time scale by a suitable factor f the composite curves are superimposable. The course of precipitation can thus be described by the general relation:

$$\mathrm{X} = F(f \,.\, t),$$

where f depends on the supersaturation ratio S, the method of mixing and the specific solutions used. Turnbull interprets this relation as indicating that the number of precipitation nuclei formed after homogenization of the solution is negligible in comparison with the number produced during the homogenization (mixing) process. The dependence of X on $(f \,.\, t)$ is then determined by the rate of growth of the n_i particles which were formed during homogenization. For the most reproducible method of mixing, Turnbull estimates that the number of nuclei formed is 560 times greater for S equal to 19·0 than for S equal to 12·2.

It is surprising, as Turnbull indicates, that a slower rate of precipitation is obtained with the method that might be expected to produce the higher local excess of supersaturation, namely, addition of a relatively concentrated barium solution. Turnbull also observed a similar effect when barium nitrate and potassium sulphate were used. However, in those cases where a concentrated sulphate solution was added to the barium solution, the rate of precipitation was much faster than in the opposite case. Turnbull states that "the effect may be associated with the use of a very small volume of a particular solution rather than with the mixing method". Dependence of the induction period and precipitation rate on the method of mixing has also been observed by Lucchesi[15] with $BaSO_4$ and with $SrSO_4$, and by Davies and Jones[8] with AgCl.

O'Rourke and Johnson[18] are in disagreement with Turnbull's view that the number of nuclei of barium sulphate formed after homogenization is small compared to that formed in the homogenization process itself. They base their argument that nuclei are formed *after* homogenization on their observation that the number of particles of barium sulphate formed is nearly independent of concentration when equal volumes of reagents of equimolar solutions of barium and sulphate were mixed. The concentrations of the solutions mixed ranged from 2·5 to $25 \times 10^{-4}M$; after rapid mixing and allowing the solution to stand until precipitation was complete, the particles of barium sulphate were counted. The number of particles per litre amounted to about $1{\cdot}2 \times 10^9$ (*cf.* the value of 10^8 obtained by Nielsen[17]) over the range of concentrations studied. In view of Nielsen's observation of the effect of cleaning of reaction vessels on the number of particles, it is possible that the constant number of particles formed was due to a fixed concentration of foreign nuclei, *i.e.*, heterogeneous nucleation could occur on each foreign nucleus, thus resulting in a constant number of particles.

Although it would appear that precipitation from homogeneous solution should avoid the effect of mixing fluctuations and some of the attendant uncertainities, O'Rourke and Johnson believe that other complications might arise because of the steadily increasing flow of nuclei brought into the crystal growth reaction stage. However, once the formation of crystals is effected, the solution concentration rapidly decreases to a value below the auto-nucleation point. In addition, the rate of formation of a reactant in precipitation from homogeneous solution is usually quite small, so that at any one time there will not be any great excess of the reactant, particularly in the presence of crystals. It thus does not seem reasonable to expect that new nuclei will be formed during precipitation from homogeneous solution in the presence of solid phase unless the critical supersaturation ratio is very small or the influx of precipitant is extremely high. Examination of crystals formed by the process of precipitation from homogeneous solution does not reveal the presence of small crystals; in fact, the crystals are usually quite large and fairly uniform in size.

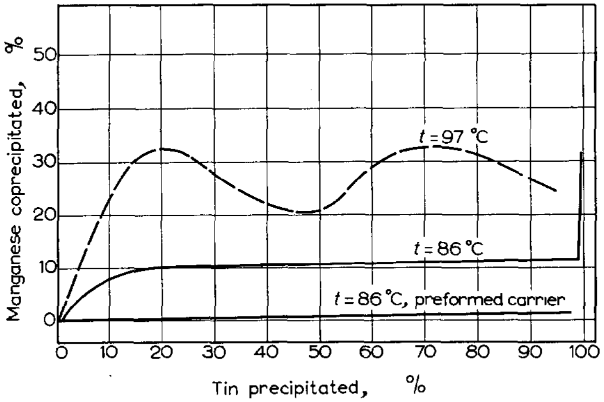

FIG. 2.—Co-precipitation of manganese with basic stannic sulphate precipitated from homogeneous solution.

Davies and Jones[8] have studied the precipitation of silver chloride to determine its critical supersaturation.

These investigators mixed dilute solutions of silver nitrate and potassium chloride and determined the change of conductance with time. By extrapolating a plot of the average rate of fall in conductivity for very slow precipitations over the first hour or two after mixing against ionic concentration product, Davies and Jones found the critical ionic concentration product at which nucleation occurred to be $3{\cdot}14 \times 10^{-10}$. These authors give the ion activity product constant, $K_{\text{S.P.}}$, as $1{\cdot}81 \times 10^{-10}$; the supersaturation ratio is thus of the order of 1·3. In these experiments the initial ionic ratio of $[\text{Ag}^+]$ to $[\text{Cl}^-]$ was one. When the ratio was varied, from 0·25 to 4, it was found that a critical supersaturation limit existed for each case, but that the supersaturation product depended on the ionic ratio.

Davies and Jones obtained the same values for the critical supersaturations in a different way, by carrying out moderately slow precipitation runs and by plotting the rate of precipitation against the amount of AgCl precipitated. They found that precipitation accelerated to a maximum, and that shortly thereafter the rate curve changed at a fairly well-defined point to a nearly linear rate of decrease. The turning-point at which the change takes place was interpreted as the stage at which fresh nuclei ceased to be formed. The concentration products at the turning-point correlated well with the critical concentration products obtained by the previous method. It would be of considerable interest to determine if the variable concentration product obtained with different [Ag] to [Cl] ratios would be constant if the technique of precipitation from homogeneous solution were applied in a manner similar to that by LaMer and Dinegar in the case of barium sulphate.

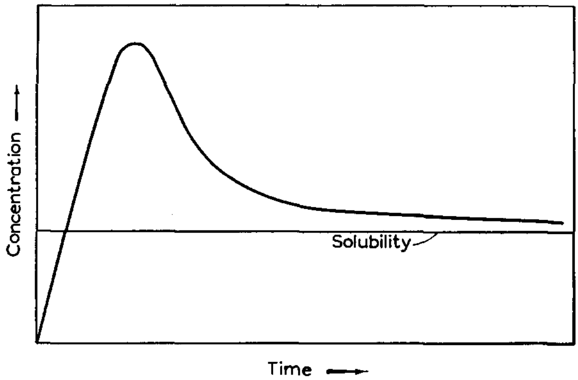

FIG. 3.—Schematic representation of concentration of elemental sulphur formed during precipitation from homogeneous solution.

The investigation of Gordon, Teicher and Burtt[10] showed the effect of the nucleation process on co-precipitation. The results are shown in Fig. 2. When basic stannic sulphate was precipitated in the presence of manganese^{II} by hydrolysing urea at 97°, the extent of co-precipitation of the manganese as a function of the fraction of tin precipitated followed a somewhat erratic pattern. When the rate of precipitation of basic stannic sulphate was made smaller, by hydrolysing urea at 86°, it was found that co-precipitation of manganese occurred in the early stages of the precipitation process where less than 25% of the tin present was precipitated and that from that point on there was virtually no co-precipitation of manganese until the fraction of tin precipitated reached the value of about 99%, at which value the removal of manganese began to be appreciable. As can be seen from Fig. 2, the co-precipitation curve (eliminating the portion due to the initial rise) is characteristic of a system of small distribution coefficient.[11] As is also shown in Fig. 2, the presence of pre-formed basic stannic sulphate eliminated the initial co-precipitation. Basic stannic sulphate was allowed to nucleate and precipitate to the extent of about 25% of the total present but without manganese initially present in the reaction mixture. Manganese was then added and the reaction allowed to proceed in order to precipitate different fractions of the tin present. As can be seen from the figure, the co-precipitation curve is identical, although displaced downward, to that obtained when manganese was initially present.

LaMer and Dinegar[13] have proposed a model for precipitation from homogeneous solution which explains these observations. Fig. 3 is essentially their plot of concentration vs. time for the precipitation of sulphur. The concentration increases with time until the critical supersaturation ratio is reached, whereupon nucleation occurs. The initial rate of precipitation is quite rapid because of the high supersaturation. Not until the supersaturation has decreased appreciably does the slow process characteristic of precipitation from homogeneous solution take place. Extending this scheme to the observations of Gordon, Teicher and Burtt, the anomalous early co-precipitation can be attributed to the high supersaturation required for nucleation, and the resultant initial non-homogeneous precipitation. In the experiments with pre-formed carrier, manganese was not added until the initial supersaturation of the system was relieved and precipitation was occurring at a controlled rate.

CONCLUSION

The relationships between nucleation and the properties of a precipitate will undoubtedly be more fully developed as the nucleation process is further elucidated. The classic investigation of von Weimarn[22] was instrumental in establishing some of the basic rules used by analytical chemists in precipitation, such as using dilute solutions of reagents, adding the precipitant slowly and using vigorous stirring. These precipitation rules were suggested primarily as a guide to produce more nearly perfect growth of the crystals of precipitate by controlling supersaturation. Nucleation studies carried out thus far indicate that these precipitation rules will need revision in some cases to allow for the effect of nucleation. Turnbull[19] finds that barium sulphate precipitates more slowly and presumably more perfectly, when a highly concentrated reagent is added rapidly to a dilute one as opposed to the mixing of two dilute solutions. Nielsen[17] finds that stirring during the early stages of precipitation fractures the small crystallites to form more nuclei, and thus leads to a greatly diminished final particle size. Such facts as these indicate the need for extending the precipitation rules to include nucleation phenomena. During the nucleation period the number of particles and the final size are fixed. Nucleation determines the surface area on which precipitation can take place, and consequently establishes the tempo of the precipitation. Further study of the nucleation process will be of great aid in understanding, and thus increasing the sensitivity and delicacy of separation by precipitation.

Zusammenfassung—Die Fällung beinhaltet zwei Prozesse: Kristallkeimbildung und anschliessendes Kristallwachstum. Der Vorgang der Kristallkeimbildung ist von ausserordentlicher Wichtigkeit für die Zahl und Grösse der am Ende vorhandenen Kristallpartikeln. Die Bedeutung von experimentellen Studien über Kristallkeimbildung wird erörtert und auf die Notwendigkeit weiterer Untersuchungen hingewiesen.

Résumé—La précipitation comporte deux processus: la formation des germes et la croissance subséquente des cristaux. La formation des germes a une très grande importance pour la détermination du nombre et de la taille des particules cristallines obtenues finalement. On discute l'importance des études expérimentales sur la nucléation et montre la nécessité de faire de plus amples recherches à ce sujet.

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DETERMINATION OF HYDRAZINE AND HYDRAZINE DERIVATIVES USING BROMINE MONOCHLORIDE AS STANDARD SOLUTION

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(*Received* 14 *February* 1958)

Summary—A method was evolved for the determination of hydrazine and hydrazine derivatives (such as phenylhydrazine, semicarbazide, *iso*-nicotinic hydrazide) with the use of standard bromine monochloride solution. The titration values are not affected by the degree of acidification or by the nature of the acid used.

On the basis of the experimental results the principle of the Kurtenacker method of hydrazine determination is interpreted.

SCHLÖTTER was the first to evolve a bromometric method for the determination of hydrazine. His method, however, yielded only approximate values, due to interfering side reactions. The use of copper and iron salts or molybdate as catalysts capable of eliminating these side reactions was suggested by Hodgkinson.[2] Conditions of oxidizing hydrazine by potassium bromate were studied by Browne and Shetterly[3] who found that in a sulphuric acid medium hydrazine is oxidized to hydrazoic acid and ammonia.

The first precise bromometric method, which is still in use, for the determination of hydrazine was evolved by Kurtenacker and Wagner,[4] who determined hydrazine in strong hydrochloric acid, in the presence of indigo carmine as indicator, by direct titration with a standard bromate solution. The Kurtenacker method has been subjected to a thorough critical examination by Kolthoff[5] who found that the accuracy of the method depends to a great extent on the concentration of hydrochloric acid. When the solution initially contains hydrochloric acid in concentrations below 20%, the results will be lower than the actual values. The precision of the method is reduced because the indigo carmine indicator consumes bromate. Methyl red, proposed by Kolthoff, behaves similarly.

The use of *p*-ethoxychrysoïdine as an indicator in bromometry was suggested by Schulek and his co-workers[6]. Wojahn[7] actually applied this indicator to the bromometric determination of *iso*nicotinic hydrazide.

Conditions for the bromometric determination of hydrazine and its derivatives in the presence of *p*-ethoxychrysoïdine as indicator were examined by Laszlovszky.[8] It appeared that with low concentrations of hydrochloric acid the method yielded low values. When high concentrations of hydrochloric acid were applied, the results were affected by consumption of bromate by the indicator.

As this short literature survey discloses, the bromometric determination of hydrazine and hydrazine derivatives yields reliable results only under strictly controlled experimental conditions.

In the course of our earlier experiments,[9] we succeeded in preparing a 0·1N standard solution of bromine monochloride the titre of which showed changes of not more than 3–5% after storage for 2–3 months under appropriate conditions. An attempt was made to determine hydrazine and hydrazine derivatives by a standard solution of bromine monochloride. The preparation and properties of the standard solution have been discussed elsewhere in detail[9]. The solution was stored in a Winkler burette with a stock flask.

The titre of the standard solution was determined by iodometry. The titre of the reagent was established daily. *p*-Ethoxychrysoidine was applied as indicator. The effect of the nature and concentration of acid on the titration results were examined.

EXPERIMENTAL

Determination of hydrazonium sulphate

It was previously established that hydrazine is quantitatively oxidized to elementary nitrogen by bromine monochloride, as shown by the equation:

$$N_2H_4 + 2BrCl \rightarrow N_2 + 2HBr + 2HCl$$

In this reaction the equivalent weight of hydrazine is equal to 1/4 of its molecular weight (32·53).

Experiments were carried out to establish how changes in the nature and concentrations of acids affect the results of measurements. A 0·2% ethanolic solution of *p*-ethoxychrysoïdine was applied as indicator.

It can be seen from Table I that the degree of acidification and the nature of acid applied do not affect the reaction. Moreover, an aqueous solution of hydrazine sulphate can be titrated directly with bromine monochloride solution, without any acidification.

No deviations were observed between the results of titrations conducted in the presence of sulphuric and hydrochloric acid. The only difference was that in the case of quick titration, the indicator was consumed more rapidly in a sulphuric acid medium than in a hydrochloric acid solution. One extra drop of indicator was required in such cases, the addition of which did not affect the titration results. (This phenomenon is attributed to the fact that the higher chloride content of the hydrochloric acid solution suppresses the dissociation of the bromine monochloride complex, thus reducing the redox potential.[9])

It appears from Table I that hydrazine sulphate can be determined with an appreciable precision by means of standard bromine monochloride. The maximum titration error ranges were 0·2%.

It is known[10] that hydrazine sulphate is a non-hygroscopic substance of stoichiometric composition which can readily be purified by recrystallisation and dried at 150°. This is why it is frequently used in acidimetry as a primary standard.

On this basis, hydrazine sulphate is suggested as a primary standard for bromine monochloride solution.

Determination of phenylhydrazine hydrochloride

The reaction which takes place during the titration of phenylhydrazine with bromine monochloride

$$C_6H_5NH{\cdot}NH_2 + 2BrCl + H_2O = N_2 + C_6H_5OH + 2HBr + 2HCl,$$

has been subjected to investigation. The equivalent weight of phenylhydrazine in this reaction is equal to 1/4 of its molecular weight (36·14).

It was found that, as for hydrazine, the degree of acidification and the nature of the acid applied did not affect the determination (Table II).

It is of interest to note that solutions containing *p*-ethoxychrysoïdine as indicator, when allowed to stand for a while after titration, turn red in 15–20 minutes, because of the reducing action of the phenol formed in the oxidation of phenylhydrazine.

TABLE I.—RESULTS OF HYDRAZINE DETERMINATIONS

No.	Hydrazine sulphate, weighed, *mg*	0·1*N* BrCl, consumed, *ml*	Hydrazine sulphate, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl, *ml*	2*N* H_2SO_4, *ml*
1	18·26	5·61	18·25	−0·01	−0·05	2	—
		5·61	18·25	−0·01	−0·05	2	—
		5·63	18·32	+0·06	+0·3	5	—
		5·61	18·25	−0·01	−0·05	5	
		5·61	18·25	−0·01	−0·05	10	—
		5·61	18·25	−0·01	−0·05	10	—
2	15·15	4·65	15·13	−0·02	−0·13	—	—
		4·65					
		4·65	15·13	−0·02	−0·13	5	—
		4·65					
		4·65	15·13	−0·02	−0·13	—	10
		4·65					
3	30·05	9·25	30·09	+0·04	+0·13	—	—
		9·25					
		9·25	30·09	+0·04	+0·13	5	—
		9·23	30·03	−0·02	−0·06	5	—
		9·25	30·09	+0·04	+0·13	—	10
		9·25				—	10
		9·25	30·09	+0·04	+0·13	—	20
		9·25				—	20
4	36·21	11·13	36·21	0·00	0·00	2	—
		11·13					
		11·12	36·18	−0·03	−0·08	5	—
		11·13	36·21	0·00	0·00	5	—
		11·13	36·21	0·00	0·00	10	—
		11·13					

Determination of semicarbazide hydrochloride

The oxidation of semicarbazide, in direct titration with bromine monochloride, takes place according to the scheme

$$NH_2NH{\cdot}CO{\cdot}NH_2{\cdot}HCl + 2BrCl + H_2O \rightarrow N_2 + NH_4Cl + CO_2 + 2HBr + 2HCl.$$

The equivalent weight is equal to 1/4 of the molecular weight (27·88).

As before, the oxidation of semicarbazide by bromine monochloride is not affected, either, by the degree of acidification or the nature of acid (Table III).

It must be noted that in the case of semicarbazide the colour change of the indicator is not as

TABLE II.—RESULTS OF DETERMINATIONS OF PHENYLHYDRAZINE

No.	Phenylhydrazine hydrochloride weighed, *mg*	0·1*N* BrCl consumed, *ml*	Phenylhydrazine hydrochloride, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl, *ml*	2*N* H_2SO_4 *ml*
1	12·15	3·37 3·37	12·18	+0·03	+0·2	2	—
		3·37 3·37	12·18	+0·03	+0·2	5	—
		3·37 3·37	12·18	+0·03	+0·2	10	—
2	15·55	4·30 4·30	15·54	−0·01	−0·06	—	—
		4·30	15·54	−0·01	−0·06	5	—
		4·31	15·58	+0·03	+0·2	5	—
		4·29	15·50	−0·05	−0·3	—	10
		4·30	15·54	−0·01	−0·06	—	10
		4·30 4·30	15·54	−0·01	−0·06	—	20
3	24·10	6·69	24·18	+0·08	+0·3	2	—
		6·67	24·10	0·00	0	2	—
		6·67 6·67	24·10	0·00	0	5	—
		6·67	24·10	0·00	0	10	—
		6·69	24·18	+0·08	+0·3	10	—
		6·67 6·67	24·10	0·00	0	—	20
4	30·83	8·50 8·50	30·72	−0·11	−0·4	5	—
		8·50	30·72	−0·11	−0·4	—	10
		8·49	30·68	−0·15	−0·5	—	10
		8·50 8·50	30·22	−0·11	−0·4	—	20

readily observed as with other hydrazine derivatives. The colour of the indicator entirely disappears 0·5 to 1·0 drop before the end point, and it turns yellow only when a further half or whole drop is added, whereas with other hydrazine derivatives the colour change of the indicator takes place instantly, on adding a fraction of a drop. However, the application of an indicator correction is not considered necessary.

TABLE III.—RESULTS OF DETERMINATIONS OF SEMICARBAZIDE

No.	Semicarbazide hydrochloride, weighed, *mg*	0·1*N* BrCl consumed, *ml*	Semicarbazide hydrochloride, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl *ml*	2*N* H_2SO_4 *ml*
1	16·59	5·97 5·97	16·65	+0·06	+0·36	2	—
		5·96	16·62	+0·03	+0·2	5	—
		5·97	16·65	+0·06	+0·36	5	—
		5·96 5·96	16·62	+0·03	+0·2	10	—
		5·96 5·96	16·62	+0·03	+0·2	—	10
		5·97	16·65	+0·03	+0·2	—	20
		5·96	16·62	+0·06	+0·36	—	20
		5·96 5·96	16·62	+0·03	+0·2	—	—
2	32·90	11·77 11·77	32·82	−0·08	−0·24	5	—
		11·76	32·79	−0·11	−0·3	—	10
		11·77	32·82	−0·08	−0·24	-	10
		11·76	32·79	−0·11	−0·3	—	20
		11·77	32·82	−0·08	−0·24	—	20

Determination of iso*nicotinic hydrazide*

*iso*Nicotinic hydrazide, can also be titrated with a 0·1*N* solution of bromine monochloride. The reaction proceeds according to the equation:

$$C_5H_4NCO{\cdot}NH{\cdot}NH_2 + 2BrCl + H_2O \rightarrow N_2 + C_5H_4NCOOH + 2HBr + 2HCl.$$

The equivalent weight is equal to 1/4 of the molecular weight (34·28).

The results are not affected by the nature of the mineral acid or by its concentration (Table IV).

In contrast to the previous compounds, *iso*nicotinic hydrazide does not undergo acid hydrolysis on dissolving, therefore it cannot be measured without acidification (too low values). When, however, it is converted into its hydrochloride or sulphate, it is suitable for titration with bromine monochloride solution without further acidification.

TABLE IV.—RESULTS OF DETERMINATIONS OF *iso*NICOTINIC HYDRAZIDE

No.	*iso*Nicotinic hydrazide, weighed, *mg*	0·1*N* BrCl, consumed, *ml*	*iso*Nicotinic hydrazide, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl, *ml*	2*N* H_2SO_4, *ml*
1	18·01	5·24	17·96	−0·05	−0·3	2	—
		5·26	18·03	+0·02	+0·1	2	—
		5·24	17·96	−0·05	−0·3	5	—
		5·24					
		5·26	18·03	+0·02	+0·1	10	—
		5·27	18·06	+0·05	+0·3	10	—
		5·24	17·96	−0·05	−0·3	—	20
		5·26	18·03	+0·02	+0·1	—	20
2	15·22	4·37	14·98	−0·24	−1·6	—	—
		4·37					
		4·46	15·29	+0·07	+0·5	—	10
		4·46					
		4·43	15·19	−0·03	−0·2	—	20
		4·46	15·29	+0·07	+0·5	—	20
		4·46	15·29	+0·07	+0·5	5	—
		4·43	15·19	−0·03	−0·2	5	—
3	30·17	8·66	29·69	−0·48	−1·6	—	—
		8·66					
		8·78	30·10	−0·07	−0·2	5	—
		8·77	30·06	−0·11	−0·4	5	—
		8·85	30·34	+0·17	+0·6	—	20
		8·82	30·23	+0·06	+0·2	—	20
		8·82	30·23	+0·06	+0·2	—	10
		8·82					
4	35·71	10·38	35·58	−0·13	−0·4	5	—
		10·38					
		10·38	35·58	−0·13	−0·4	10	—
		10·32	35·38	−0·33	−0·9	10	—

Procedure for hydrazine and hydrazine derivatives

On the basis of the experiments described the following method is proposed for the determination of hydrazine and hydrazine derivatives.

About 0·30 g substance is weighed accurately, transferred quantitatively into a 100-ml measuring flask and made up to volume with distilled water. 5–10-ml portions of this stock solution are diluted with distilled water to 30–50 ml, and 2–10 ml of 20% hydrochloric acid or 10–20 ml of 2*N* sulphuric acid and 1 drop of *p*-ethoxychrysoïdine indicator are added. The resulting solution is titrated with 0·1*N* bromine monochloride solution.

1 ml of 0·1*N* bromine monochloride is equivalent to 2·253 mg of hydrazine sulphate, 3·614 mg of phenylhydrazine hydrochloride, 2·788 mg of semicarbazide hydrochloride or 3·428 mg of *iso*nicotinic hydrazide.

DISCUSSION

As a result of these experiments the principle of the bromometric determination of hydrazine by the Kurtenacker method[4] can be interpreted.

In sulphuric acid, hydrazine is known to react with bromate to form hydrazoic acid and ammonia,[3] whereas in strong hydrochloric acid a nearly instantaneous reaction between bromate and hydrochloric acid takes place, with formation of bromine monochloride. In the Kurtenacker method[4] for hydrazine, bromine monochloride developed in this way during titration oxidizes hydrazine to elementary nitrogen, and thus controls the oxidation.

The rate of the reaction between bromate and hydrochloric acid diminishes with decreasing concentration of hydrochloric acid. Thus, bromate can react directly with hydrazine, and this side reaction is responsible for deviations in results. In titration with a solution of bromine monochloride, therefore, acidification with hydrochloric acid is not necessary.

Zusammenfassung—Es wird eine Methode für die Bestimmung von Hydrazin und seinen Derivaten (z.B. Phenylhydrazin, Semicarbazid, *iso*-Nikotinsäurehydrazid) mit einer Brom-chlorid-Masslösung entwickelt.

Die Titrations-Werte werden von Art und Menge der Säure nicht beeinflusst.

Auf Grund der exprimentellen Resultate konnte das Prinzip der Kurtenacker-Methode für die Bestimmung von Hydrazin erklärt werden.

Resume—On a élaboré une méthode pour le dosage de l'hydrazine et des dérivés de l'hydrazine (tels que la phénylhydrazine, le semicarbazide, l'hydrazine *iso*nicotique) au moyen d'une solution titrée de chlorure de brome. Les valeurs du titrage ne sont affectées ni par le degré d'acidité ni par la nature de l'acide utilisé.

Par suite des résultats expérimentaux on a interprété la principe de la méthode de Kurtenacker pour le dosage de l'hydrazine.

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Talanta, 1958, Vol. 1, pp. 351–354. Pergamon Press Ltd., London.

GRAVIMETRIC DETERMINATION OF OSMIUM WITH 1:2:3-BENZOTRIAZOLE

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(*Received* 3 *July* 1958)

Summary—A method for the direct gravimetric determination of osmium with 1:2:3-benzotriazole in acetic acid-sodium acetate buffer is presented. The method is accurate and reproducible, and the conditions used in the determination are not critical. The precipitate is a stoichiometric compound which is stable from room temperature up to 200°. It appears that 1:2:3-benzotriazole is probably the first organic reagent to be used successfully in the direct gravimetric determination of osmium.

THE gravimetric determination of osmium[1,3] has been a subject of study in recent years. Thionalide was reported[1] as the first organic reagent to be used successfully for the indirect gravimetric determination of osmium. In these studies, strychnine sulphate, and certain substituted thioureas and thiazoles were recommended for the gravimetric or colorimetric determination of osmium. Though osmium is easily separated from the other platinum metals as its volatile tetroxide by distillation, its quantitative titrimetric and gravimetric determinations[1,3,4] are tedious and/or time consuming. However, in the aforementioned gravimetric procedure for osmium with thionalide, Wagner, Hall, and Markle[5] have given a detailed account of the gravimetric determination of osmium with thionalide which would seem to require approximately 15 hours for a single determination.

Since there is great need for a rapid and direct method for the gravimetric standardization of osmium in solution, the present investigation is concerned with a determination of osmium with 1:2:3-benzotriazole which is direct and involves a stoichiometric compound, whose pH of precipitation in acetic acid-sodium acetate buffer and drying temperature are not critical, and which requires less than 2 hours for a complete determination.

EXPERIMENTAL

Reagents and solutions

A 2.0153-g sample of osmium tetroxide, obtained from A. D. Mackay, Inc., was dissolved in 500 ml of 0.2*M* sodium hydroxide and diluted to 1 litre with distilled water using the procedure of Ayres and Wells.[2] This solution was standardized by the method of Klobbie.[4] All other materials used were reagent-grade chemicals. All precipitates were filtered using medium-porosity, sintered-glass crucibles.

Apparatus

A Beckman Model H2 Glass electrode pH meter was employed to take pH readings. Osmium tetroxide was distilled from solution using a modification of the distillation apparatus described by Westland and Beamish.[6]

Properties of osmium–1:2:3-benzotriazole precipitate

The interaction of osmium with 1:2:3-benzotriazole in acid media[7] gives a beige precipitate when precipitated from solution and after drying. Temperatures up to 200° were safe for drying as indicated graphically by thermogravimetric data presented by Wilson and Baye.[8] Constant weight was obtained for the precipitates after they had been dried at 110° for 30 minutes. The precipitates are readily coagulated in acetic acid-sodium acetate buffer. The effect of pH on precipitation of osmium by the recommended procedure given below is shown in Table I in which varying amounts of acetic acid were added. The pH of the solution containing the red coloured complex before addition of any acetic acid was 7.7. On the addition of acetic acid, the precipitate which began first to form at a pH of 4.2 was not coagulated.

TABLE I.—EFFECT OF pH ON PRECIPITATION OF 15.08 MILLIGRAMS OF OSMIUM

pH	Wt. of ppt. *mg*	Os found *mg*
7.7	—	—
4.2	—	—
4.0	47.6	15.13
4.0	47.4	15.06
4.0	47.5	15.10
3.5	47.5	15.10
3.5	47.4	15.06
3.5	47.5	15.10
3.0	47.5	15.10
3.0	47.5	15.10
3.0	47.5	15.10
2.7	47.5	15.10
2.7	47.5	15.10
2.7	47.6	15.13
2.5	47.6	15.13
2.5	47.5	15.10
2.5	47.5	15.10
2.3	47.5	15.10
2.3	47.4	15.06
2.3	47.4	15.06

Recommended procedure

Ten millilitres of the standard osmium solution which contained 1.51 mg of Os per ml were added to a flask containing 1 ml of ethanol. To this solution were added 25 ml of 2% aqueous 1:2:3-benzotriazole to form the red complex. After heating the solution containing the red complex on a steam bath for 15 minutes, the pH is adjusted roughly to 3 using acetic acid. The resulting precipitate and solution are digested for 15 minutes to coagulate the precipitate. Then the precipitate is filtered on a weighed, medium-porosity, sintered-glass crucible and washed several times with hot distilled water. The precipitate is dried at 110° for 1 hour to constant weight. The theoretical factor for osmium corresponding to the formula $Os(OH)_3(C_6H_4NHN_2)_3$ is 0·3178, the value used to calculate the osmium content of the precipitate. Experimental data shown in Table II were in good agreement with the theoretical factor 0.3178.

Data obtained from several determinations of osmium, after distilling this element as its tetroxide from nitric acid solution, are shown in Table III. The osmium tetroxide was distilled over into 0.1*M* sodium hydroxide using a distillation apparatus similar to the one described by Westland and Beamish.[6]

DISCUSSION

A gravimetric method for the direct determination of osmium is presented, which involves the precipitation of osmium as $Os(OH)_3(C_6H_4NHN_2)_3$. This method is applicable to the determination of osmium after having distilled this element as its

TABLE II.—GRAVIMETRIC DETERMINATION OF OSMIUM

Os taken *mg*	Wt. of ppt. *mg*	Os found *mg*	Difference *mg*
1.51	4.7	1.49	−0.02
1.51	4.8	1.53	+0.01
1.51	4.7	1.49	−0.02
3.02	9.5	3.02	0.00
3.02	9.6	3.05	+0.03
3.02	9.6	3.05	+0.03
4.52	14.2	4.51	−0.01
4.52	14.3	4.54	0.02
4.52	14.1	4.48	-0.04
7.54	23.5	7.47	−0.07
7.54	23.7	7.53	−0.01
7.54	23.6	7.50	−0.04
12.06	38.1	12.11	+0.05
12.06	38.0	12.08	+0.02
12.06	37.9	12.04	−0.02
15.08	47.5	15.10	+0.02
15.08	47.4	15.06	−0.02
15.08	47.5	15.10	+0.02
22.62	71.1	22.60	−0.02
22.62	71.2	22.63	+0.01
22.62	71.1	22.60	−0.02

TABLE III.—GRAVIMETRIC DETERMINATION OF OSMIUM AFTER THREE DIFFERENT DISTILLATION SEPARATIONS

Osmium, *mg*	
Taken	Found
15.08	15.10
15.08	15.10
15.08	15.06

tetroxide from solution. The method is believed to offer certain advantages over the recently-published thionalide procedure. The osmium-1:2:3-benzotriazole procedure, as compared to the thionalide procedure, is direct, saves time, and the determination requires only simple equipment.

Acknowledgment—The authors wish to express their sincere thanks for a National Science Foundation grant which supported this study.

Zusammenfassung—Eine Methode zur direkten gravimetrischen Bestimmung von Osmium mittels 1:2:3-Benzotriazole in Essigsäure-Natriumacetat-Puffer wird angegeben. Die Methode ist genau, gut reproduzierbar und die Arbeitsbedingungen sind einfach. Der Niederschlag ist eine stöchiometrische Verbindung, die von Zimmertemperatur an bis auf 200° stabil ist. Es scheint, dass

1:2:3-Benzotriazol das erste organische Reagens ist, das in der direkten gravimetrischen Bestimmung von Osmium erfolgreich verwendet worden ist.

Résumé—Les auteurs présentent une méthode de dosage par gravimétrie directe de l'osmium par le 1:2:3-benzotriazol en tampon acide acétique-acétate de sodium. Cette méthode est précise et reproductible, et les conditions de dosage ne sont pas critiques. Le précipité est un composé stoechiométrique qui est stable de la température ordinaire jusqu'à 200°. Il est probable que le 1:2:3-benzotriazol est le premier réactif organique à être utilisé avec succès dans le dosage de l'osmium par gravimétrie directe.

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CERIMETRIC DETERMINATION OF URANIUM^{IV}

USE OF TRIPHENYLMETHANE DYES AS INTERNAL INDICATORS

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(*Received* 5 *February* 1958)

Summary—The use of the triphenylmethane dyes (erioglaucine, eriogreen, and xylene cynol FF) as internal indicators in the cerimetric titration of uranium^{IV} has been investigated. The titration is possible in the cold with sufficient rapidity and accuracy, the indicator colour change appearing sharply at the equivalence point. The indicator reactions are rapid and reversible within a wide range of acidity, from 0·5*N* to 8·0*N*, unlike other indicators, *e.g.* diphenylbenzidine, N-phenylanthranilic acid or ferroïn, which require specified conditions for their proper functioning. These indicators can also beused for titration of uranium^{IV} with ceric ammonium nitrate in perchloric acid medium (but not in nitric acid medium).

FURMAN and Schoonover[1] were the first to employ ceric sulphate for the titrimetric determination of a mixture of uranium^{III} and uranium^{IV}. The titration was carried out potentiometrically in an inert atmosphere at 80°. They found that the first break in the potential corresponds to the stoichiometric oxidation of uranium^{III} to uranium^{IV}, and the second break to the complete oxidation of uranium^{IV} to uranium^{VI}. According to Luyckx,[2] the end-point corresponding to the oxidation of uranium^{III} is accurate only when the titration is carried out at 80°. Heal[3] stated that the potential-break occurs too late at room temperature, probably because of the slow oxidation of the hydrogen layer by the titrant. Belcher, Gibbons and West[4] have used uranium^{IV} chloride as a titrimetric (reductimetric) reagent for the determination of permangante, dichromate, vanadate, iron^{III} and cerium^{IV}. They observed that in the potentiometric titration of dichromate, cerate, permanganate and vanadate solutions with uranium^{IV} it is necessary to work at elevated temperatures. They obtained satisfactory and consistent results when the titrations were carried out at 60°. In spite of the statements of earlier workers, we believe that the need for the use of a high temperature for the potentiometric titration of uranium^{IV} by ceric sulphate is not because of the sluggishness of the reaction between uranium^{IV} and cerium^{IV}, but because of the difficulty in the ready establishments of steady potentials. It is of interest to note in this connection that Belcher, Gibbons and West observed that although permanganate was decolorized in the cold by uranium^{IV}, no change in the oxidation potential of the system occurred. It may also be noted that even the reaction between uranium^{IV} and iron^{III} is reported to be rapid at room temperature, although the potentiometric titration of iron^{III} by uranium^{IV} requires a higher temperature. Rodden[5] has recorded the observations of Korach, Nessle, Sinclair and Casto on this reaction and writes as follows:—"The rate of oxidation of uranium^{IV} by iron^{III} in 5% sulphuric acid has been studied by means of the absorption maximum of uranium^{IV} at 650 mμ. Since it was found that the rate of oxidation is faster than the time of addition and the absorption measurements (approximately 1 min), it appears that titrations at room temperature would be feasible if some method could be found to speed the rate of establishment of potential equilibrium at the electrode."

Ferroïn was first used by Willard and Young[6] as an internal indicator for the cerimetric titration of uranium^{IV}. They found that it was necessary to raise the temperature to 50° to obtain a sharp end-point. Birnbaum and Edmonds[7] investigated the use of this indicator further and found that it does not function properly at 50°, because of its dissociation at the higher temperature. The pink colour fades perceptibly long before the end-point is reached, They found that in titrations where the approximate titre is not known, the ceric sulphate has to be added slowly, and the colour fades entirely, so that it is necessary to add more indicator near the end of the titration. Moreover, it becomes necessary to protect the solution from aerial oxidation. Birnbaum and Edmonds[7] are of the opinion that the titration at room temperature is unsatisfactory, apparently because of the slowness of the reaction between the ceric ion and quadrivalent uranium. These authors observed that in the presence of phosphoric acid the titration at room temperature gives a sharp end-point. In contrast to the earlier workers, Sill and Peterson[8] recently stated that the reaction between cerium^{IV} salt and uranium^{IV} is very rapid at room temperature. They found that "Sulphatoceric acid can be added to a dilute sulphuric acid solution of uranium^{IV} at the full speed of delivery of the burette without producing the yellow colour of excess of cerium^{IV}." Sill and Peterson adduced evidence in favour of the view that the beneficial action of phosphoric acid observed by Birnbaum and Edmonds is more concerned with the catalysis of the slow reaction between uranium^{IV} and the oxidized indicator than with the rection between uranium^{IV} and cerium^{IV}. Recently Pandurango Rao, Murty and Gopala Rao[9] have confirmed the findings of Sill and Peterson.

Vogel[10] states that the titration of uranium^{IV} with ceric sulphate can be carried out at 50°, using N-phenylanthranilic acid as indicator.

Pandurango Rao, Murty and Gopala Rao[9] have recently stated that the need for a higher temperature is not because of the slow speed of the reaction between uranium^{IV} and cerium^{IV} at room temperature but because of the unsatisfactory functioning of the indicators. They have developed suitable conditions for the titration of uranium^{IV} by ceric sulphate at the room temperature, with diphenylbenzidine or N-phenylanthranilic acid as indicators using suitable catalysts. We have now investigated the use of triphenylmethane dyes as internal indicators in this tiration. The dyes tested are erioglaucine A, eriogreen B and xylene cyanol FF. We have found that the reaction between the indicator and ceric sulphate is quite rapid even in very dilute solutions. For instance, the addition of a drop of 0·01N ceric sulphate solution to 50 ml of 1·0N sulphuric acid solution, containing 0·5 ml of a 0·1% solution of the dye, changes the colour immediately from yellow to orange red. The orange-red colour is stable for about two minutes. We have also observed that the reaction between oxidised erioglaucine and uranium^{IV} is very rapid, unlike the reaction between ferrin (oxidised ferroïn) and uranium^{IV}. Similar results have been obtained with eriogreen B and xylene cyanol FF. It has also been observed by us that uranium^{IV} salt has no retarding effect on the indicator-ceric sulphate reaction or the oxidised indicator-uranium^{IV} reaction. In the light of these findings, we believe that erioglaucine A, eriogreen B and xylene cyanol FF are particularly suitable for the direct titration of uranium^{IV} with ceric sulphate at the room temperature.The transition at the equivalence point can be taken as yellow to orange-red. The indicator reactions have been observed to be simple, rapid and reversible within a wide range of acidity investigated (0·5 to 8·0*N*). We have found that in titrations with 0·05*N* ceric sulphate, the indicator correction is negligible; an indicator correction of 0·04 ml is necessary with a 0·01*N* solution of ceric sulphate. Of the three dyes tried, we found that erioglaucine A is to be preferred for it gives a more sensitive colour change than the other two. These indicators can also be used with success in hydrochloric acid solution.

Procedure

The following procedure is recommended:—To a known volume of uranium^{IV} solution taken in a conical flask, 0·50 ml of 0·1% erioglaucine solution is added. The solution is diluted and titrated with ceric sulphate with constant stirring. A sharp change of colour from yellow to orange-red indicates the end-point. Some typical values are given in Table I.

TABLE I

Amount of uranium^{IV} taken *m-moles*	Amount of uranium^{IV} found by titration with ceric sulphate *m-moles*		
	with Erioglaucine A as indicator	with Eriogreen B as indicator	with Xylene cyanol FF as indicator
0·0250	0·0252	0·0252	0·0252
0·0500	0·0502	0·0502	0·0504
0·1000	0·1006	0·1004	0·1008
0·3180	0·3188	0·3186	0·3190
0·4488	0·4496	0·4498	0·4498

Similar results have been obtained in the titration of uranium^{IV} with ceric ammonium nitrate in perchloric acid medium, using these dyes as internal indicators. We have found that they cannot be used in the titration of uranium^{IV} with ceric ammonium nitrate in 1·0 to 2·0*N* nitric acid medium. In such titrations, it has been observed that the indicator gives a green-coloured product with the addition of even one or two drops of 0·05*N* ceric ammonium nitrate solution.

The advantages of erioglaucine A, eriogreen B and xylene cyanol FF as indicators in the titration of uranium^{IV}

The preparation of the indicator solution is easy, as the dyes are readily soluble in water and the resulting solutions are stable over a long period. The reaction between the dye and ceric sulphate is quite rapid at the room temperature, as also is the reverse reaction between the oxidised indicator and uranium^{IV}. Titrations of uranium^{IV} are possible with this class of indicators in a wide range of acidity, 0·5*N* to 8·0 *N* H_2SO_4. With the other internal indicators so far investigated, *e.g.* diphenylbenzidine, N-phenylanthranilic acid, and ferroïn, the indicator reactions are not so rapid, and require the use of special conditions of acidity and the use of catalysts like phosphoric acid. These indicators can be used for the titration of uranium^{IV} even with ceric ammonium nitrate in perchloric acid medium (but not in nitric acid medium).

Acknowledgement—One of us, V. Panduranga Rao, desires to thank the Government of India for the award of a National Research Fellowship, which has enabled him to work on the problem.

Züsammenfassung—Es wird der Gebrauch von Triphenylmethanfarbstoffen, Erioglaucin, Eriogrün und Xylenolcyanol FF als innere Indikatoren der cerimetrischen Titration von Uran-IV untersucht. Die Titration ist in der Kälte mit genügender Geschwindigkeit und Genauigkeit möglich, wobei die Farbänderung des Indikators am Äquivalenzpunkt scharf eintritt. Die Reaktionen des Indikators sindschnell und im Aciditätsbereich von 0,5N bis 8,0N reversibel, im Gegensatz zu anderen schon untersuchtenIndikatoren, z.B. Diphenylbenzidin, N-phenylantranilsäure oder Ferroin, die nur unter genau bestimmten Bedingungen funktionieren-. Man kann auch die Triphenylmethan-Indikatoren bei Titration von Uran-IV mit Ceri-Ammonnitrat in Perchlorsäure, aber nicht in Saltpetersäure benutzen.

Résumé—Les colorants triphénylméthanes, érmoglaucine, ériogreen et xylene cyanole FF ont été utilisés comme indicateurs internes pour le titrage cérimétrique de l'uranium-IV. Le titrage peut s'effectuer à froid avec une rapidité et une précision suffisantes, le virage des indicateurs étant très net au point d'équivalence. Les réactions des indicateurs sont rapides et réversibles dans les limites à d'acidité assez étendues de 0,5N à 8,0N. D'autres indicateurs examinés, par exemple la diphénylbenzidine, l'acide N-phénylanthranilique et la ferroine, nécessitent, au contraire, pour être efficaces des conditions bien définies. Les indicateurs triphénylméthanes permettent également le titrage de l'uranium-IV avec le nitrate céri-ammoniaque en milieu acide perchlorique (non pas en milieu acide nitrique).

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ON THE INDUCED REDUCTION OF CHLORATE IONS

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(*Received* 13 *June* 1958)

Summary—The induced reduction of chlorate ions can be carried out only by 1-equivalent oxidising agents. As^{IV} is formed by these, and this reduces chlorate very rapidly. The properties and mechanism of the induced reduction are discussed in detail.

For the determination of chlorate ions a reliable method is given, based on this induced reduction.

IT is well known that the reaction between chloric acid and arsenious oxide is very slow, but with the aid of osmium tetroxide the reaction can be accelerated very markedly.[1] However, the catalysed reaction is not sufficiently rapid for a direct titration of chlorate ion. According to Gleu[2] the determination can be carried out only by adding arsenious acid in excess and back-titrating with ceric sulphate or potassium permanganate. During the back-titration an induced reaction takes place resulting in the instantaneous reduction of chlorate ions.

The analytical features of the reduction of chlorate were discussed in Gleu's work exhaustively, but no information about the mechanism of induced reaction was obtained. The present paper deals mainly with the mechanism of induced chlorate reduction.

EXPERIMENTAL

Reagents

$0{\cdot}1N$ arsenious acid, $0{\cdot}1N$ cerium^{IV} sulphate, $0{\cdot}1N$ potassium permanganate and $0{\cdot}1N$ potassium dichromate solutions were prepared from c.p. substances and standardised in the customary way. $0{\cdot}1N$ cobalt^{III} sulphate solution was prepared by electrolytic oxidation according to Swann and Xanthakos:[3] $0{\cdot}1N$ manganese^{III} sulphate solution by oxidation of manganese^{II} sulphate with permanganate: the stock solution of $0{\cdot}1N$ ($M/60$) potassium chlorate was prepared by dissolving Merck c.p. material: $0{\cdot}01M$ osmium tetroxide in $0{\cdot}1N$ sulphuric acid: 0·025 Ferroïn indicator solution.

Procedure

10·0 and 20·0 ml of $0{\cdot}1N$ arsenious acid solution, respectively, were acidified with an adequate quantity of 20% sulphuric acid, and 5·0 and 10·0 ml of $0{\cdot}1N$ potassium chlorate solution, respectively, were added. After adding 2 drops of osmium tetroxide as catalyst the excess of arsenious acid was titrated with one of the abovementioned oxidising standard solutions.

1. *The rate of reaction between arsenious acid and chlorate ions in presence of osmium tetroxide*

The effectiveness of OsO_4 catalyst was tested as follows: To samples consisting of 10 ml $0{\cdot}1N$ As_2O_3 + 4·96 ml $0{\cdot}1N$ $KClO_3$ + 5 ml 20% H_2SO_4 and 2 drops of $0{\cdot}01M$ OsO_4, after varying times, 5 ml $0{\cdot}1M$ H_2O_2 solution was added. The excess of arsenious acid was thus oxidised to arsenate instantaneously, and the reduction of chlorate was stopped. After this 5·0 ml $0{\cdot}1N$ $AgNO_3$ was pipetted into the solution and the excess measured with $0{\cdot}1N$ KCl solution potentiometrically. Since in acidic solution osmium tetroxide decomposes hydrogen peroxide very slowly, after the titration of the silver ions the hydrogen peroxide remaining could also be determined. The extent of reduction of chlorate ions was determined, on the one hand, by titrating the chloride ions formed, and, on the other hand, by determination of the excess of the arsenious acid. Their mean values are summarised in Table I. From the data it can be seen that the catalysed reduction of chlorate is not complete even after 6 hours.

This reaction being too slow for direct determination can be accelerated by an induced reaction so as to take place instantaneously.

TABLE I. RATE OF REACTION BETWEEN ARSENIOUS ACID AND CHLORATE CATALYSED BY OSMIUM TETROXIDE

Waiting time *min*	0·1*N* $KClO_3$, *ml*		Reduction of chlorate %
	Taken	Found	
2	4·96	3·55	71·5
5	4·96	4·11	82·8
10	4·96	4·32	87·0
30	4·96	4·54	91·5
60	4·96	4·70	94·5
360	4·96	4·95	99·5

TABLE II. TITRANT, 0·1*N* CERIUM$^{\text{IV}}$ SULPHATE

Initial volume	20% H_2SO_4 *ml*	Duration of titration *sec*	0·1*N* $KClO_3$, *ml*		Difference *ml*
			Taken	Found	
50	0·5	40	9·92	10·21	0·29
50	1·0	39	9·92	10·18	0·26
50	0·5	40	9·92	10·10	0·18
50	10·0	38	9·92	10·06	0·14
50	20·0	43	9·92	10·00	0·08
50	20·0	30	9·92	9·95	0·03
50	20·0	41	9·92	9·99	0·07
50	20·0	103	9·92	10·05	0·13
50	20·0	124	9·92	10·07	0·15
50	20·0	194	9·92	10·12	0·20
50	20·0	40	9·92	9·98	0·06
100	40·0	40	9·92	10·53	0·61
200	80·0	38	9·92	10·73	0·81
300	120·0	40	9·92	11·06	1·17

Samples were deaerated by 1 g $KHCO_3$ before adding OsO_4.

2. *Titration with cerium$^{\text{IV}}$ sulphate solution*

Measurements carried out by cerium$^{\text{IV}}$ sulphate titration have supported Gleu's observation completely. The reduction of chlorate ions is accompanied by rapid air-oxidation, causing a considerable positive error in the amount of chlorate obtained. The magnitude of this error depends markedly on the concentration of acid and on the speed of the titration as well as on the volume of the titrated solution. The results in Table II show that on increasing the acid concentration the error is decreased; on adding 20 ml of 20% sulphuric acid (in 50 ml volume) it is less than 1%. On increasing the speed of titration the error becomes also smaller. Titrating the solution very rapidly (30 sec) the error is no longer considerable. Increasing the volume of the sample (keeping the acid concentration of the solution constant) the error increased proportionally, showing that the 1 g added $KHCO_3$ is not sufficient for the de-aeration of the larger volume.

It is known that during the reaction between arsenious acid and cerium^{IV}-sulphate air oxidation does not occur. Therefore we must examine how the reaction between arsenious acid and oxygen can take place coupled with the reduction of the chlorate ions. To a solution of the composition: 5 ml 0·1*N* $KClO_3$ + 5 ml 20% H_2SO_4 + 10 ml 0·1*N* As_2O_3 + 20 ml water, 2 drops of osmic acid catalyst were added and after exactly 120 sec the excess of arsenious acid was determined with cerium^{IV} sulphate. The time of titration was 75 sec. A positive error of 0·6 ml (12%) was found. (Table III, Experiments 1, 2, 3). When after 120 sec the absorbed oxygen was expelled from the solution by means of 2 g $KHCO_3$ (experiments 4, 5, 6) the error decreases to about one-third. On the contrary, when the solution was deaerated at the beginning, an error of only 0·2% was found (experiments 7, 8 and 9). The oxidation of the arsenious acid by atmospheric oxygen must therefore take place in the course of the reaction between arsenious acid and chlorate catalysed by OsO_4 as well as in that induced by cerium^{IV}-sulphate.

TABLE III. TITRANT, 0·1*N* CERIUM^{IV} SULPHATE

No.	$KHCO_3$ *g*		0·1*N* $KClO_3$, *ml*		Difference *ml*
	A	B	Taken	Found	
1	—	—	4·96	5·58	0·62
2	—	—	4·96	5·55	0·59
3	—	—	4·96	5·53	0·57
4	2	—	4·96	5·14	0·18
5	2	—	4·96	5·13	0·17
6	2	—	4·96	5·14	0·18
7	—	2	4·96	4·96	0·0
8	—	2	4·96	4·96	0·0
9	—	2	4·96	4·97	0·01

A: $KHCO_3$ applied 120 sec after adding the catalyst.
B: $KHCO_3$ added at the beginning.

Recently the determination of chlorate ions in the presence of a large amount of perchloric acid has been carried out by Smith and Veraguth[4] according to Gleu's procedure and no oxidation by atmospheric oxygen was observed at all. Checking this observation, it was found that perchlorate ions are completely inactive, but that the presence of large amounts of perchloric acid (due to the great hydrogen ion concentration) markedly decreases air-oxidation. However, in the presence of 1·0*N* acid a considerable positive error was still observed.

During the induced reduction of chlorate a strong smell of chlorine dioxide was observed and in the initial stage of titration the solution also remains weakly yellow in colour after the reduction of cerium^{IV} ions. In the course of the catalysed reaction between chlorate ions and arsenious acid the formation of chlorine dioxide is also observed, but its amount is very small compared with that formed during the induced reduction.

Halide ions inhibit the induced reduction of chlorate ions. An equivalent effect is exerted by 0·05 ml of 0·1*N* KI, 2·0 ml of 0·1*N* KBr and 20 ml of 0·1*N* KCl. The order of effectiveness is therefore $I^- > Br^- > Cl^-$ (at about 400 : 10 : 1). This agrees with the order observed in the catalysis of the reaction between arsenious acid and cerium^{IV} sulphate.[5]

3. *Titration with potassium permanganate*

The induced reduction of chlorate can also be carried out by titrating it with potassium permanganate. A striking difference in comparison with the titration with cerium^{IV} sulphate is that the induced reduction is considerably slower. Quantitative reduction of chlorate ions is not attained, by rapid titration (Table IV, Column A) while in the determinations with cerium^{IV} sulphate the reduction is complete even in the case of a more rapid titration (Table II.).

Recently we have observed[8] that the difference between the reactions of cerium^{IV} sulphate and permanganate is chiefly due to the fact that the Ferroïn indicator acts as a catalyst, and accelerates the reaction of cerium^{IV} ions. Consequently experiments were carried out to determine whether the difference in the rate of the reduction of the chlorate is caused by the catalytic characteristics of the Ferroïn. As can be seen from Table IV, column B, Ferroïn accelerates the reduction of chlorate but there still remains an additional difference between the titrations carried out with permanganate and cerium^{IV} sulphate.

Table IV. Titrant, 0·1N potassium permanganate

Duration of titration *sec*	0·1N $KClO_3$, *ml*			Difference, *ml*	
	Taken	Found			
		A	B	A	B
42	9·92	9·35	9·87	−0·57	−0·11
73	9·92	9·84	9·96	−0·08	+0·04
90	9·92	10·17	10·17	+0·25	+0·25
170	9·92	10·27	10·34	+0·35	+0·42

A: without Ferroïn indicator.
B: in presence of 1 drop 0·025M Ferroïn solution.

Otherwise the characteristics of the titration with permanganate agree qualitatively very well with those of the titration with cerium^{IV} sulphate. Strong air oxidation also takes place and this depends in the same way on the experimental conditions.

4. *Titrations by means of* Br_2, $KBrO_3$, Cl_2, KIO_4 *cobalt*^{III} *and manganese*^{III} *sulphate solutions*

Using Br_2 or $KBrO_3$ solutions, for the back-titration of the excess arsenious acid, reduction of chlorate takes place only to an extent of 70%. This fact is in good agreement with the results in Table I. On this basis it may be concluded that the reaction of arsenious acid with Br_2 or with $KBrO_3$, cannot induce the reduction of chlorate ions.

Similarly when the back-titration of the arsenious acid is carried out with Cl_2 or KIO_4 solutions, the chlorate reduction is only 70%. Since each of these reagents oxidises in 2-equivalent steps, it appears that *the induced reduction of chlorate ions cannot take place with 2-equivalent reagents.*

Cerium^{IV} sulphate, which is very effective, always oxidises with 1-equivalent; potassium permanganate can also react in 1-equivalent steps. Thus it is possible that the induced reduction of chlorate ions can be carried out by means of other 1-equivalent reagents. To examine this, titrations with cobalt^{III}, manganese^{III} sulphate and dichromate solutions were carried out.

From the results summarised in Table V, it is apparent that the cobalt^{III} and manganese^{III} ions behave as very strong inducing agents. Quantitative chlorate reduction is attainable when arsenious acid is used in only 20% excess. In the case of both reagents, but particularly with manganese^{III} sulphate, strong chlorine dioxide evolution can be observed. The inducing effect of potassium dichromate (which also can oxidise with 1-equivalent) was found very poor.

Finally it was found that silver^{I} ions accelerate the reduction of chlorate ions. When to a solution containing chlorate and arsenious acid, in which silver nitrate is present, osmium tetroxide is added, sudden precipitation of AgCl is observed. In the presence of silver ions, in 2 minutes, chlorate ions were reduced to an extent of about 90%, while without silver the reduction is only about 70%. A few seconds after the addition of osmium tetroxide the precipitate becomes brownish. This tint completely disappears during 30–40 sec and the solution becomes milk-white due to the silver chloride formed.

It is worth noting that in the presence of silver^{I} ions the oxidation of arsenious acid by atmospheric oxygen decreases considerably (Table VII).

TABLE V

	0·1N As_2O_3 *ml*	0·1N $KClO_3$, *ml*		Difference *ml*
		Taken	Found	
A	20·00	9·92	10·12	+0·20
	15·00	9·92	10·06	+0·14
	12·00	9·92	10·05	+0·13
	20·00	9·92	9·90*	−0·02
B	20·00	9·92	10·46	+0·54
	15·00	9·92	10·23	+0·31
	12·00	9·92	10·13	+0·21
	20·00	9·92	9·94*	+0·01

A: Titrant, 0·1N $Mn_2(SO_4)_3$. B: Titrant, 0·1N $Co_2(SO_4)_3$.
* Oxygen expelled before measurement by means of $KHCO_3$.

TABLE VI. TITRANT, 0·1N POTASSIUM DICHROMATE

Waiting time *min*	0·1N $KClO_3$, *ml*		Reduction of chlorate %
	Taken	Found	
2	9·92	8·69	87·5
5	9·92	9·33	94·0
10	9·92	9·65	97·2
60	9·92	9·90	99·7

Since the rate of reaction between arsenious acid and potassium dichromate under the experimental conditions is not sufficiently rapid for a direct titration, the reaction between chlorate and arsenious acid was stopped after the given waiting time by adding potassium dichromate in excess and back-titration potentiometrically with arsenious acid.

TABLE VII. TITRANT 0·1N CERIUM^{IV} SULPHATE

0·1N $AgNO_3$ *ml*	$KHCO_3$, *g*		0·1N $KClO_3$, *ml*		Difference *ml*
	A	B	Taken	Found	
—	—	—	4·96	5·55	+0·59
—	—	2	4·96	4·96	0·0
5	—	—	4·96	5·11	+0·15
5	—	—	4·96	5·10	+0·14
5	—	—	4·96	5·11	+0·15
5	2	—	4·96	5·07	+0·11
5	2	—	4·96	5·08	+0·12
5	2	—	4·96	5·06	+0·10
5	—	2	4·96	4·96	0·0
5	—	2	4·96	4·98	+0·02
5	—	2	4·96	4·95	−0·01

A: $KHCO_3$ added 2 min after OsO_4. B: $KHCO_3$ added before OsO_4 catalyst.

DISCUSSION

The reaction between arsenious acid and chlorate ions has been found to be bimolecular by Stefanovskii and Zan'ko.[7]

$$HClO_3 + As^{III} \rightarrow HClO_3^- + As^{IV}$$

This equation offers an adequate explanation of the observations by Rutter[8] and by McDougall,[9] that during the reaction chlorine dioxide forms. Alternatively arsenious acid may reduce the chlorate to chlorite, the chlorous acid then giving chlorine dioxide in a rapid reaction:

$$HClO_2 + HClO_3 \rightarrow 2ClO_2 + H_2O$$

The formation of As^{IV} during the reaction between the chlorate ions and arsenious acid on the basis of Gleu's observation must be considered to be possible. Gleu[10] found that during the reaction between arsenious acid and chlorate catalysed by osmium tetroxide, vanadate is reduced to vanadium^{IV}. As arsenious acid cannot reduce vanadate even in the presence of osmium tetroxide, it is reasonable to suppose that the inducing reaction produces As^{IV}, which is more effective than As^{III}.

To elucidate the mechanism of the induced reduction of the chlorate the inducing reaction between cerium^{IV} and arsenious acid must be examined. According to Stefanovskii[11] the rate-determining step of this reaction is bimolecular, and arsenite will be oxidised to AsO_2. Recently the cerium^{IV} arsenious acid reaction was re-investigated by Moore and Anderson,[12] who found that within a small range of concentration (0·0122–0·0230 mol/l cerium^{IV}) the reaction is 3rd order. Although the values of the termolecular rate constant vary considerably on changing the experimental conditions (*e.g.* with change of concentration) yet according to Moore and Anderson the postulation of the formation of As^{IV} is not permissible.

Although kinetic data do not furnish a satisfactory decision, we are of the opinion that to postulate the formation of As^{IV} is justified, because of the inducing effect of the reaction mentioned. The results obtained prove unequivocally that inducing effects are shown only by 1-equivalent reagents, while 2-equivalent reagents are inactive. The production of As^{IV} is also supported by the observation that during the inducing reaction chlorine dioxide is evolved in considerable quantity. Evolution of chlorine dioxide is also observed in every case where chlorate is attacked with 1-equivalent reducing agents (*e.g.* with vanadium^{III}).

In our opinion during the inducing reaction the As^{IV} formed reduces the chlorate very rapidly to chlorine dioxide. The chlorine dioxide reacts with arsenious acid relatively slowly and according to Bray[13] chlorite ions forms. During this latter reaction As^{IV} formed reduces the chlorite to ClO, from which finally chloride will be obtained.

It was mentioned that halide ions inhibit the induced reduction of chlorate. This effect can be explained by a change in the mechanism of the reaction between cerium^{IV} and arsenious acid: that is, that the ceric ions oxidise the iodide, bromide and chloride ions into iodine, bromine and chlorine; the free halogens then convert arsenite into arsenate directly and rapidly. Therefore the presence of halide ions decreases and (when a suitable quantity is present) exclude the formation of As^{IV}. Consequently the induced reduction of chlorate ions decreases or is prevented.

During the induced reduction of chlorate, strong oxidation by atmospheric oxygen can be observed. On the contrary, in the course of the reaction between arsenious acid and cerium^{IV} there is no oxidation by air. Therefore it appears that As^{IV} is not a sufficiently strong reducing agent to attack molecular oxygen. Considering the behaviour of As^{IV} in the induced reduction, it can be said that the standard oxidation potential of the As^{IV}/As^{V} couple is about 0·3–0·4 V. By analogy with the corresponding couples of antimony the same value can be deduced.

As As^{IV} is inert from the point of view of the reaction with the O_2 molecule, one of the reduction products of the chlorate ion must be responsible for the observed strong oxidation by air. This is supported by the fact that the oxidation by air, *i.e.* the extent of the positive error, is proportional to the progress of the induced reduction.

Chlorate, chlorine dioxide and chlorite ions are inactive toward atmospheric oxygen, while the ClO radical easily reacts with oxygen, according to the reaction

$$ClO + O_2 \rightleftharpoons ClO_3$$

which is about thermoneutral (Szabó[14]). The ClO_3 formed in all probability can be reduced more easily than chlorate.

In our opinion the effect of silver salts is to accelerate the reduction of chlorite ions to chloride. In consequence of this catalysis, there is only a very small amount of ClO, or none, formed from the chlorite. In the absence of oxygen-carrying substance, due to the presence of silver ions, the oxidation by atmospheric oxygen must be ruled out.

Our conception of the induced reduction of chlorate may be summarised in the following scheme:

Inducing reaction:

$$Ce^{IV} + As^{III} \rightarrow Ce^{III} + As^{IV}$$

Induced reactions:

(1) $$HClO_3 + As^{IV} \rightarrow As^{V} + HClO_3^- \rightleftharpoons ClO_2 + OH^-$$

(2) $$ClO_2 + As^{III} \rightarrow As^{IV} + ClO_2^-$$

(3) $$HClO_2 + As^{IV} \rightarrow As^{V} + HClO_2^- \rightleftharpoons ClO + OH^-$$

(4) $$2\,ClO + 4H^+ + 3As^{III} \rightarrow 2Cl^- + 2H_2O + 3As^{V}$$

Induced oxidation by air:

$$ClO + O_2 \rightleftharpoons ClO_3$$

$$ClO_3 + 6H^+ + 3As^{III} \rightarrow Cl^- + 3As^{V} + 3H_2O$$

Finally, the accelerating and inhibiting effect of silver ions can be applied to the determination of chlorate ions to obtain more accurate data. For the titration of the chlorate ions the following procedure is recommended:

Acidify the sample containing 3–35 mg chlorate with 10–20 ml of 20% sulphuric acid, add 5–10 ml 0·1*N* silver nitrate and dilute the solution to 50–60 ml. After de-aerating the solution by means of 1–2 g $KHCO_3$, add arsenious acid in excess and 2 drops of 0·01*M* OsO_4 as a catalyst. After 1–2 min back-titrate the arsenious acid with standard cerium^{IV} sulphate solution.

Errors are as small as 0·1%.

Acknowledgement—Thanks are due to Prof. Z. G. Szabó for his kind interest in this work and the valuable discussions.

Zusammenfassung—Man kann die induzierte Reaktion von Chlorat-Ionen nur mittels 1-Äquivalent-Oxydiermittel durchführen. Mit diesen Substanzen wird Arsen(IV) gebildet, und dies reduziert Chlorat sehr rasch. Die Eigenschaften und Mechanik der induzierten Reaktion werden umständlich erörter. Zur Bestimmung von Chlorat-Ionen wird eine zuverlässige auf dieser induzierten Reduktion basierte Methode gegeben.

Résumé—La reaction induite des ions chlorates ne s'effectue qu'en présence des oxydants "l-équivalent". Au moyen de ces réactifs on obtient l'arsenic-IV qui réduit très rapidement les ions chlorates. On discute en détail les propriétés et la mechanisme de la réaction induite.

On décrit une méthode sûre de dosage des ions chlorates basée sur cette réaction induite.

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SPOT TEST DETECTION OF PHENYLHYDRAZINE AND ARSONIC ACIDS*

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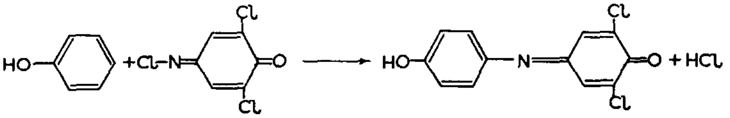
(*Received* 13 *May* 1958)

Summary—If phenylhydrazine or its salts are heated with arsenic acid or with one of its organic derivatives (aliphatic or aromatic arsonic acids) phenol results. The latter can easily be detected in the gas phase by the indophenol reaction with 2:6-dichloroquinone-4-chloroimine. This has been made the basis of characteristic tests for phenylhydrazine (also phenylhydrazones and osazones) as well as for arsonic acids. When conducted within the bounds of spot test analysis, the limits of detection are microanalytical.

IT has been shown elsewhere[1] that the indophenol reaction of phenols with 2 : 6-dichloroquinone-4-chloroimine[2] discovered by Gibbs[3] may be employed in spot test analysis for the detection of volatile phenols or of phenols that are being carried along by water vapour. The condensation



can be accomplished for analytical purposes by allowing the phenol vapours to come into contact with filter paper which has been impregnated with the reagent by bathing the paper in a saturated benzene solution of the imine. Phenols produce a brown-yellow to light yellow stain on the reagent paper and on exposure to ammonia vapour the stain turns blue because of the formation of the ammonium salt of the indophenol. This colour reaction will reveal as little as 0·3 μg of carbolic acid.

The procedure provides a reliable preliminary test for aromatic compounds which contain oxygen in the nucleus or in a side chain, since such compounds almost invariably yield phenols on pyrolysis. (Certain azo dyes containing phenolic OH groups do not follow this rule.) Furthermore, it was possible to work out tests[1] for phenyl esters and phenyl ethers which were based on the finding that these compounds yield phenols through pyrohydrolysis or dealkylation at 150°. The pyrohydrolysis[2] is accomplished by heating the sample with oxalic acid dihydrate; the dealkylation ensues if the compound is heated with a mixture of potassium iodide and oxalic acid dihydrate. All of these tests can be successfully conducted within the bounds of spot test analysis.

This paper describes two additional tests in this category, based on the production of phenol.

It has long been known[4] that phenylhydrazine is oxidatively decomposed even at room temperature by arsenic acid:

$$C_6H_5NH\,NH_2 + 2H_3AsO_4 \rightarrow 2H_3AsO_3 + N_2 + H_2O + C_6H_5OH$$

---

* Translated by R. E. Oesper, University of Cincinnati, U.S.A.

If this redox reaction is conducted at 100°, the phenol is carried along with the water vapour and gives the indophenol reaction in the gas phase. An excellent test for phenylhydrazine has been constructed on this finding and the test may be extended to its condensation products with aldehydes and ketones.

It has furthermore been found that aliphatic and aromatic arsonic acids resemble their parent acid in the ability to oxidize phenylhydrazine to produce phenol. Consequently, a reliable test for arsonic acids has resulted.

I. DETECTION OF PHENYLHYDRAZINE

Procedure: One drop of the test solution is mixed in a micro test tube with a drop of concentrated arsenic acid solution. The mouth of the tube is covered with a disc of filter paper impregnated with a saturated benzene solution of 2:6-dichloroquinone-4-chloroimine and placed in a boiling water bath for 3–4 minutes. In the presence of phenylhydrazine a pale brown stain appears on the paper and turns blue when held over ammonia vapour. The blue colour is not permanent, but it can be restored by again exposing the reagent paper to ammonia vapour.

Limit of detection: 5 μg phenylhydrazine.

Phenylhydrazones and phenylosazones can likewise be detected by the above procedure.

A preliminary separation is essential if phenols are present. This is readily accomplished by shaking the alkaline test solution with an organic liquid which is immiscible with water (ether, benzene, etc.). The phenolate remains in the water layer.

II. DETECTION OF ARSONIC ACIDS

Procedure: A little of the solid or 1 drop of its aqueous solution is placed in a micro test tube along with an additional drop of water and several cg of phenylhydrazine hydrochloride. The mouth of the test tube is covered with a disc of filter paper that has been bathed in a saturated benzene solution of 2:6-dichloroquinone-4-chloroimine. The tube is kept in a boiling water bath for about 5 minutes. The paper is then exposed to strong ammonia vapour. A positive response is indicated by the development of a blue stain.

The procedure revealed:

5 μg *p*-aminophenylarsonic acid
5 μg *p*-hydroxyphenylarsonic acid
10 μg *p*-dimethylamino-azo-phenylarsonic acid

Zusammenfassung—Bei Erwärmung von Phenylhydrazin und dessen Salzen mit Arsensäure oder deren organischen Derivaten (aliphatische und aromatische Arsonsäeuren) entsteht Carbolsäeure, die in der Gasphase durch die Indophenolreaktion mit 2,6-dichloroquinone-4-chlor-imin empfindlich nachweisbar ist. Dies ermöglicht charakteristische Nachweise von Phenylhydrazin (auch Phenylhydrazone und Ozazone), sowie von Arsonsäuren, die in der Technik der Tüpfelanalyse ausgeführt mikroanalytische Erfassungsgrenzen besitzen.

Résumé—En chauffant la phénylhydrazine ou ses sels avec de l'acide arsénique ou avec un de ses dérivés organiques (acides arsoniques aliphatiques ou aromatiques) on obtient du phénol. On peut facilement déceler en phase gazeuse ce dernier comme indophénol par réaction avec la 2:6-dichloroquinone-4-chloroimine. On a également utilisé cette réaction comme base des essais caractéristiques pour la phénylhydrazine (et pour les phénylhydrazones et les osazones) ainsi que pour les acides arsoniques. Lorsque l'on opère dans les conditions de l'analyse à la touche les limites de détection sont microanalytiques.

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Talanta, 1958, Vol. 1, pp. 369–373. Pergamon Press Ltd., London.

DETERMINATION OF VANADIUM IN HIGH ALLOY STEELS BY ISOTOPE-DILUTION

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(*Received* 7 *July* 1958)

Summary—An isotope-dilution method has been developed for the determination of vanadium in high-alloy steels. Vanadium is titrated amperometrically after removal of chromium as chromyl chloride. Vanadium losses due to adsorption were corrected for radiometrically. The procedure was tested on N.B.S. steel samples and showed good precision and accuracy.

IN the analysis of tungsten-containing high alloy steels, vanadium, among other elements, is adsorbed on the precipitate of tungstic acid that is formed during solution of the sample. For accurate results it would therefore be necessary to analyse the precipitate as well as the solution for vanadium content. An isotope-dilution procedure, however, readily permits a correction for vanadium losses in the precipitate to be made. As a gravimetric determination is rather impracticable, an amperometric procedure has been used for the determination of the vanadium content of the solution.

Choice of method

As an amperometric titration is sensitive as well as accurate, this method was chosen for the determination of vanadium. The procedure adopted has been studied by Parks and Agazzi[1] and by Rulfs and coworkers.[2]

V^V is titrated with Fe^{II} after first being oxidised by means of $KMnO_4$ in slight excess. Parks and Agazzi destroy the excess of permanganate by means of NaN_3, whereas Rulfs uses $NaNO_2$-urea. From results on pure vanadium solutions in perchloric acid medium it appears that $NaNO_2$-urea is to be preferred, as NaN_3 often gives rise to intermediate manganese oxides which are reduced only with difficulty.

EXPERIMENTAL

Apparatus

Micro-platinum anode, 5 mm long, wire gauge 25, driven by a synchronous motor at 360 rpm.

Standard Calomel Electrode as reference connected through a 3% $(NH_4)_2SO_4$ bridge to the solution to avoid interference of chloride ions.

Kipp No. A70 galvanometer.

Tracerlab Superscaler and P20–A well-type NaI(Tl) detector.

5-ml microburette.

Reagents

0·01*N* ferrous ammonium sulphate stock solution in 2% H_2SO_4, standardised against $K_2Cr_2O_7$. The normality of this solution is kept constant by inserting an aluminium wire in the stock solution.[3]

0·01*N* NH_4VO_3 stock solution in 2% H_2SO_4 standardised by potentiometry and amperometry against ferrous ammonium sulphate solution. Before titration the vanadium is oxidised with $KMnO_4$, as the solution is slowly reduced to the V^{IV} state.

Amperometric titration

In a series of determinations made on pure vanadium solutions, accurate results were obtained using a polarising voltage of 0·85 volts measured against the S.C.E. For vanadium solutions containing 4 μ equivalents/50 ml to 40 μ equivalents/50 ml the mean deviation was better than 0·45%; the accuracy always being better than 1%.

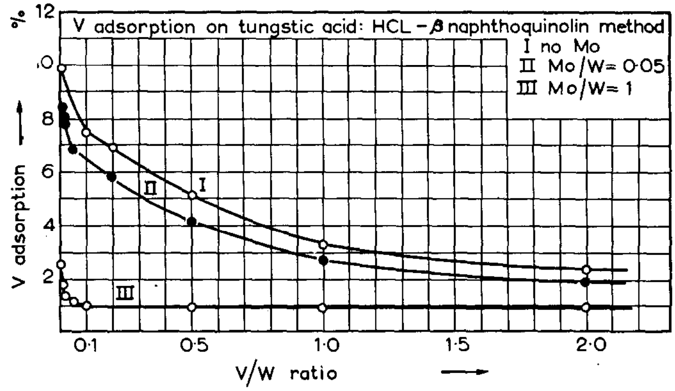

FIG. 1.

Tracer vanadium

Carrier-free ^{48}V ($t_{\frac{1}{2}}$ = 16·2d; β^+ : 0·69; γ : 0·99, 1·32, 2·23 MeV) was used as a tracer. This isotope was prepared by the bombardment of a titanium target with 12-MeV deuterons in the Louvain cyclotron. The procedure for the carrier-free separation of ^{48}V has already been described.[4] A modification of this procedure using di-*iso*butyl ketone will be reported in detail elsewhere.

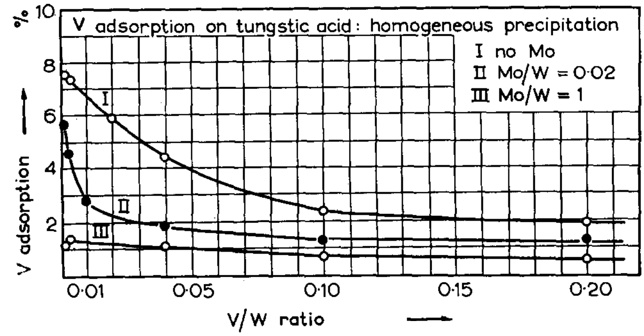

FIG. 2.

Vanadium adsorption on tungstic acid

Tracer vanadium was used to study the importance of the adsorption on the tungstic acid precipitate. The tungstic acid was precipitated by the method of Claeys[5] with β-naphthoquinoline, as this reagent is preferable to the generally used cinchonine. In these experiments 100 mg tungsten (as tungstate) were used, to which increasing amounts of vanadium carrier were added as well as a constant activity of carrier-free ^{48}V. The results are summarized in Fig. 1. It appears that the vanadium adsorption is closely dependent on the vanadium-molybdenum ratio, as well as on the vanadium-tungsten ratio. A high molybdenum content to reduce the vanadium adsorption.

As the presence of organic material is to be avoided in the subsequent titration of vanadium, and since a quantitative precipitation of tungsten is not required, the adsorption of vanadium on tungsten was also studied using perchloric acid in the presence of hydrogen peroxide on 100-mg amounts of tungsten. In this case a solution of pertungstate is obtained which slowly decomposes on heating and causes homogeneous precipitation of tungstic acid. As can be seen from Fig. 2, vanadium adsorption is considerably reduced but is still quite important. Accurate results can therefore not be obtained if the solution only is analysed for vanadium content.

Interference of chromium

From amperometric titrations of synthetic samples, it appeared that large amounts of chromium interfere. For a Cr/V ratio of 250 for instance, the results are too high by 6%. This is obviously due to a partial oxidation of Cr^{III} to Cr^{VI} by the excess permanganate. Chromium was therefore separated as CrO_2Cl_2 before the titration. This can easily be achieved quantitatively by passing *dry* HCl into the hot perchloric acid solution. The use of dry HCl is necessary, as aqueous HCl causes reduction of Cr^{VI} to Cr^{III}. Tracer experiments with ^{51}Cr showed that the removal was quantitative after 10 minutes.

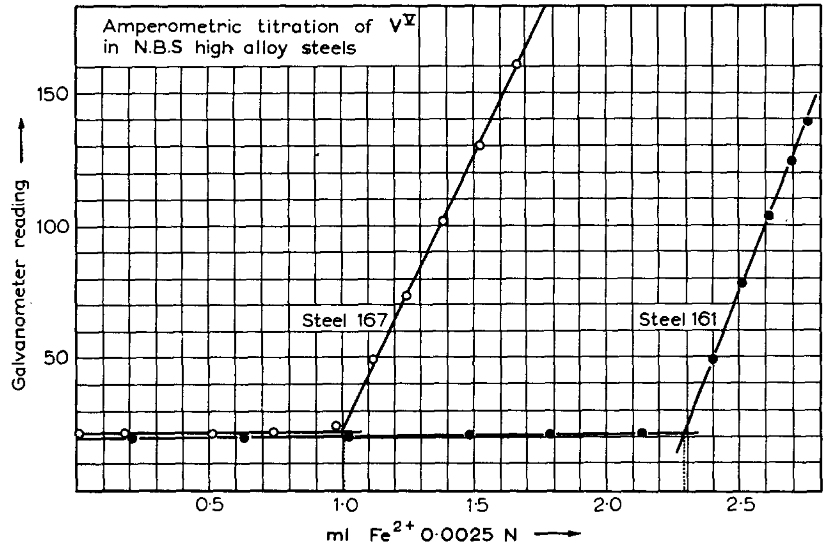

FIG. 3.

Procedure

0·1 to 1 g of steel turnings is dissolved in 30 ml of concentrated HCl. After the reaction has subsided 20 ml of HNO_3 ($d = 1·40$) are added and the solution is evaporated on a hot plate. 30 ml of $HClO_4$ are added to the residue and the solution is taken to fumes, eliminating HCl and HNO_3. The solutuoi and the precipitate are transferred quantitatively into a platinum dish together with 4 ml HF, and a suitable amount of carrier-free ^{48}V is added (about 500,000 counts/min). The precipitate, consisting mainly of hydrates of SiO_2, WO_3, Nb_2O_5, Ta_2O_5, TiO_2 and adsorbed elements, goes into solution on heating. The solution is taken to fumes again, driving out HF as well as SiF_4, and causing precipitation of the insoluble acids. After dilution with approximately 20 ml of water, the solution is filtered into a 250-ml beaker through an asbestos filter and again evaporated to fumes of $HClO_4$ on a hot plate. 20 Ml of $HClO_4$ are added and *dry* HCl gas is passed through the boiling solution for about 10 minutes eliminating chromium as brown fumes of CrO_2Cl_2. After the removal of the chromium, boiling is continued to remove HCl and the solution is finally diluted with water to approximately 50 ml. A few drops of 1% ferrous sulphate in 2% H_2SO_4 are added to reduce vanadium to V^{IV}. 0·05*N* $KMnO_4$ is then added in just enough excess to give a slightly pink colour. The excess $KMnO_4$ is destroyed after standing 5 minutes at 20° by adding 2–3 drops of 2% $NaNO_2$ followed by 500 mg of urea. Vanadium is then titrated amperometrically with *ferrous sulphate* added from a micro-burette. (The normality of the ferrous sulphate solution varied from 0·0025*N* to 0·025*N* depending on the vanadium content of the sample.) The rotating Pt electrode should not be introduced into the solution before the removal of the excess $KMnO_4$. A typical titration is represented in Fig. 3.

After the titration the solution is partially evaporated, transferred to a 50-ml graduated flask and diluted to the mark. 4 Ml of this solution are counted in the well-type detector.

TABLE I. DETERMINATION OF V IN HIGH-ALLOY STEELS

NBS steel	NBS results		Isotopic dilution analysis		
	mean value $\overline{m}$	mean error $\overline{\Delta}$	%V found	mean value $\overline{m}$	mean error $\overline{\Delta}$
132_{A}[a]	1·94%	0·009%	1·931	1·93^{1}%	0·008%
			1·940		
			1·942		
			1·928		
			1·913		
153[b]	2·04	0·022	2·02^{4}	2·04^{7}	0·02^{6}
			2·07^{8}		
			2·04^{7}		
			2·08^{1}		
			2·00^{7}		
123_{B}[c]	0·05 provis. certif.		0·054	0·053	0·001
			0·052^{3}		
			0·055		
			0·055		
			0·053		
101_{D}[d]	0·049	0·0022	0.049^{1}	0·048^{8}	0·0007
			0·047^{4}		
			0·048^{3}		
			0·049		
			0·050		
161[e]	0·029	0·005	0·030^{6}	0·030^{7}	0·000^{3}
			0·030^{6}		
			0·031^{1}		
			0·031^{1}		
			0·030^{1}		
167[f]	0·01 provis. certif.		0·0080^{7}	0·0080^{7}	0·0000^{9}
			0·0082^{6}		
			0·0080		
			0·0079^{6}		

Composition in % according to N.B.S. certification

[a] Mn 0·268; Ni 0·137; Cr 4·21; Mo 4·51; W 6·20

[b] Mn 0·219; Ni 0·107; Cr 4·14; Co 8·45; Mo 8·39; W 1·58

[c] Mo 0·17; W 0·18; Ta 0·20; Nb 0·75

[d] Mn 0·39; Ni 9·05; Cr 18·68; Co 0·058; Mo 0·11

[e] Mn 1·28; Ni 64·3; Cr 16·9; Co 0·47; Mo 0·005

[f] Mn 1·64; Ni 20·65; Cr 20·00; Co 42·9; Mo 3·90; W 4·50; Ta 0·08; Nb 3·75.

Calculation of the results

The V content of the sample is given by:

$$\%\mathrm{V} = \frac{50{\cdot}95}{10\,.\,a}\left[\frac{v\,.\,t}{1-\alpha}\right]$$

where t = normality of the ferrous solution,
a = sample weight in g,
v = volume in ml of ferrous sulphate,

$$1-\alpha = \frac{A_x \cdot 50}{A_{\mathrm{tot}} \cdot 4} = \text{fractional vanadium yield:}$$

A_{tot} = total activity of ^{48}V added:
A_x = activity of ^{48}V in the 4-ml sample.

TABLE II. DETAILED SURVEY OF THE ISOTOPE-DILUTION ANALYSIS OF NBS STEEL 167

a_g	${}^{v}\mathrm{Fe}^{\mathrm{II}}$, *ml*	% V uncorrected	$(1 - \alpha)$	% V corrected	NBS results
2000·2	1·003	$0{\cdot}0064^9$	0·804	$0{\cdot}0080^7$	0·01 provis. certif.
2009·5	1·026	$0{\cdot}0065^9$	0·800	$0{\cdot}0082^6$	
2000·2	1·023	$0{\cdot}0066^0$	0·827	$0{\cdot}0080^0$	
2000·1	0·881	$0{\cdot}0057^0$	0·716	$0{\cdot}0079^6$	
		$\overline{m} = 0{\cdot}0063^5$ $\overline{\Delta} = 0{\cdot}0003^2$		$\overline{m} = 0{\cdot}0080^7$ $\overline{\Delta} = 0{\cdot}0000^9$	

RESULTS

The procedure described was tested on a number of U.S. National Bureau of Standards high-alloy steel samples.

Results are summarized in Table I and a detailed survey of NBS steel 167 is given in Table II.

Acknowledgements—Thanks are due to the Louvain and Amsterdam cyclotron groups for irradiation facilities given, and to Dr. W. C. Orr, who corrected the English of the manuscript.

Zusammenfassung—Er wird eine Isotopenverdünnungsmethode ausgearbeitet zur Bestimmung von Vanadin in hochlegierten Stahlen. Das Vanadin wirt amperometrisch titriert nach Verflüchtigung vom Chrom als Chromyl-chloride. Die Vanadin Verluste durch Adsorption sind radiometrisch korrigiert worden.

Die Methode, geprüft an einer Anzahl NBS Stahlen, erwies sich als genau und reproduzierbar.

Résumé—On a mis au point une méthode de dosage du vanadium dans les aciers hautement alliés.

La méthode est basée sur une titration ampérométrique, le chrome étant éliminé comme CrO_2Cl_2.

Une correction radiométrique pour les pertes de vanadium dues à l'adsorption a été introduite au moyen de ^{48}V. Les résultats obtenus avec des aciers du NBS démontrent que la méthode est précise et reproductible.

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A SPECTROPHOTOMETRIC METHOD OF DETERMINING SULPHURIC ACID CONCENTRATION*

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(*Received* 28 *July* 1958)

Summary—A spectrophotometric method of determining the per cent sulphuric acid in the concentration range 85 to 99% sulphuric acid was developed. It provides a rapid easy way of determining the concentration of sulphuric acid to within about ±0·3%. Quinalizarin is used as the colour-forming reagent.

A SPECTROPHOTOMETRIC method of determining the per cent sulphuric acid in the concentration range from 85 to 99% sulphuric acid has been developed. It involves the use of 1:2:5:8-tetrahydroxyanthraquinone (quinalizarin) as the reagent. The absorption spectra of quinalizarin dissolved in various concentrations of sulphuric acid shows absorbance maxima at 537 mμ, 575 mμ and 605 mμ and an isosbestic point at 585 mμ. The addition of water to the system increases the absorbance at 537 mμ and 575 mμ and decreases it at 605 mμ (Fig. 1).

The relationship between the ratios of absorbance at certain chosen wavelengths and the concentration of sulphuric acid has been studied to determine the best wavelengths to use.

EXPERIMENTAL

The exact concentration of quinalizarin used was not important since the ratio of the absorbances at two wavelengths is a constant for varying concentrations of coloured materials. Enough quinalizarin was used to ensure that the absorbance was within the measurable range on the spectrophotometer. Measurements of absorbance were made using a Beckman model B spectrophotometer. Ratios of the absorbances at the following pairs of wavelengths were determined and plotted versus per cent sulphuric acid: 535 mμ and 600 mμ, 535 mμ and 630 mμ, 575 mμ and 600 mμ.

The ratio of the absorbances at 535 mμ and 630 mμ gives the graph with the most favourable slope. A smooth curve is obtained from 85 to 99% sulphuric acid. The ratio reaches a minimum between 99 and 99·5% sulphuric acid and then increases sharply as the concentration of sulphuric acid is increased.

The ratios of absorbances were determined from three sets of experimental values for each acid concentration used. The acid concentration of each sample was determined by the titration of aliquot samples with standard sodium hydroxide. All of the experimentally determined points fell on the curve within ±0·3% of the acid concentration (Fig. 2).

This method provides a rapid, easy way of determining the concentration of sulphuric acid to within about ±0·3% sulphuric acid in the concentration range, 85 to 99% by weight.

Procedure

After a calibration curve has been determined, the only manipulations required are:

1. Dissolve a small amount of quinalizarin in about 3–5 ml of the acid. (The exact amount need not be known.)

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* Abstracted from a thesis submitted by Elaine Zimmerman in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1958.

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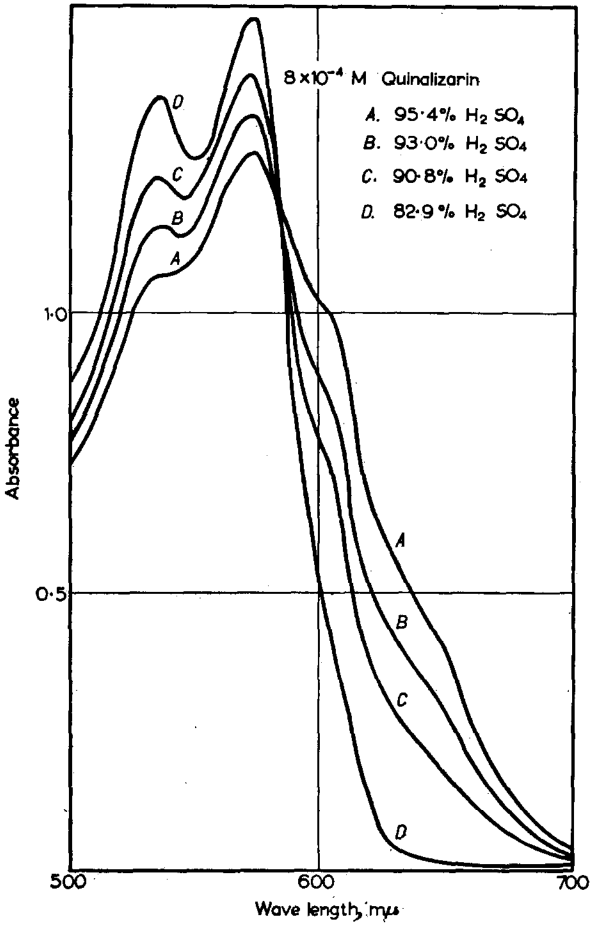

FIG. 1. Absorption spectra of quinalizarin in H_2SO_4.

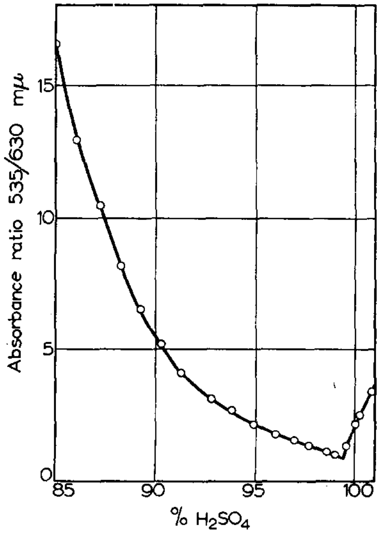

FIG. 2. Relationship between H_2SO_4 concentration and the relative absorbances of quinalizarin solutions at 535 mμ and 630 mμ.

2. Measure the absorbance of the solution at 535 mμ and at 630 mμ.
3. Calculate the ratio of the absorbances and read the percentage of sulphuric acid in the sample from the graph.

If coloured material is present in the sulphuric acid, the absorbances at 535 mμ and 630 mμ must be measured both before and after the quinalizarin is added. The ratio of the increase in absorbance at the two wave lengths is used to determine the percentage of sulphuric acid.

The presence of boric acid or borates in the sulphuric acid solution interferes. When borates are present the value for sulphuric acid concentration determined by this method is too high.

Acknowledgements—The authors wish to express their appreciation for the financial support given this project by the Standard Oil Research Foundation.

Zusammenfassung—Es wird eine spektralfotometrische Methode zur Bestimmung des procentigen Schwefelsäure-Gehalts in der Konzentrations-Reihe von 85 bis 99% von Schwelfelsäure entwickelt. Sie liefert ein rasches und einfaches Verfahren zur Bestimmung der Schwefelsäure-Konzentration bis innerhalb ungefähr ±0·5%. Man gebraucht Chinalizarin als das farbenbildende Reagens.

Résumé—Les auteurs ont mis au point une méthode spectrophotométrique qui permet de déterminer la teneur en acide sulfurique lorsque la concentration en acide sulfurique est comprise entre 85 et 99%. Cette méthode permet de déterminer d'une façon rapide et facile la concentration en acide sulfurique avec une précision voisine de ±0,3%. Le réactif qu'on utilise pour former la coloration est la quinalizarine.

Talanta, 1958, Vol. 1, pp. 377–395. Pergamon Press Ltd., London.

ARGENTOMETRISCHE TITRATIONEN MIT REDOXINDICATION

BESTIMMUNG VON HALOGENIDEN, CYANIDEN, RHODANIDEN UND KALIUM IN GEGENWART VON VARIAMINBLAU

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(*Received* 20 *March* 1958)

Zusammenfassung—Bei der argentometrischen Bestimmung von Halogeniden, Rhodaniden, Cyaniden und Kalium kann Variaminblau als Redoxindicator vorteilhaft angewendet werden. Durch Einstellung eines geeigneten pH-Wertes zeigt es den ersten Tropfen des Silbernitratüberschusses an. Potentiometrische Messungen mit einer Platinelektrode bezeugen die potentialbestimmende Rolle des Indicators am Anfang der Titration. Das Verfahren ist auch zur Silberbestimmung mit Kaliumjodidmasslösung geeignet. Kalium bestimmt man massanalytisch durch argentometrische Titration des Tetraphenylborats in Gegenwart des Redoxindicators.

Das System Ag–Ag$^+$ verhält sich infolge seines hohen Redoxnormalpotentials (+0,80 Volt) gegenüber Redoxindicatoren des Types Variaminblau als Oxydationsmittel. Wir berichteten schon darüber wie man diesen Umstand bei der ascorbinometrischen Silbertitration verwerten kann.[1]

Das Variaminblau[2] (4-Amino-4'-methoxy-diphenylamin HCl) umwandelt im pH-Gebiet 2–6 auf Einwirkung von milden oder geringen Mengen Oxydationsmitteln zu einem chinhydronartigen stark blauen Oxydationsprodukt (III), das teilweise zu Semichinonen (IV) dissociiert. In stärker oxydierenden Lösungen umsetzt das Chinhydron (III) zu einem Chinonimin (II). In stark sauren Lösungen (pH < 2) zersetzt sich das Chinonimin (II) rasch irreversibiler Weise infolge Hydrolyse zu Chinon-mono-4-methoxyanil (V), das keine Redoxindicatoreigenschaften mehr besitzt. Über pH 6 verschwindet infolge der freien Basenbildung (VI) die Chinhydronstruktur und die Lösung wird gelb (Abb. 1).

Das Umschlagspotential des Variaminblaus ändert im pH-Gebiet 2–6 laut Gleichung

$$E_i = +0{,}712 - 0{,}058\,\mathrm{pH}$$

Durch Änderung des pH-Wertes der Lösung kann man also den Umschlagspunkt des Indicators innerhalb 364–596 mV beliebig einstellen. Das Umschlagsintervallum des Indicators erbreitet sich über ein Redoxpotentialgebiet von ±29 mV (Abb. 2.). Bei der Ermittelung dieser Daten beobachteten wir, dass die Redoxpotentiale des Systems Variaminblau Ox/Red, ähnlich dem System Chinon-Hydrochinon, sich sofort auf sehr gut definierte Werte einstellen. Diese Tatsache weist darauf, dass das System reversibel ist und sich als ein sehr guter Mediator verhält. Setzt man aus einer frisch bereiteten farblosen Indicatorlösung einige Tropfen zu einer Pufferlösung von gegebenem pH-Wert, so kann man in der Lösung mit Hilfe einer Platinelektrode sofort gut definierte Redoxpotentialwerte messen. Die reduzierte Form und die auf Einwirkung des Luftsauerstoffes sich bildende geringe Menge der oxydierten Form stellen sogleich einen Redoxpotentialwert ein, der in der noch farblosen Lösung mit 55–60 mV weniger als das Umschlagspotential beträgt.

Das Prinzip der Redoxindication über welche die vorliegende Mitteilung berichten wünscht, wird eingehender am Beispiel der argentometrischen Chloridbestimmung dargelegt.

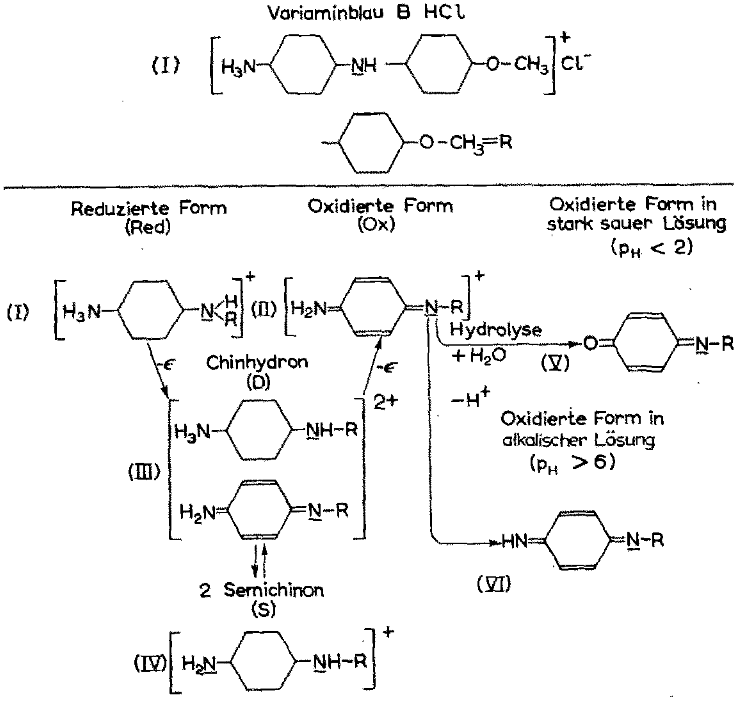

Abbildung 1. Redoxmechanismus des Indicators Variaminblau B.

Wird eine chloridhaltige Lösung mit einer Silbernitratmasslösung titriert, so nimmt die Silberionenaktivität $[Ag^+]$ der Lösung in der Nähe des Äquivalenzpunktes sprunghaft zu, demzufolge wird das Redoxpotential der Lösung im Endpunkte der Titration ebenfalls positiver. Der Redoxpotentialwert stimmt in Gegenwart von Silbermetallspuren mit dem Elektrodenpotential des Silbers überein. Man kann diesen Wert aus folgender Gleichung berechnen:

$$E = +0{,}800 + 0{,}058 \log [Ag^+]; \qquad \text{(bei } 20^\circ\text{)}$$

In neutraler und saurer Lösung ist der Elektrodenpotentialwert vom pH unabhängig. In Anwesenheit eines Chloridüberschusses berechnet man die Silberionenaktivität mit Hilfe des Löslichkeitsproduktes des Silberchlorids:

$$L = [Ag^+] \cdot [Cl^-] = 1{,}56 \cdot 10^{-10} \qquad \text{(bei } 20^\circ\text{)}$$

Das Redoxpotential des Äquivalenzpunktes berechnet aus dem Löslichkeitsprodukt des Silberchlorids beträgt

$$E_{\text{Äp}} = +0{,}800 + 0{,}058 \log \sqrt{L} = 0{,}520 \text{ Volt}$$

In Abb. 3 ist die potentiometrische Titrationskurve von 10 ml 0,1, 0,01 und 0,001 n Natriumchloridlösung zu sehen, d.h. die aus obigen Daten berechnete Abhängigkeit der Redoxpotentiale von dem Grad der Titration (τ). Führte man die potentiometrische Titrationen in Gegenwart einer Silberindikatorelektrode aus, so erhielt man genau die theoretischen Werte.

Benützt man jedoch statt einer Silberelektrode eine Platinelektrode, so sind die Potentialwerte positiver als in Abb. 3 und auch unsicherer, im Äquivalenzpunkt aber erfolgt auch in diesem Falle ein deutlicher Potentialsprung (Abb. 3). E. Müller[3] erklärt diese Erscheinung damit, dass in der Lösung in sehr geringer Menge Argentoionen (Ag_2^+) anwesend sind. Das Redoxpotential der Lösung wird durch das System Ag^+—Ag_2^+ bestimmt.*

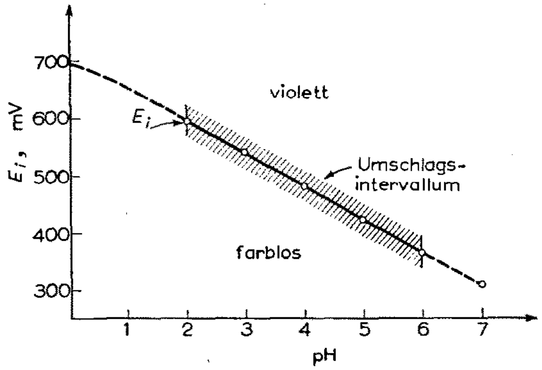

Abbildung 2. Änderung des Umschlagspotentials als Funktion des pH.

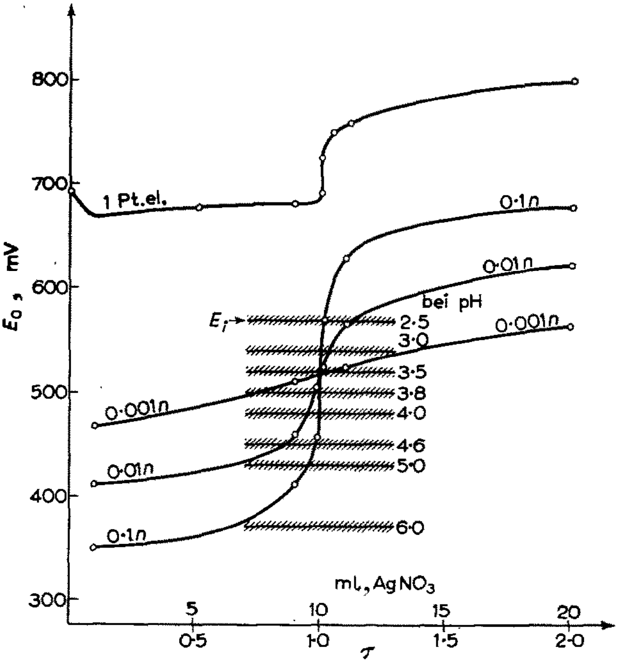

Abbildung 3. Potentiometrische Titrationskurve von Chloridionen.

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* Man gelangt zum mit Müller gleichen Resultat, wenn man annimmt, dass infolge der im Laufe der Messungen unvermeidlich eintretenden geringen Polarisation die Oberfläche der Platinelektrode mit wenig Silber legiert wird.

Den Potentialsprung des Endpunktes verursacht die sprunghafte Zunahme der Silberionenkonzentration. Besondere Verhältnisse entstehen dann, wenn die Titration in Gegenwart von Variaminblau in Anwesenheit einer Platinelektrode durchgeführt wird (Abb. 4). In diesem Falle bestimmt nämlich, solange die Chloridionen im Überschuss sind, das Variaminblau das Redoxpotential. Das als Indicator benützte reduzierte Variaminblau enthält nämlich immer eine bedeutende Menge (1—2%) der oxydierten Form. Dieses Redoxsystem übernimmt also in diesem Falle die Potentialbestimmung von dem in sehr geringer Konzentration anwesenden System $Ag^+—Ag_2^+$ Vor dem Äquivalenzpunkt hält also das Variaminblausystem ein von dem pH zwar abhängiges, aber während der Titration sehr beständiges Potential in der Lösung aufrecht. (Im Falle der Abb. 4 ungefähr 480 mV.) Diese Potentialwerte fallen immer unter das in Abb. 2 dargestellte Umschlagsgebiet. Nach dem Äquivalenzpunkt nimmt jedoch die Silberionenkonzentration sprunghaft zu, das Potential des Systems $Ag^+—Ag_2^+$ wird positiver als das des Systems Variaminblau Ox/Red, demzufolge wird das reduzierte Variaminblau oxydiert und es scheidet eine äquivalente Menge von metallischem Silber in Form eines feinen Pulvers aus:

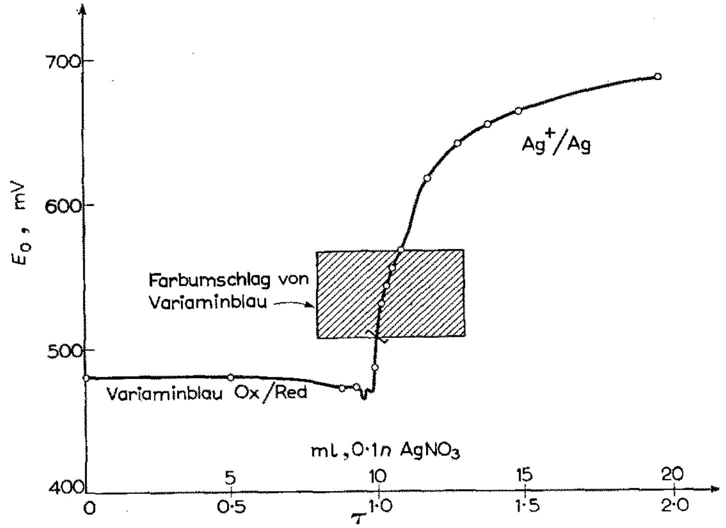

Abbildung 4. Potentiometrische Titrationskurve von Chloridionen in Anwesenheit von Variaminblau

$$\text{Variaminblau (Red)} + Ag^+ \rightleftharpoons \text{Variaminblau (Ox)} + Ag_{\text{Metall}}$$

Wird mit dem Silbernitratzusatz noch weiter verfahren, so bestimmt nun schon das System $Ag^+—Ag$ das Potential, folglich stimmen die Potentiale mit den in Abb. 3 bei $\tau > 1$ messbaren Potentialen überein.

Chlorid

Abb. 3 enthält auch die Umschlagspotentialwerte des Variaminblaus bei verschiedenen pH-Werten. Das Umschlagspotential des Indicators ist bei pH-Wert 3,6 mit dem Potential des Äquivalenzpunktes (+520 mV) gleich. Aus den Titrationskurven ist es ersichtlich, dass man in 0,1 und 0,01 n Mass die Titration auch in essigsaurer Lösung (pH ~ 3) ohne einen nennenswerten Indicatorfehler ausführen kann. In

0,001 n Mass ist es jedoch zweckmässig den pH-Wert mit einer Essigsäure-Natriumacetatpufferlösung vom pH 3,6 einzustellen. Potentiometrische Titrationen in Gegenwart des Indicators rechtfertigten diese Vorstellungen.

Wir gelangten im wesentlichen zu denselben Ergebnissen bei der Untersuchung der potentiometrischen Titrationskurven von Bromiden, Jodiden, Rhodaniden und Cyaniden. Führte man die Titrationen in Gegenwart einer Silberindicatorelektrode aus, so zeigten die Kurven einen mit dem Theoretischen übereinstimmenden Ablauf (Abb. 5, 6, 7). Im Falle der Anwendung einer Platinelektrode bestimmte vor dem Äquivalenzpunkt das System Variaminblau, danach das System Ag^+—Ag das Potential. Die Messungen zeigten, dass das Variaminblau vor dem Äquivalenzpunkt mit 55–60 mV niedrigere Potentiale gestaltet als das bei dem betreffenden pH-Wert beobachtbare Umschlagspotential; dies weist darauf, dass die Indicatorlösung 1–2 % oxydiertes Variaminblau enthält, wenn auch die Lösung noch farblos ist. Nach dem Äquivalenzpunkt stimmen die Potentiale mit den unter Anwendung einer Silberelektrode gemessenen Potentialwerten. Abb. 5, 6, 7 enthalten auch die Umschlagspotentialwerte des Variaminblaus bei verschiedenen pH-Werten.

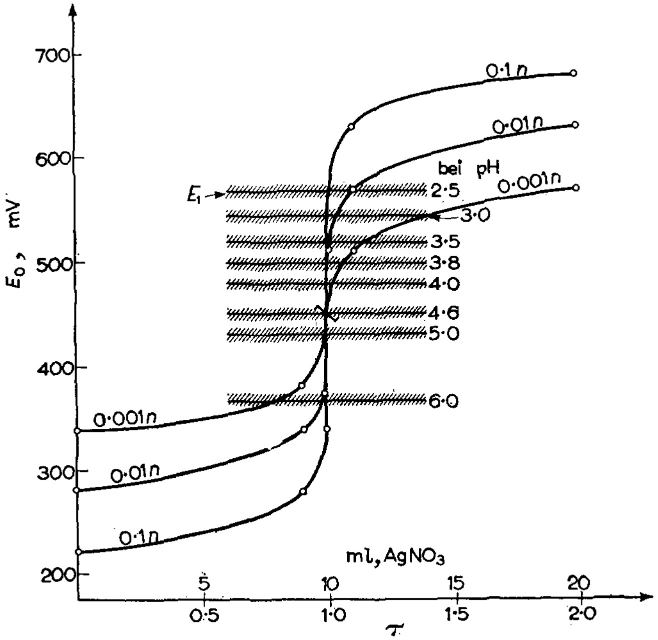

Abbildung 5. Potentiometrische Titrationkurve von Bromid- und Rhodanidionen.

Bromid und Rhodanid

Auf Grunde der Abb. 5 ist es leicht festzustellen, dass im Falle der Titration von Bromiden und Rhodaniden das Redoxpotential des Äquivalenzpunktes +460 mV beträgt, weiterhin, dass das Umschlagspotential des Variaminblaus in Lösungen vom pH-Wert 4,6 denselben Wert besitzt. Infolge der Steilheit der Titrationskurven zeigt jedoch der Indicator in Lösungen von über 0,01 n zwischen den pH-Werten 3–6, in 0,001 n Konzentration dagegen beim pH-Wert 4,5 mit befriedigender Genauigkeit (±0,2 %) den Endpunkt an. Den geeigneten pH-Wert kann man also mit Essigsäure oder im Falle von sehr verdünnten Lösungen mit einer entsprechenden Pufferlösung einstellen.

Jodid

Die potentiometrischen Titrationskurven der argentometrischen Jodidbestimmung sind in Abb. 6 dargestellt. Das Äquivalenzpotential liegt in Anwesenheit einer Silberindicatorelektrode bei +330 mV. Das Variaminblau funktioniert bei pH-Werten über 6 nicht mehr gut als Redoxindicator, deshalb kann man sein Umschlagspotential nicht auf den Äquivalenzpunkt einstellen. Da jedoch in der Nähe des Äquivalenzpunktes die Titrationskurven sehr steil verlaufen, kann man den Indicatorfehler in Lösungen zwischen den pH-Werten 3,5–6 in 0,01 n und konzentrierterem Mass vernachlässigen. In 0,001 n Lösungenzeigt das Variaminblau zwischen den pH-Werten 4,6–6 genau den Endpunkt. In Gegenwart von Standardacetatpufferlösungen kann man folglich die Titration auch in sehr verdünnten Lösungen mit befriedigender Genauigkeit (±0,2%) beenden. In 0,1 n Mass genügt ein Ansäuern mit Essigsäure.

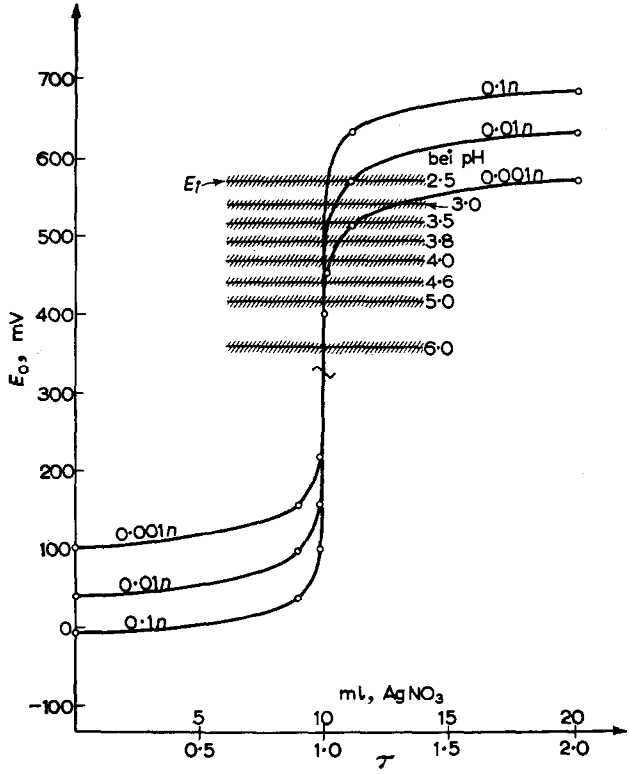

Abbildung 6. Potentiometrische Titrationskurve von Jodidionen.

Cyanid

Die neben Silberelektrode aufgenommene argentometrische Titrationskurve der Cyanide zeigt zwei scharfe Potentialsprünge (Abb. 7.) Der erste Potentialsprung kündigt den Endpunkt der Reaktion

$$2CN^- + Ag^+ = Ag(CN)_2^-$$

der zweite den von

$$Ag(CN)_2^- + Ag^+ = Ag[Ag(CN)_2]$$

an. Aus den Redoxpotentialwerten des Variaminblaus folgt, dass der Indicator nur zur Anzeige des zweiten Äquivalenzpunktes im Betracht kommen kann. Den Potentialwert dieses Punktes (+460 mV) nähert das Umschlagspotential des Variaminblaus am besten bei pH-Wert 4,3 an. Der Indicatorfehler ist aber praktisch auch noch in 0,001 n Lösungen vernachlässigbar, wenn der pH-Wert der Lösung zwischen 4–4,6 fällt. In Standardacetatpufferlösungen kann man also die Titration bei jeder praktisch in Betracht kommender Konzentration ausführen. In konzentrierteren Lösungen sind die Titrationskurven steiler, das pH-Intervallum ist folglich breiter. Im Falle der Titration von 0,01 n Cyanidlösungen kann der pH-Wert der Lösung zwischen den pH-Werten 3,5–5, im Falle von 0,1 n Cyanidlösungen zwischen 2,5–5 liegen. Dies bedeutet, dass in und über 0,01 n Mass zur Titration ein Ansäuern von Essigsäure genügt.

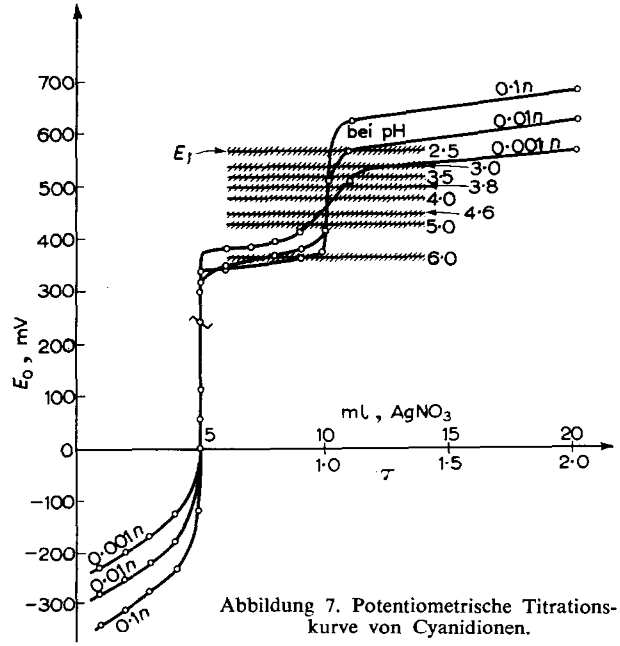

Abbildung 7. Potentiometrische Titrationskurve von Cyanidionen.

Die Variaminblauindication ermöglicht auch eine Cyanidbestimmung neben anderen Halogeniden. In diesem Falle titriert man die Cyanide nach Liebig bis zum Erscheinen der ersten beständigen Trübung, dann fügt man Variaminblau zur Lösung und titriert weiter bis dieses umschlägt. Subtrahiert man aus dem Gesamtmasslösungsverbrauch das Doppelte der nach Liebig verbrauchten Masslösungsmenge, so erhält man das den neben dem Cyanid anwesenden Haloiden äquivalente Volumen der Masslösung.

Titration von Silberionen

Die potentiometrische Titration einer Silberlösung neben einer Platinindicatorelektrode mit irgend einer Haloidenlösung zeigte, dass das Variaminblau im Äquivalenzpunkte nicht umschlug und dass das Redoxpotential der titrierten Lösung höher als das Umschlagspotential des Variaminblaus war. Nur im Falle einer Kaliumjodidmasslösung erfolgte ein Umschlag des Indicators und nur in diesem Falle gestaltete sich nach dem Äquivalenzpunkt das Redoxpotential der Lösung negativer als das Umschlagspotential des Variaminblaus. Diese Beobachtung wird folgendermassen erklärt: In einer silberhaltigen Lösung wird das Variaminblau sofort oxydiert und feinverteiltes Silber scheidet aus:

$$\text{Variaminblau (Red)} + Ag^+ \rightleftharpoons \text{Variaminblau (Ox)} + Ag_{\text{Metall}}$$

Titriert man nun die Lösung mit einer Chloridmasslösung, so reisst das sich bildende Silberchlorid das Silber mit sich, hüllt es ein, so dass letzteres das Variaminblau nun nicht mehr reduzieren kann. Das Silberhaloid erniedrigt also die Aktivität des metallischen Silbers in der Lösung, deshalb sich in der Lösung ein positiveres Redoxpotential nach dem Äquivalenzpunkt gestaltet, als es wäre falls die Silberaktivität nicht abgenommen hätte. Dies beweist auch ein Versuch, bei welchem zu einer titrierten Lösung feinverteiltes Silberpulver gestreut wurde. Auf Einwirkung des letzteren verschwand die Farbe des Variaminblaus und das Redoxpotential gestaltete sich negativer als das Umschlagspotential. Anders ist es im Falle von Kaliumjodid. Hier bestimmt nach dem Äquivalenzpunkt das System Jod-Jodid ($E_0 = +620$ mV) das Potential. Da der Kaliumjodidüberschuss Jod höchstens in Spuren enthalten kann, ist das Redoxpotential der überschüssiges Jodid enthaltenden Lösung negativer als das Umschlagspotential des Variaminblaus. Das Variaminblau wird folglich reduziert:

$$2\ \text{Variaminblau (Ox)} + 2J^- \rightleftharpoons 2\ \text{Variaminblau (Red)} + J_2$$

Bei den anderen Halogeniden kann so ein Redoxvorgang deshalb nicht stattfinden, weil die Normalpotentiale der Systeme Chlor-Chlorid bzw. Brom-Bromid wesentlich positiver sind.

Die Silberbestimmung mit Kaliumjodid führt man zweckmässig in fast neutralem Medium (pH = 4,6–6) aus und erwärmt im Endpunkte die Lösung auf 40–50 C° um den durch die Silberabsorption verursachten Fehler zu erniedrigen. In sehr verdünnter Lösung ($>0,01$ n) kann man jedoch diesen Fehler nicht mehr beseitigen, die Bestimmung ist also nur bis zu 0,01 n Mass ausführbar.

EXPERIMENTELLER TEIL

Lösungen

1 % *ige Variaminblauacetat-Indicatorlösung*: Die technische Variaminblau B Base ist ein salzsaures Salz, dessen Chloridgehalt einen Fehler bei der argentometrischen Titration verursacht. Deshalb benützt man Variaminblauacetat, das auch beständiger als das Chlorid ist. Man bereitet es folgendermassen: Man wägt 0,2 g Variaminblau B Base in einen 100 ml Scheidetrichter, setzt 0,05–0,1 g Ascorbinsäure hinzu und löst das Gemisch unter kräftigem Umschütteln in 20 ml Wasser. Die Ascorbinsäure reduziert den ewentuell oxydierten Farbstoff. Dann fällt man mit 5 ml n Natriumhydroxydlösung die schlechtlösliche Variaminblau B Base, vermischt die niederschlaghaltige Lösung mit 20 ml Benzol, filtriert dann die benzolige Phase durch ein ebenfalls mit Benzol benetztes Filterpapier in einen zweiten Scheidetrichter. Die Extraktion wiederholt man nochmals mit 2–5 ml Benzol. Aus der gesammelten benzoligen Lösung bringt man das Variaminblau mit 20 ml 20 % iger Essigsäure in die wässrige Phase zurück, die man dann durch ein benetztes Filterpapier in eine Tropfflasche filtriert. Aus dieser ungefähr 1 % iger Indicatorlösung benützt man 3–6 Tropfen zu einer Titration. Die Indicatorlösung kann man 3 Wochen hindurch benützen. Man kann natürlich als Indicator auch das salzsaure Salz in 1 % iger wässriger Lösung gebrauchen, man muss jedoch in diesem Fall

den aus dem Chloridgehalt des Indicators sich ergebenden Fehler in Betracht nehmen. 1 ml 1%ige Variaminblau HCl–Lösung verbraucht 0,28 ml 0,1 n Silbernitratlösung.

Pufferlösung vom pH 3,6: 10,2 ml Eisessig und 2,8 g krist. Natriumacetat verdünnt man mit Wasser auf 1 Liter. 10 ml dieser Lösung fügt man zur neutralisierten, zu titrierenden Lösung.

Pufferlösung vom pH 4,6: Man löst 5,7 ml Eisessig und 13,6 g krist. Natriumacetat in Wasser und ergänzt auf 1 Liter. Aus dieser Lösung fügt man 10 ml zur neutralisierten, zu titrierenden Lösungen.

0,1 *n Essigsäurelösung*: Man verdünnt 6–7 ml Eisessig mit Wasser auf 1 Liter. Zur neutralisierten, zu titrierenden Lösungen fügt man davon 10 ml.

Alle diese Reagenzien und Lösungen prüft man mit Silbernitrat auf Chloridfreiheit.

Bestimmung von Chloridionen

Die 1–150 mg Chlorid enthaltende Lösung neutralisiert man mit chloridfreier Natriumhydroxydlösung oder Salpetersäure gegen Phenolphtalein bis die rosa Farbe eben erscheint, dann setzt man so viel 0,1 n Essigsäure hinzu, bis die Färbung wieder verschwindet. Nun versetzt man die Lösung mit 10 ml Pufferlösung vom pH 3,6 und 3 Tropfen Variaminblaulösung und titriert mit der entsprechenden Silbernitratmasslösung. In der Nähe des Endpunktes fügt man die Masslösung tropfenweise zu und schüttelt nach jedem Tropfen gründlich um. 1 ml 0,1 n Silbernitratmasslösung entspricht 3,5457 mg Chlorid.

Bemerkung: Beträgt die Konzentration der vorbereiteten neutralen Chloridlösung 0,01 n oder mehr, so kann man statt einer Pufferlösung mit 10 ml 0,1 n Essigsäure das pH einstellen.

Ergebnisse derartiger Titrationen sind in Tab. I dargestellt und wie ersichtlich sind sie sehr genau. Zur Ermittelung der Genauigkeit und der Standarddeviation des Verfahrens führten wir 12–12 parallele Titrationen aus, deren Ergebnisse in Tab. VII ersichtlich sind.

Aus den Daten sieht man, dass die Genauigkeit des Verfahrens die der Titration nach Mohr übertrifft. Ein weiterer Vorteil besteht in der Möglichkeit der Bestimmung in saurer Lösung. Diese Vorteile sind besonders bei der Bestimmung des Chloridgehaltes von natürlichen Wässern angenehm. Bei dem Mohr-schen Verfahren lässt der Farbumschlag des Chromatindicators viel zu wünschen, und es ergibt sich infolge des Indicatorfehlers ein bedeutender Masslösungsüberverbrauch.[4] Diese Fehler resultieren einerseits in der Streuung der Ergebnisse, anderseits dass mehr Chlorid gefunden wird als sollte. Den Indicatorfehler muss man deshalb hier immer in Korrektion nehmen.[4,5] Diese Korrektion beträgt laut Kolthoff in 150 ml Titrierendvolumen 0,6 ml 0,01 n Silbernitratlösung. Die Endpunktsindication mit Variaminblau ist viel besser wahrnehmbar, der Indicatorfehler (0,05 ml 0,01 n Silbernitratlösung in 100 ml Endvolumen) kann vernachlässigt werden. Tab. II enthält die Ergebnisse einiger Chloridbestimmungen von natürlichen Wässern mit Variaminblau und nach Mohr. Wie ersichtlich ist die Streuung der Variaminblautitrationen wesentlich geringer und die Ergebnisse liegen auch ohne Korrektion viel näher zum richtigen Wert als beim Mohr-schen Verfahren.

Bestimmung von Bromiden, Jodiden, Rhodaniden und Cyaniden

Die Lösung wählt man so, dass sie zwischen 0,4–400 mg Bromid, 0,6–600 mg Jodid, 0,3–300 mg Rhodanid, 0,1–140 mg Cyanid enthält. Diese Lösung neutralisiert man mit chloridfreier Natriumhydroxydlösung bzw. Salpetersäure bis Erscheinung der rosa Farbe des Phenolphtaleins, dann versetzt man sie mit soviel 0,1 n Essigsäure, dass die Färbung eben verschwindet, dann mit 10 ml Pufferlösung vom pH-Wert 4,65 und 3–6 Tropfen Variaminblauacetatlösung und titriert sie mit Silbernitratlösung. In der Nähe des Endpunktes fügt man die Masslösung tropfenweise zu und schüttelt nach jedem Tropfen kräftig um. 1 ml 0,1 n Silbernitratlösung entspricht 7,9916 mg Bromid, 12,691 mg Jodid, 5,9093 mg Rhodanwasserstoff bzw. 2,7027 mg Cyanwasserstoff.

Bemerkung: Bei oder über 0,01 n Halogenidkonzentration genügt zur pH-Einstellung 10 ml 0,1 n Essigsäure. Im Falle von Cyaniden wendet man zur pH–Einstellung in jeder Konzentration eine Pufferlösung von pH 4,65 an.

In Tab. III–VI sind die Ergebnisse von verschiedenen Halogenidbestimmungen dargestellt. In 12–12 parallelen Titrationen wurde die Standarddeviation und die Streuung der Ergebnisse bei 20 ml Masslösungsverbrauch ermittelt. (Tab. VII.) Wie daraus ersichtlich, liefert das Verfahren in 0,1 und 0,01 n Mass sehr genaue und auch noch in 0,001 n Mass befriedigende Ergebnisse.

TABELLE I.—TITRATION VON VERSCHIEDENEN MENGEN NATRIUMCHLORID MIT SILBERNITRAT IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n und 0,001 n NaCl-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
5,05	5,07 5,04 5,05	5,05	±0,0	5,11 5,12 5,09	5,11	+1,20	5,05 4,99 5,00	5,01	−0,80
10,07	10,03 10,03 10,06	10,04	−0,33	10,12 10,11 10,14	10,12	+0,50	9,76 9,84 9,79	9,80	−2,70
20,02	20,02 20,04 20,03	20,03	+0,05	20,06 20,06 20,07	20,06	+0,20	19,95 19,87 19,92	19,91	−0,55
30,00	29,98 29,96 29,99	29,98	−0,07	29,97 30,04 30,00	30,00	±0,0	29,23 29,33 29,31	29,29	−2,40
49,96	49,86 49,83 49,83	49,84	−0,24	49,81 49,90 49,97	49,89	−0,14	48,26 48,21 48,27	48,25	−3,40

Tabelle II.—Chloridbestimmung in Trinkwässern. Titration von Trinkwässern (je 100 ml) verschiedener Herkunft mit 0,01 n Silbernitratlösung in Anwesenheit von Variaminblauacetat und Kaliumchromat als Indicatoren

	In Anwesenheit von Variaminblauacetat (Korr. = — 0,05 ml)			In Anwesenheit von Kaliumchromat (Korr. = —0,40 ml)		
	Verbrauch an 0,01 n $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Gefunden Cl^- *mg/Lit*	Verbrauch an 0,01 n $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Gefunden Cl^- *mg/Lit*
Wasserleitungswasser unseres Laboratoriums	3,08 3,10 3,09	3,09 3,04*	11,0 10,8*	3,37 3,60 3,25	3,41 3,01*	12,1 10,7*
Wasserleitungswasser von Ujpest	2,84 2,81 2,81	2,82 2,77*	10,0 9,8*	2,95 3,41 3,19	3,18 2,78*	11,3 9,9*
Donauwasser von Vác	1,90 1,86 1,88	1,88 1,83*	6,7 6,5*	2,22 2,08 2,45	2,25 1,85*	8,0 6,6*
Wasserleitungswasser von Budafok	3,70 3,71 3,71	3,71 3,66	13,2 13,0*	3,86 4,14 4,06	4,02 3,62*	14,3 12,8*
Brunnenwasser von Budafok	4,81 4,77 4,80	4,79 4,74*	17,0 16,8*	5,13 5,01 5,34	5,16 4,76*	18,3 16,9*

* Die mit Sternchen bezeichneten Zahlen bedeuten die mit den Korrekturwerten verbesserten Ergebnisse.

TABELLE III.—TITRATION VON VERSCHIEDENEN KALIUMBROMIDLÖSUNGMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n 0,01 n und 0,001 n KBr-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
5,05	5,07 5,06 5,06	5,06	+0,02	5,10 5,08 5,11	5,10	+1,00	5,34 5,30 5,39	5,34	+5,80
10,07	10,05 10,08 10,07	10,07	±0,0	10,11 10,14 10,13	10,13	+0,60	10,24 10,15 10,24	10,21	+1,40
20,01	20,01 20,00 20,01	20,01	±0,0	20,12 20,12 20,09	20,11	+0,50	20,19 20,30 20,28	20,26	+1,25
29,98	29,97 29,92 29,94	29,94	−0,11	30,05 30,03 30,06	30,05	+0,23	30,30 30,30 30,21	30,27	+0,97
49,93	49,75 49,73 49,75	49,74	−0,38	49,93 49,91 49,96	49,93	±0,0	50,09 50,12 49,98	50,06	+0,26

TABELLE IV.—TITRATION VON VERSCHIEDENEN KALIUMJODIDLÖSUNGSMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR.

Einwaage 0,1 n, 0,01 n u. 0,001 n KJ-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
4,99	4,99 5,00 5,00	5,00	+0,20	4,99 5,00 5,00	5,00	+0,20	5,10 5,21 5,22	5,18	+3,8
9,91	9,92 9,93 9,94	9,93	+0,20	9,93 9,92 9,93	9,93	+0,20	10,12 10,11 10,02	10,08	+1,7
19,94	19,91 19,94 19,94	19,93	−0,05	19,98 19,97 19,96	19,97	+0,15	20,38 20,35 20,32	20,35	+2,05
29,91	29,88 29,91 29,90	29,89	+0,07	29,90 29,90 29,93	29,91	±0,0	30,52 30,48 30,40	30,47	+1,87
49,89	49,82 49,86 49,82	49,83	−0,12	49,90 49,87 49,90	49,89	±0,0	50,77 50,72 50,85	50,78	+1,78

TABELLE V.—TITRATION VON VERSCHIEDENEN KALIUMCYANIDLÖSUNGSMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n u. 0,001 n KCN–lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %
4,72	4,71 4,71 4,71	4,71	−0,21	4,58 4,54 4,59	4,57	−3,18	4,44 4,30 4,43	4,39	−6,99
9,43	9,41 9,42 9,40	9,41	−0,21	9,29 9,31 9,26	9,29	−1,49	9,21 9,13 9,23	9,19	−2,55
18,86	18,83 18,82 18,82	18,82	−0,21	18,63 18,58 18,70	18,64	−1,17	18,30 18,18 18,27	18,25	−3,23
28,29	28,19 28,20 28,20	28,20	−0,32	27,94 28,00 28,03	27,99	−1,06	27,70 27,88 27,87	27,82	−1,66
47,15	47,10 47,13 47,10	47,11	−0,08	46,79 46,72 46,83	46,78	−0,78	46,48 46,70 46,56	46,58	−1,21

TABELLE VI.—TITRATION VON VERSCHIEDENEN AMMONIUMRHODANIDLÖSUNGSMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n u. 0,001 n NH_4SCN-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
5,04	5,05 5,04 5,04	5,04	±0,0	5,06 5,02 5,04	5,04	±0,0	5,08 5,20 5,13	5,14	+2,00
10,05	10,09 10,09 10,10	10,09	+0,40	10,05 10,08 10,08	10,07	+0,20	10,18 10,04 10,14	10,12	+0,70
19,96	19,97 19,94 19,94	19,95	−0,05	20,11 20,07 20,10	20,09	+0,65	20,12 20,25 20,17	20,18	+1,10
29,94	30,01 29,98 29,98	29,99	+0,17	30,10 30,08 30,12	30,10	+0,53	30,38 30,37 30,30	30,35	+1,37
49,86	49,93 49,91 49,92	49,92	+0,12	50,12 50,05 50,07	50,08	+0,44	50,52 50,47 50,39	50,46	+1,20

TABELLE VII.—GENAUIGKEIT DER METHODE

Bestimmte Ionen	Konzentration n	Abweichung vom Sollwert %	Standarddeviation %
Cl^-	0,1	±0,0	±0,05
	0,01	+0,30	±0,08
	0,001	+0,50	±0,25
Br^-	0,1	±0,0	±0,06
	0,01	+0,40	±0,10
	0,001	+0,65	±0,19
J^-	0,1	±0,0	±0,04
	0,01	+0,15	±0,08
	0,001	+0,54	±0,16
CN^-	0,1	−0,32	±0,05
	0,01	−1,17	±0,12
	0,001	−3,22	±0,25
SCN^-	0,1	−0,10	±0,07
	0,01	+0,24	±0,13
	0,001	−0,96	±0,23
Ag^+	0,1	±0,0	±0,06
	0,01	+1,98	±0,51

Bestimmung des Jod- und Jodidgehaltes von Jodtinktur

Eine besondere praktische Bedeutung hat die Anwendung des neuen Verfahrens zur Wirkungswertbestimmung von Jodtinkturlösungen. Das neue Verfahren kann nämlich hier gut mit unserer ascorbinometrischen Jodtitration[6] verknüpft werden.

Verfahren: 2 ml der Jodtinktur pipettiert man in einen Titrierkolben, verdünnt sie mit 10 ml 50% igem Alkohol, titriert das Jod mit 0,1 n Ascorbinsäurelösung bis hellgelber Farbe, dann fügt man zur Lösung 20 ml Pufferlösung vom pH-Wert 4,65 und 3 Tropfen Variaminblaulösung und titriert bis Verschwinden der violetten Farbe. Aus dem Verbrauch berechnet man den freien Jodgehalt der Lösung. 1 ml 0,1 n Ascorbinsäurelösung entspricht 12,691 mg Jod.

Die mit Ascorbinsäure bis Farblosigkeit titrierte Lösung titriert man mit 0,1 n Silbernitratlösung weiter, bis die violette Farbe erscheint. Aus diesem Masslösungsverbrauch subtrahiert man das Volumen der aufs Jod verbrauchten Ascorbinsäurelösung. Die Differenz entspricht dem Kaliumjodidgehalt der Tinktur. 1 ml 0,1 n Silbernitratlösung entspricht 12,691 mg Jodid.

Bemerkung. Statt Ascorbinsäure kann man auch eine Natriumthiosulfatmasslösung neben Variaminblauindication benützen. Unsere Ergebnisse verglichen wir mit den Resultaten des Verfahrens nach der Vorschrift des ung. Arzneibuches VI; das zur Jodbestimmung eine Natriumthiosulfatmasslösung, zur Jodidbestimmung eine Silbernitratmasslösung und p-Äthoxychrisoidin als Indicator benützt. Die Ergebnisse stimmen ausgezeichnet überein. Unser Verfahren besitzt jedoch den Vorteil, dass es nur einen einzigen Indicator benötigt, dessen Umschlag sehr scharf ist (Tab. VIII).

TABELLE VIII.—JOD- UND KALIUMJODIDGEHALTBESTIMMUNG IN JODTINKTUR

1. Mit dem Verfahren des Ungarischen Arzneibuches

Einwaage Jodtinktur *ml*	Verbrauch an 0,1 n $Na_2S_2O_3$-lsg *ml*	Gefunden Jod *mg*	Mittelwert *mg*	Verbrauch an 0,1 n $AgNO_3$-lsg *ml*	Gefunden KJ *mg*	Mittelwert *mg*
2,00	8,57	108,7	108,6	11,29	45,2	45,3
	8,55	108,5		11,26	45,0	
	8,55	108,5		11,30	45,7	

2. Endpunktindication mit Variaminblau

Einwaage Jodtinktur *ml*	Verbrauch an 0,1 n Ascorbinsäure *ml*	Gefunden Jod *mg*	Mittelwert *mg*	Verbrauch an 0,1 n $AgNO_3$-lsg. *ml*	Gefunden KJ *mg*	Mittelwert *mg*
2,00	8,56	108,6	108,5	11,26	45,0	44,9
	8,55	108,5		11,26	45,0	
	8,54	108,4		11,25	44,8	

Silberbestimmung mit Kaliumjodidmasslösung

Die 5–550 mg Silberionen enthaltende Lösung neutralisiert man wie schon beschrieben, säuert dann mit einigen Tropfen 0,1 n Essigsäure an, versetzt mit 1–3 Tropfen Indicatorlösung und titriert mit 0,1 bzw. 0,01 n Kaliumjodidmasslösung. In der Nähe des Endpunktes erwärmt man auf 40–50 C° und titriert weiter bis Entfärbung der Lösung. 1 ml 0,1 n Kaliumjodidmasslösung entspricht 10,788 mg Silber.

Bemerkung: In Tab. IX. sind die Ergebnisse einiger Silbertitrationen dargestellt. Wie ersichtlich liefern die Bestimmungen bei verschiedenen Silberkonzentrationen gute Resultate. Die aus 12–12 parallelen Titrationen bestimmten Genauigkeits- und Deviationsdaten sind für den Fall der Bestimmung von 20 ml 0,1 n und 0,01 n Lösungen in Tab. VII zusammengefasst. Daraus geht hervor, dass in 0,1 n Mass sehr gute, in 0,01 n Mass noch annehmbare Resultate erzielt wurden.

Bestimmung von Kalium

Wir fanden, dass die Variaminblauindication auch zur argentometrischen Bestimmung der Tetraphenylborationen geeignet ist. Dieses Verfahren wurde zur volumetrischen Bestimmung der Kaliumionen erweitert. Wie bekannt, gibt das Natriumtetraphenylborat (Kalignost) mit Kaliumionen einen in Wasser sehr schlechtlöslichen Niederschlag,[7] der jedoch in Aceton löslich ist. Das Silbersalz des Tetraphenylborats, $Ag[B(C_6H_5)_4]$, ist jedoch sowohl in Wasser als auch in Aceton unlöslich. Das Tetraphenylboratanion kann man gleich den Halogeniden argentometrisch bestimmen:

$$[B(C_6H_5)_4]^- + Ag^+ = Ag[B(C_6H_5)_4]$$

Den Endpunkt dieser Titration kann man mit Variaminblauacetat auch in acetoniger Lösung ausgezeichnet indizieren. Der Vorteil dieser Indication gegenüber denen mit Adsorptionsindicatoren[8] bzw. Chromat[9] besteht darin, dass man sie unmittelbar ausführen kann und dass der Indicatorfehler und die Standardstreuung wesentlich geringer als bei den erwähnten anderen Verfahren sind.

Lösungen: 0,1 m *Natriumtetraphenylborat-(Kalignost)-lösung*: 3,42 g Natriumtetraphenylborat löst man in 100 ml Wasser. Zwecks Beseitigung einer ewentuellen Trübung klärt man die Lösung

Tabelle IX.—Titration von verschiedenen Silbernitratlösungsmengen mit Kaliumjodidlösung in Anwesenheit von Variaminblauacetat als Indicator

Einwaage 0,1 n, 0,01 n AgNO$_3$ *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen		
	Verbrauch an KJ *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an KJ *ml*	Mittelwert *ml*	Abweichung %
4,95	4,92 4,94 4,92	4,93	−0,40	5,06 5,25 5,17	5,16	+4,2
9,86	9,84 9,83 9,84	9,84	−0,20	10,26 10,31 10,13	10,23	+3,8
19,64	19,63 19,66 19,63	19,64	±0,0	19,91 20,16 20,06	20,04	+2,0
29,43	29,34 29,35 29,33	29,34	−0,31	30,12 30,39 30,25	30,25	+2,8
49,01	48,88 48,90 48,90	48,89	−0,25	49,77 50,56 50,24	50,19	+2,4

durch 5 minutiges Schütteln mit 0,5 g Aluminiumhydroxyd oder Aluminiumoxyd und filtriert. 1 ml der Lösung ist zur Fällung von 3,5 mg Kalium geeignet. Es ist zweckmässig die Lösung stets frisch zu bereiten.

Waschflüssigkeit: 0,1 g des nach obiger Vorschrift gefällten und mit Wasser ausgewaschenen Kaliumtetraphenylboratniederschlages wird mit 250 ml Wasser während 30 Minuten geschüttelt, zur trüben Lösung dann 0,5–1 g Aluminiumhydroxyd oder Aluminiumoxyd gesetzt, einige Minuten hindurch umrührt, filtriert und die ersten 20 ml des Filtrats neuerdings auf das Filterpapier gegossen. Die Waschflüssigkeit muss vollständig klar sein.

Verfahren: Die 10–100 mg Kalium enthaltende Lösung verdünnt man auf 100 ml, säuert mit n Essigsäure gegen Lakmus eben an, dann setzt man zur Lösung in ungefähr 1,5-fachen Überschuss tropfenweise die 0,1 n Natriumtetraphenylboratlösung zu, filtriert in 5 Minuten durch ein dichtes Filterpapier und wäscht dann den Niederschlag mit der Waschflüssigkeit solange bis das Filtrat mit Silbernitrat schon kaum eine Reaktion zeigt. Das Filterpapier gibt man samt Niederschlag in das Glas, wo die Fällung erfolgte, zurück, giesst es mit 10–20 ml Aceton auf und löst den Niederschlag unter Umrühren mit einem Glasstab. Die acetonige Lösung säuert man mit 2 ml n Essigsäure an, fügt 3 Tropfen Variaminblaulösung hinzu und titriert mit der Silbernitratmasslösung bis zum Erscheinen der violetten Farbe. Gegen Ende der Titration titriert man tropfenweise und schüttelt nach jedem Tropfen kräftig um. 1 ml 0,1 n Silbernitratlösung entspricht 3,9096 mg Kalium.

TABELLE X.—MASSANALYTISCHE KALIUMBESTIMMUNG MIT HILFE VON KALIGNOST IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage K^+ *mg*	Gefunden K^+ *mg*		Mittelwert *mg*	Abweichung %
11,75	11,75 11,71 11,71	11,66 11,69 11,66	11,70	−0,43
29,52	29,40 29,50 29,66	29,58 29,56 29,44	29,52	±0,0

Bemerkung: Ergebnisse von Kaliumbestimmungen sind in Tab. X ersichtlich. Wie es zu sehen ist, ist das Verfahren sehr genau.

Die Menge des zur Lösung gebrauchten Acetons kann die Genauigkeit der Bestimmung beeinflussen. Ein grosser Überschuss von Aceton löst nämlich eine nicht vernachlässigbare Menge des Silbertetraphenylboratniederschlages. Ist jedoch das Aceton zu wenig, dann scheidet in dem im Laufe der Titration sich allmählich verdünnenden Wasser–Acetongemisch auch das Kaliumtetraphenylborat aus. Beide Vorgänge verursachen einen negativen Fehler. Man wählt deshalb zweckmässig ein solches Acetonvolumen, dass es das zur Titration benötigte Masslösungsvolumen nicht übertrifft. Im allgemeinen sind im Falle der Bestimmung von Mengen unter 25 mg des Kaliums 10 ml Aceton genügend.

Benützt man zur Fällung eine Natriumtetraphenylboratlösung von bekanntem Volumen und Wirkungswert, so kann man auch derart verfahren, dass man die überschüssige Fällungslösung ohne Acetonzusatz rücktitriert. Dieses Verfahren liefert besonders im Falle von höheren Mengen Kaliums verlässliche Ergebnisse.

Summary—Variamine-blue can be used with advantage as a redox indicator in the argentometric determination of halide, thiocyanate, cyanide and potassium. At a suitable pH the first drop of silver nitrate in excess can be detected. The procedure may also be used for the determination of silver by means of potassium iodide. Potassium can be determined titrimetrically by argentometric titration of the tetraphenylboron compound in the presence of the indicator.

Résumé—On peut utiliser avec profit le bleu de variamine comme indicateur d'oxydo-réduction dans le dosage argentométrique des halogénures, du thiocyanate, du cyanure et du potassium. Il est possible de déceler, à un pH convenable, la première goutte de nitrate d'argent en excès. Le procédé permet également de déterminer l'argent au moyen de l'iodure de potassium. On peut effectuer le dosage titrimétrique du potassium par le titrage argentométrique du composé tétraphénylbore en présence de l'indicateur.

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Talanta, 1958, Vol. 1, pp. 396-407. Pergamon Press Ltd., London.

THE QUANTITATIVE DETERMINATION OF FISSION AND NUCLEAR REACTION PRODUCTS

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(*Received* 4 *July* 1958)

Summary—Definitions are given to the terms "per cent atom burn-up" and "per cent atoms consumed" as applied to nuclear fuel analysis at the Argonne National Laboratory. The radiochemical and analytical methods which have been adapted and developed especially for this type of analysis are discussed. The analysis of nuclear reaction products by paper chromatographic methods and scintillation spectrometry is emphasised and demonstrated.

INTRODUCTION

INCREASED and more general operation of nuclear reactors for power will create a wider interest in the methods of determining the absolute numbers or the ratios of various nuclear events which have occurred in reactor fuels, blanket materials, moderators, and structural materials. The purpose of this paper is to summarise some of the calibrations and techniques employed, to indicate the type of instrumentation applicable, and to define and elucidate some special problems encountered in this type of analysis. The quantitative determination of radioactive nuclides in an extremely wide range of materials is becoming of increasing interest and importance. A relatively large part of the discussion is devoted to the methods which we have developed for determining the fraction of fissile atoms consumed by fission in nuclear fuels. This determination illustrates many of the basic methods of detection and calibration which are also applicable to the analysis of many other nuclear reaction products.

Although the counting methods are generally applicable, the particular decay scheme of each radioactive isotope must be considered when applying the various absolute counting techniques. This point is illustrated with the decay scheme of the fission product caesium-137, which has been useful in monitoring the number of fission events or per cent atom burn-up in nuclear fuels.

DEPLETION OF FUEL IN A NUCLEAR REACTOR

In the development of power reactors, nuclear fission is the most significant reaction. The fraction of fissile atoms which have undergone fission is an important quantity in analysing reactor performance. The number of other nuclear events which have occurred during the same time is compared to the total fission events to obtain the over-all neutron economy. Also, the total number of fission events which have occurred in a given fuel element is correlated with many other physical or chemical phenomena, such as dimensional changes, corrosion, phase changes, and other effects which take place during irradiation. Certain ambiguous terminology which has not been defined previously has developed in describing the total number of various events which occur in reactor fuel. This is especially true of the term "burn-up." The following definitions are suggested as generally applicable, and will be used here:

$$\text{Per cent total atom burn-up} = \frac{f_T}{(M_1{}^0 + M_2{}^0 + \ldots)\, 6{\cdot}02(10^{23})}\, 100 \qquad (1)$$

$$\text{Per cent total atoms consumed} = \frac{(f_T + C_M + \ldots)}{(M_1{}^0 + M_2{}^0 + \ldots)\, 6{\cdot}02(10^{23})}\, 100 \qquad (2)$$

where $(M_1{}^0 + M_2{}^0 + \ldots)\, 6{\cdot}02(10^{23})$ is the number of atoms of a definite element or group of elements in the original sample. It is generally more convenient, and at higher per cent total atom burn-up necessary, to obtain the denominator by an analysis before irradiation. Mass analysis may also be applied, and the molar and isotopic content of the sample used to group only the fissile isotopes in the denominator of (1) and (2) to give the per cent fissile atom burn-up and the per cent fissile atoms consumed.

f_T is the total number of fissions detected in the original group of atoms, $(M_1{}^0 + M_2{}^0 + \ldots)\, 6{\cdot}02\, (100^{23})$. There is no reliable method to distinguish between fission of the various fissile isotopes. Therefore the selection of the original group of atoms in a complex fuel should include all the fissile atoms and non-fissile atoms which will breed fissile atoms, and result in an appreciable contribution to the value of f_T. Two of the more important examples are:

$$^{232}\text{Th} \xrightarrow{(n,\gamma)} {}^{233}\text{Th} \xrightarrow[23\text{ min}]{\beta^-} {}^{233}\text{Pa} \xrightarrow[27\text{ d}]{\beta^-} {}^{233}\text{U}$$

$$^{238}\text{U} \xrightarrow{(n,\gamma)} {}^{239}\text{U} \xrightarrow[23\text{ min}]{\beta^-} {}^{239}\text{Np} \xrightarrow[2{\cdot}3\text{ d}]{\beta^-} {}^{239}\text{Pu}$$

C_M is the total number of relatively stable non-fissile atoms in an irradiated sample which are formed by neutron capture with a fissile isotope in the selected group of atoms. These atoms may or may not have been converted to other elements by radioactive decay. It should be apparent that the term C_M cannot be defined exactly unless referred to a specific fuel composition, and even then fissile, non-fissile and nuclear stability of the non-fissile atoms are applied within the judgements of the analyst. The important point is that as burn-up values and the complexity of fuel compositions increase, the application of the term C_M must be made with reference to the system being analysed.

Other nuclear reactions with the selected group of atoms may be included in a similar manner. The per cent total atom burn-up and per cent total atoms consumed are referred to the original atom content of the sample. The analysis of the atom content, however, may only be made on a sample after the irradiation. If there is a significant burn-up and isotopic change, the elemental and isotopic content as observed on the irradiated sample should be corrected, where appropriate, to the original atom content.

Thus, the atom content of the denominators of (1) and (2) may be expressed by

$$(M_1{}^0 + M_2{}^0 + \ldots)6{\cdot}02(10^{23}) = M_1 + M_2 + \ldots)6{\cdot}02(10^{23}) + f_T + C_M{}^1 + \ldots \qquad (3)$$

where $(M_1 + M_2 + \ldots)6{\cdot}02(10^{23})$ is the atom content of the irradiated sample.

$C_M{}^1$ is the number of atoms which were formed by capture from atoms in the group $(M_1{}^0 + M_2{}^0 + \ldots)6{\cdot}02(10^{23})$, but would not be analysed as a part of the group $(M_1 + M_2 + \ldots)(6{\cdot}02)(10^{23})$ in the irradiated material.

In general, the addition of the number of atoms fissioned is sufficient to correct the analysis of the irradiated material to the original content. In many cases the neutron capture products are relatively stable and the chemical analysis will not be changed. However, if the atoms comprising the denominators of (1) and (2) are selected by both the isotopic and elemental content, the correction of the irradiated sample analysis would be applicable.

With high burn-up values, it is not possible to deduce the original fuel content accurately by analysis of the irradiated material alone. Therefore, the values of per cent total atom burn-up and per cent total fissile atoms consumed must be obtained on a confined sample whose elemental and isotopic content has been analysed before the irradiation. Other considerations which must be taken into account when analysing an unconfined sample are the state of the material, the temperature, and proper sampling. Finely divided material or a very thin sample will allow a substantial fraction of the fission fragments to recoil from the sample, and gaseous fission products will diffuse out at appreciable rates. The fission product content of the sample is then no indication of the number of fission events which have occurred in the sample. Molten uranium or plutonium will lose additional gaseous and volatile fission products. Caesium is distilled from uranium and plutonium at their melting points. Fused salts and solutions may be more troublesome because of surface deposition of fission products and loss of gaseous fission products if the sample is not confined during irradiation. Thick fuel elements will attenuate the neutron flux in the element. Consequently, fission and other nuclear reaction products will not be generated homogeneously throughout the fuel. Because of the difficulties outlined above, it is very often impossible to obtain a representative sample on unconfined reactor fuel. The sampling problems associated with attenuation of the neutron flux will, of course, affect any method of analysis.

The fission reaction requires a careful absolute fission yield calibration before any fission product may be used to determine the number of fission events which have occurred in a given material. This calibration will be discussed in the experimental section to follow. Other than fission, the only nuclear reaction which will deplete significant amounts of fissile material in a reactor is the neutron capture reaction. Other reactions, such as $(n, 2n)$, (n, α), (n, p), etc., will be of interest if the products formed have very high neutron cross sections, by virtue of the radiation effects of the products, or for theoretical reasons.

DETERMINATION OF FISSION BY FISSION PRODUCT MONITORING

The direct measurement of fission events in a sample has relatively limited practical application. Direct measuring includes counting individual fission events with a proportional ionisation counter[8,13] and measuring the total heat released by fission. Indirect methods are fission product monitoring and observation of changes in the isotopic ratio of fissile and non-fissile isotopes of a heavy element.

The measurement of total heat released is generally applied to a complete pile assembly rather than individual isolated samples. Monitoring a heavy sample by means of a light sample plus a fission counter is the most sensitive method,[8] but this has severe practical limitations. This method has been applied[13] to calibrate the indirect fission product procedure for the determination of per cent total atom burn-up in uranium-235 and plutonium-239.

Of the indirect methods, fission product monitoring is the most sensitive indicator of the number of fissions which have occurred. Isotopic analysis has advantages in that the sample is not subject to errors due to the recoil, volatilisation, or surface adsorption of fission products from an unconfined sample. The isotopic composition of the fuel, however, is affected by nuclear reactions other than fission. The ratio of σ_c/σ_f for uranium-235, for example, varies[14] with position in a typical fast reactor from 0·14 to 0·27. Also, resonance capture cross sections may be very high and give abnormal isotopic compositions at certain pile locations. In general, the sensitivity of the isotopic ratio analysis is not high enough for samples irradiated to relatively low (10^{-4} to 10^{-1} per cent) burn-up.

Only a few of the fission products are suitable for determining the number of fission events. The useful fission products are limited to the mass numbers falling on, or close to, the heavy or light fission yield peaks. Fission products located on the sharp slopes or in the valley of the fission yield curve show relatively large variations in their fissions yields with changes in neutron energy or the fissile isotope. Even on the heavy or light fission yield peaks, appreciable variations in the yield with neutron energy and fissile isotopes make accurate calibrations laborious. It is also desirable to be able to analyse a relatively wide variety of pile-irradiated samples with irradiation histories involving one to two years. In order to avoid detailed, tedious half-life corrections, it is necessary to select a long-lived fission product. The analytical chemistry of the fission product selected should be straight forward, and the counting characteristics favorable, to allow a reliable sample isolation and accurate count. Caesium-137 meets the above requirements.

The calibration of caesium-137 and absolute fission yields in fast pile flux for uranium-235 and plutonium-239 have been reported.[13] Thermal fission yields of caesium-137 for various fissile isotopes have been reported.[19] In reviewing the recent literature on some absolute fission yields and the half-life of caesium-137, one finds a discouraging lack of agreement. Thermal fission yield of caesium-137 for plutonium-239 has been reported[19] as 5·8 and also[21] as 4·94 per cent. The half-life of caesium-137 is also subjected to uncertainty. Values reported recently are 32·6 ± 2 years,[20] $30{\cdot}9 \pm {}^{0\cdot3}_{0\cdot4}$ years,[3] and 26·6 ± 0·4 years.[22] Although precision of ±1·5 per cent may be obtained be careful fission product analysis and counting techniques, our uncertain knowledge of the absolute fission yields and decay constants limits the accuracy of monitoring fission events by a fission product. Strontium-90, the only other long-lived peak-yield fission product which we have considered acceptable, is subject to essentially the same limitations in accuracy as caesium-137.

The use of $^{140}\text{Ba} \rightarrow {}^{140}\text{La}$ is not suitable except for very short irradiations. Fuel samples are usually in the pile for months or years, and the ^{140}Ba content would indicate only the most recent irradiation history of the sample.

It is possible to prepare a heavy foil of fissile material with a known number of fission events. This has been done[13] in a fast pile flux bath for uranium-235 and plutonium-239. The fission product isolated from such foils at known chemical yield may then be used to calibrate a stable counting system. This circumvents the limitations in accuracy caused by the uncertainties in absolute fission yield and decay constants. However, this is not generally applicable to all fissile materials with the required accuracy and without relatively formidable experimental difficulties. In the long run, more accurate decay constant and absolute fission yield data will be useful in improving the accuracy and general applicability of the fission product method for monitoring the number of fission events.

To complete the fission product monitoring method for the number of fission events which have occurred in a nuclear fuel sample, two additional aspects must be considered—the counting method and the chemical isolation of the fission product. Caesium-137 has been used as the monitor for fission events for the past seven years by the authors, and has been described briefly in a previous paper.[4] Caesium-137 counting was first done on calibrated, long-lived, halogen-filled Geiger counters. At present, samples of low irradiation levels are counted with a methane flow end-window proportional counter. The caesium-137 samples, with appreciable caesium-134 or caesium-136 content, are counted with calibrated sodium iodide–thallium-activated scintillation crystals. When fission foils[13] of a particular fissile element are not available, the basic calibration is made with a 4π-methane flow counter and the reported caesium-137 yield values. The techniques used in preparing 10 microgram/cm^2 resin sample films and the detector design, etc. are those described by B. D. Pate and L. Yaffe.[15–18]

The decay scheme of caesium-137 is relatively well known. The checks we have obtained between the 4π-counter and independently calibrated scintillation spectrometers are better than five per cent. The absolute calibration of scintillation crystals has been discussed by P. R. Bell.[2] In the 4π-counter 110·5 counts are recorded for every 100 caesium-137 atoms disintegrating. One hundred of these counts come directly from beta rays emitted during caesium decay, while 9·7 come from subsequent conversion electrons. These delayed conversion electrons originate from the isomeric state of barium-137, which is formed in 92 per cent of the caesium-137 decays. In 10·6 per cent of the decays of the barium-137 isomer, conversion electrons are emitted. Approximately one per cent of the remaining unconverted 661 keV gamma rays is counted in the methane flow counter. This will add an additional 0·8 count for every 100 caesium atoms disintegrating for the total 110·5 counts.

The most important contribution of the scintillation spectrometer in burn-up analysis is in correcting the caesium count for presence of caesium-134 or caesium-136. Figure 1 shows the changes in the gamma spectrum of isolated caesium from natural uranium at various per cent total uranium atom burn-up. In these samples, the caesium-136 yield was initially low and approximately sixty days cooling was required to reduce the caesium-136 activity level below detection. The method employed in making the caesium-134 correction may vary with the instrument available. A scintillation spectrometer with reasonably good resolution will almost completely resolve the caesium-134 795 keV and the caesium-137 661 keV gamma rays. By integrating from the valley between these two gamma rays, a counting rate will be obtained which is proportional to the caesium-134 content alone. Since pure caesium-134 is also easily prepared by pile irradiation of caesium-133, the proper proportionality constant can be obtained by counting pure caesium-134 under the same conditions as the mixed caesium-137, -134 isotopes. With a magnetic core multichannel analyser, the combined spectrum of caesium-137, -134 is inverted in the memory of the instrument. A pure caesium-134 sample is then counted at the same geometry until the 795 keV line is just subtracted out when the spectrum is viewed on the oscilloscope display.

Figures 2 and 3 show the gamma scintillation spectrometer response curves of pure caesium-134 and caesium-136. The caesium-136 was prepared from uranium-233 fission. The yield of the shielded nuclide caesium-136 is relatively high (0·12 per cent) for uranium-233 fission, and green caesium isolated from a short irradiation of uranium-233 has only a small caesium-137 activity level, as shown in Figure 3. The yield of caesium-136 for plutonium-239 fission is approximately 0·09 per cent, and for uranium-235 fission the yield is 0.006 per cent. Therefore, it should be noted that more cooling time is required for plutonium-239 and uranium-233 burn-up samples to reduce the caesium-136 level. The area under the full energy peak of caesium-137 can be obtained fairly accurately in the presence of some caesium-136, as the caesium-136 gamma spectrum does not contain an unresolved gamma ray in the 661 keV region.

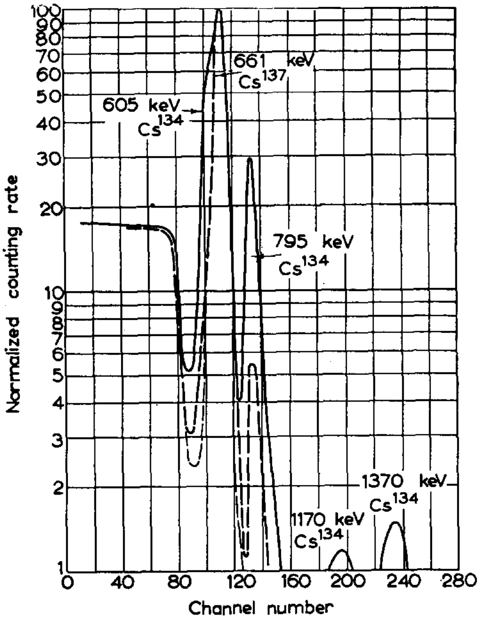


FIG. 1.—Changes in the gamma spectrum of caesium with the per cent total natural uranium atom burn-up

——— 1·7 per cent total uranium atom burn-up

— — 0·33 per cent total uranium atom burn-up

– · · · 0·04 per cent total uranium atom burn-up

Several methods are suitable for the chemical isolation of caesium. The procedure of Glendenin and Nelson[9] has been satisfactory. The chemical yield was obtained by weighing the perchlorate on a glass fibre filter mat. The area and uniformity of the sample spread were controlled by slurrying the caesium perchlorate precipitate in a glass chimney placed over the filter mat. A procedure[7] for caesium extraction with sodium tetraphenylboron and nitrobenzene has also been used successfully. Recently, amyl acetate has been substituted[6] for the less desirable nitrobenzene solvent. The method for isolating caesium at present used in this laboratory for a majority of the

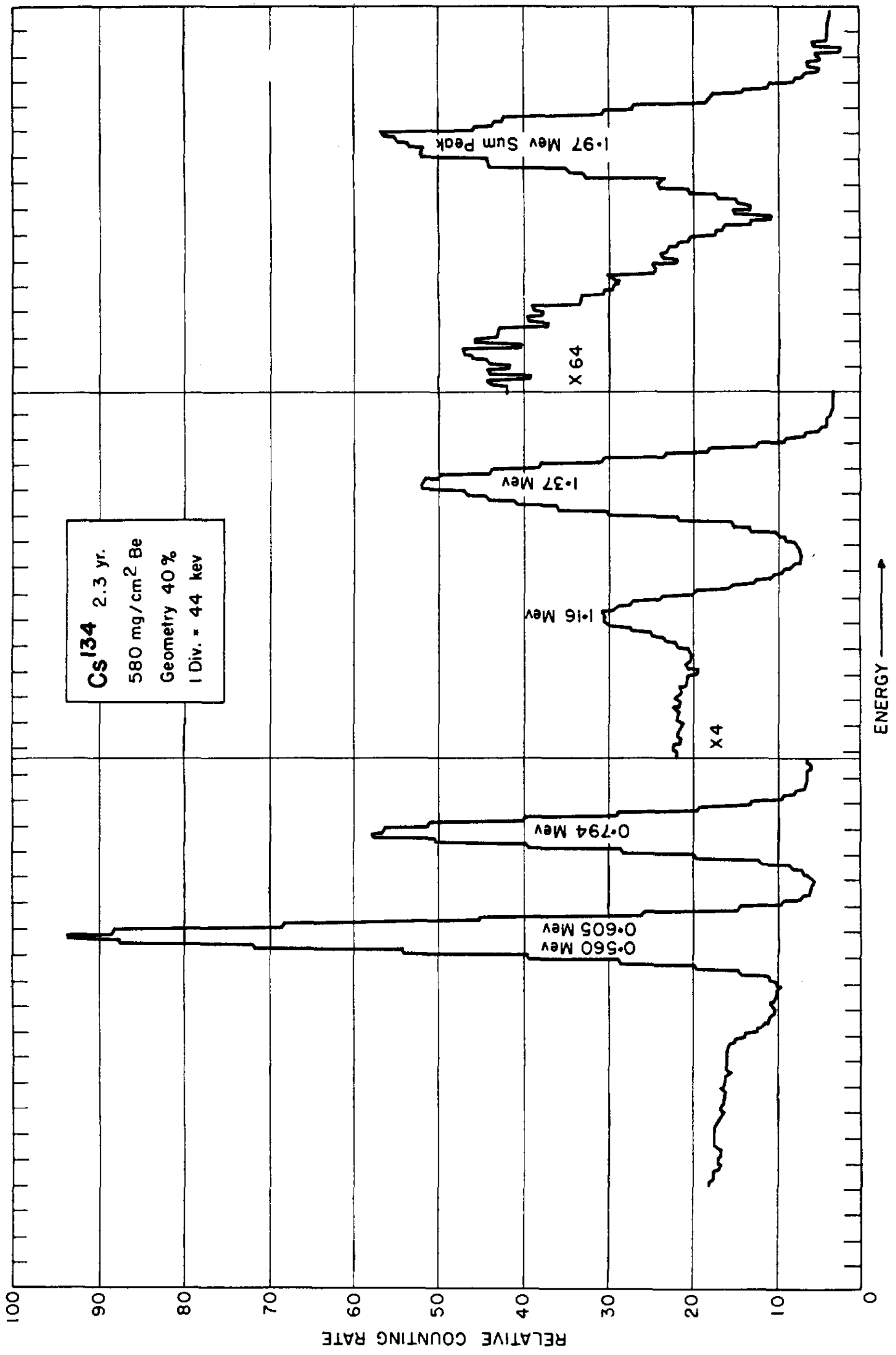

Cs134 2.3 yr.
580 mg/cm2 Be
Geometry 40 %
1 Div. = 44 kev
0·560 Mev
0·605 Mev
0·794 Mev
1·16 Mev
1·37 Mev
1·97 Mev Sum Peak
X 4
X 64
100
90
80
70
60
50
40
30
20
10
0
RELATIVE COUNTING RATE
ENERGY

Fig. 2.

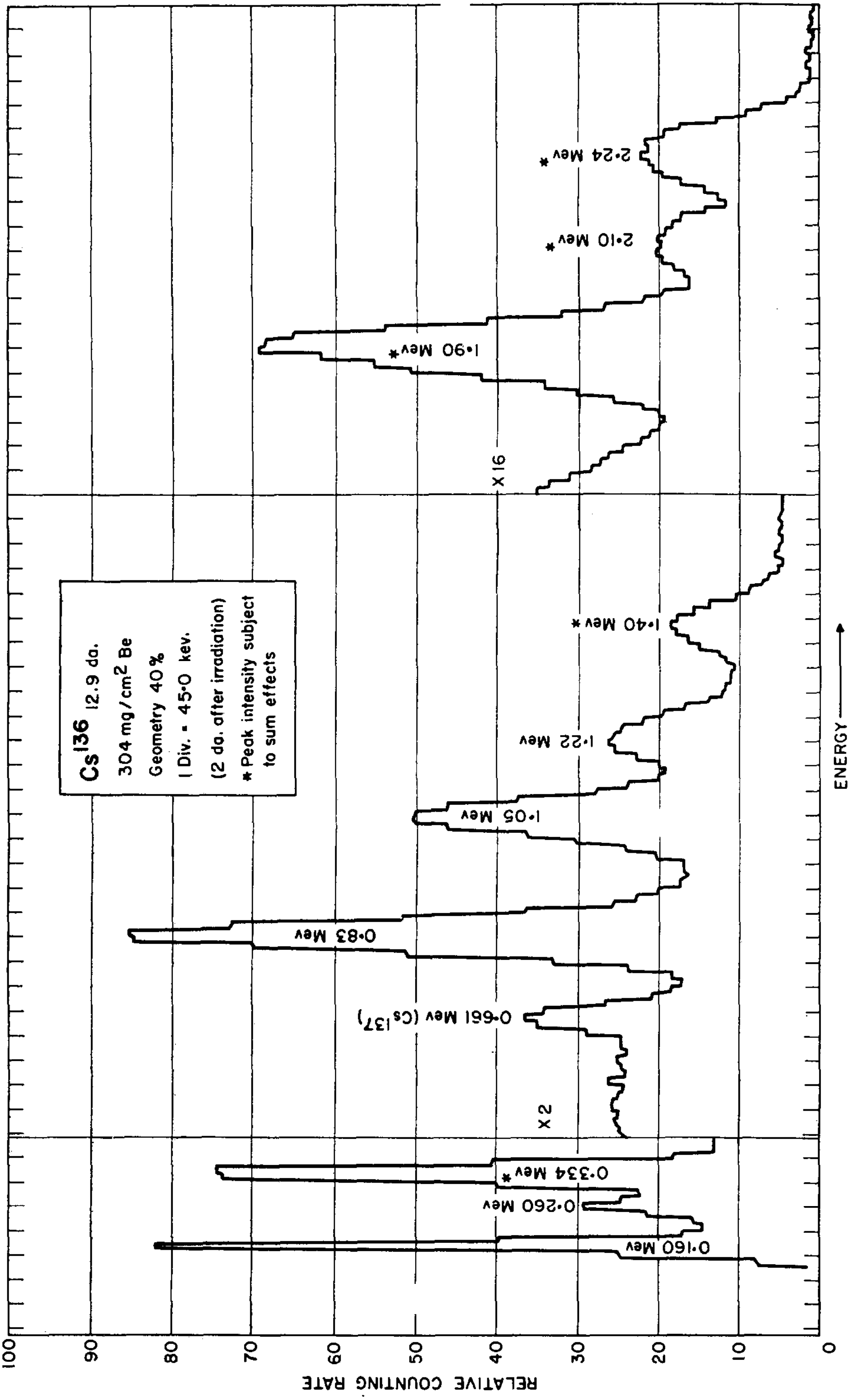

Cs¹³⁶ 12.9 da.
304 mg/cm² Be
Geometry 40%
1 Div. = 45·0 kev.
(2 da. after irradiation)
* Peak intensity subject to sum effects
0·160 Mev
0·260 Mev
0·334 Mev*
X2
0·661 Mev (Cs¹³⁷)
0·83 Mev
1·05 Mev
1·22 Mev
1·40 Mev*
X16
1·90 Mev*
2·10 Mev*
2·24 Mev*
RELATIVE COUNTING RATE
0
10
20
30
40
50
60
70
80
90
100
ENERGY

FIG. 3a.

burn-up samples is an ascending paper chromatographic analysis.[4] Samples of very low burn-up values which require analysis of a large amount of fissile fuel will still require one of the former procedures. Figure 4 shows radioautographs of a typical "fissium" fuel and a calibrated caesium-137 sample after chromatographic analysis. The yield of caesium by this analysis is 100 per cent. Sample solutions of nitric or hydrofluoric acids give somewhat better chromatograms than hydrochloric acid solutions. The fissile fuel solutions containing from 2–100 micrograms of uranium were placed in Whatman 3 MM paper and air dried. The developing solvent was a mixture of 60 g of 49 per cent hydrofluoric acid and 100 ml of dry methyl ethyl ketone. The chromatograms require 3 to 5 hours to develop. The caesium is easily located at the centre of the chromatogram with a simpler Geiger counter probe equipped with a defining slit over the window. The paper is cut and mounted between 25 mil mylar plastic and counted with a scintillation spectrometer. The absolute d/m is obtained by comparing the counting rates under the 661 keV gamma peak of the samples and $4\pi\beta$-calibrated caesium-137 solution chromatographed as shown in Figure 4.

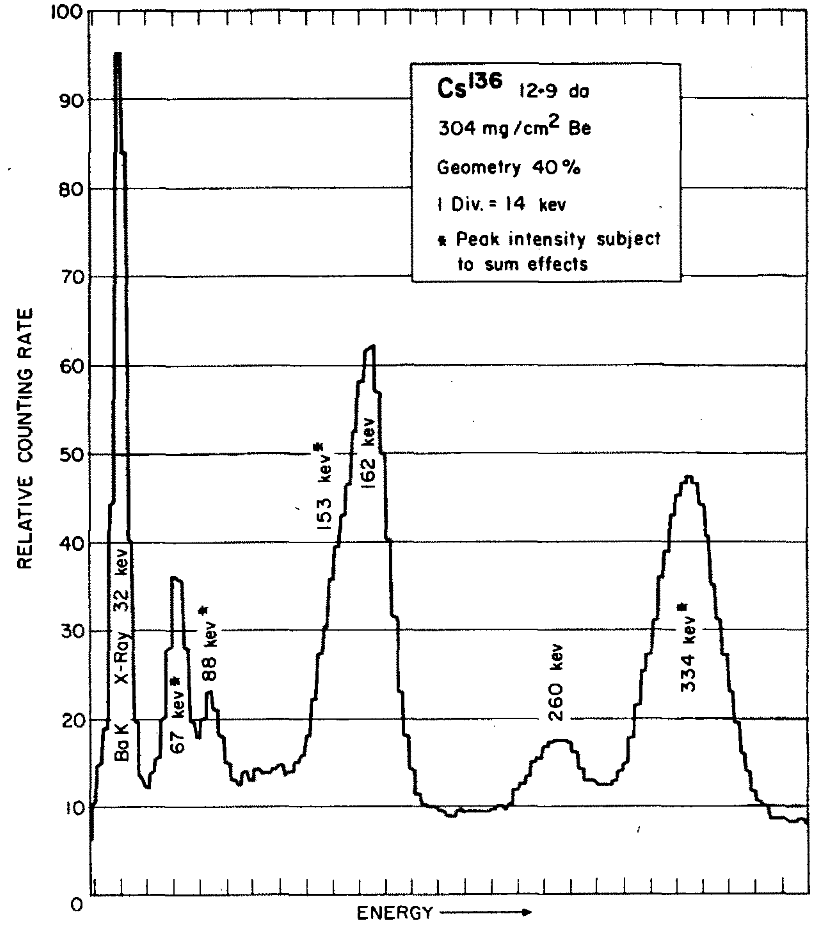
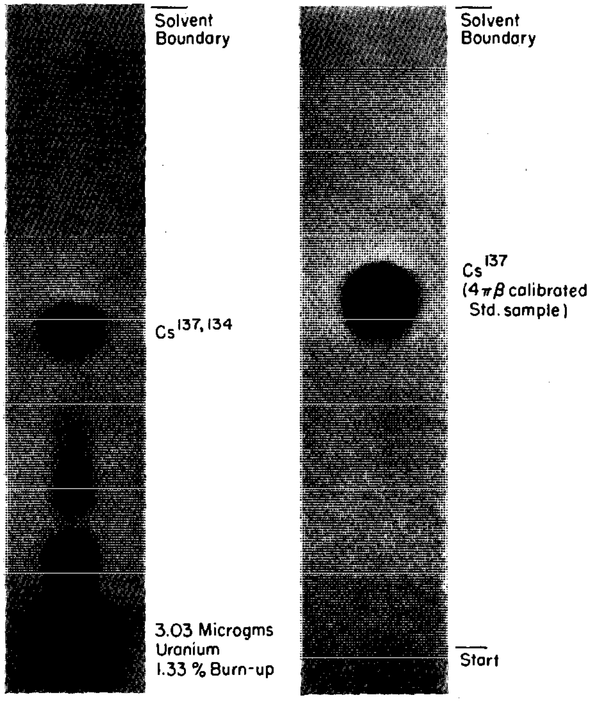


FIG. 3b.

FIGURE 4

CHROMATOGRAPHIC ANALYSIS OF CESIUM FOR PERCENT TOTAL URANIUM ATOM BURN-UP DETERMINATION

(FUEL COMPOSITION: U-95% WITH Mo, Ru, Pd, Rh, Zr AND Nb)



It has been observed that carrier-free caesium solutions show a marked tendency to adsorb on the walls of glass and plastic containers. Over 50 per cent of the carrier free caesium-137 in $2M$ hydrochloric or $2M$ nitric acid has been lost from solution in a month of storage. The addition of approximately one microgram of caesium carrier per ml has stabilised the $4\pi\beta$ calibrated solutions for a period of six months. The same amount of carrier is also added to burn-up samples during dissolution.

THE ASSAY OF NEUTRON CAPTURE AND OTHER NUCLEAR REACTION PRODUCTS

In many reactor problems, it is necessary to correlate the per cent atom burn-up with the formation of other nuclear reaction products. A typical example is the determination of the ratio of neutron capture events of a nuclide to fission events of a particular nuclide or a group of nuclides. The two most useful assay methods are radiochemical and mass spectrometric.

The methods of 4π-counting and scintillation counting are applied as discussed in the previous section for the assay of caesium-137. In each case, some knowledge of the particular decay scheme must be applied as in the case of caesium-137, which has been shown above in detail.

Many heavy element capture reactions produce unstable nuclei in which all the disintegrations go through an alpha branch. It is then possible to determine the absolute d/m to 0·5 per cent or better, with a low geometry alpha counter or a 2π-geometry alpha counter. The 2π-alpha counting will require thinner, more uniformly spread samples for an accurate assay. Jaffey[12] has given a comprehensive discussion of alpha assay instrumentation and methods. Samples which have been alpha-assayed may be used to calibrate a scintillation counter or beta counter. In many experiments, it is not possible or desirable to build up the specific activity of the capture nuclide high enough so that alpha pulse analysis or mass analysis may be applied.

Sodium iodide crystals have been standardised with alpha-assayed americium-241 samples. The intensity of the 59·6 keV gamma transition, as observed with a sodium–iodide scintillation crystal under controlled conditions, was correlated with the disintegration rate. Of the alpha transitions 36·4 per cent also involves the 59·6 keV gamma transition. Gamma assay is often preferred or necessary, rather than alpha or beta assay, because of the rigorous requirements of sample preparation for the latter. Nevertheless, the experimental conditions for calibration and scintillation counting must be carefully defined and maintained. For example, the counting rate of americium-241 under the 59·6 keV full energy peak varies, because of the escape of iodine X-rays from the sodium–iodide crystal. The fraction of X-radiation which escapes is a function of the counting geometry, being a maximum with nuclear radiation striking the crystal at the edges or with small angles of incidence with the crystal surface. Attenuation of the X-rays must be kept constant or negligible. The sample mount is also selected so that secondary scattering is not a factor in the assay.

Neptunium-239 disintegration rate has been accurately determined by $4\pi\beta$-counting. This nuclide, appearing after neutron capture by uranium-238, has an intense unresolved 106 keV gamma and a 104 keV X-ray from both Pu-239 *m* isomeric state and K-conversion. Sixty-five per cent of the disintegrations of neptunium-239 resulted in 104–106 keV photons in the energy range. ^{238}U mono-energetic neutron capture events with Van de Graaff irradiations have been monitored directly in natural uranium metal foils by the authors. A uranium foil of the same material as that irradiated is used to subtract the uranium daughter activity and background. R. C. Axtmann and J. S. Stutheit[1] have previously reported a similar method for monitoring pile-irradiated samples.

Protactinium-233, appearing after neutron capture of throium, contains relatively low energy beta radiation, which makes accurate $4\pi\beta$-counting difficult. Very pure neptunium-237, however, can be obtained and alpha-assayed absolutely. The known protactinium-233 daughter atom content in secular equilibrium with neptunium-237 can then be correlated with the gamma spectrum. The area under the group of unresolved 302–342 keV Pa-233 gamma rays has been used to calibrate scintillation crystals for the determination of protactinium-233 atom content, and thus the neutron capture events which have occurred in thorium targets.

The application of mass analysis for the determination of the number of atoms in irradiated material may require the accurate determination of abundance ratios of adjacent masses in the heavy elements to values as high as 10^5 to 10^6. It is important, therefore, to employ machines and techniques which are specially adapted to this type of analysis. A review of instruments and techniques to 1952 has been compiled by Inghram and Hayden.[10] Mass analysis of samples is obtained at present with a 60°, 12-inch radius mass spectrometer with a multiple filament ionization source. The multiple filament ionization source[11] allows the measurements to be obtained on metal ions rather than the oxide ions. The scattering background under these conditions at one mass unit from the high abundance peak of a heavy element is two parts per million. Accurate analyses of heavy element capture products have been made to 20 parts per million[14] of the adjacent high abundance peak.

Acknowledgement—The authors wish to thank Peter Kafalas, Milton Levenson, Ellis Steinberg, David Okrent, and Richard Vogel for many helpful discussions and criticisms. Also, they wish to acknowledge the assistance and co-operation of Willard McCorkle and Joseph McMillen in carrying out the pile experiments. Allen Madson and Gene McCloud have carried out experiments associated with the burn-up analyses.

Zusammenfassung—Die Definitionen der Ausdrücke "per cent atom burn-up" und "per cent atoms consumed" in ihrer Anwendung auf Kernbrennmaterial-Analyse in Argonne National Laboratorium werden angegeben. Die radiometrischen und analytischen Methoden, die für diesen Analyse-Typus besonders angepasst und entwickelt worden sind, werden erörtert. Die Analyse der Kern-reaktionprodukte durch papierchromatographische Methoden und Spektrometrie wird betont und gezeigt.

Résume—On donne les définitions des termes "per cent atom burn-up" et "per cent atoms consumed" dont on se sert dans l'analyse de combustible nucléaire dans le Laboratoire National d'Argonne. Les méthodes radiochimiques et analytiques qui ont été adaptées et mises au point exprès pour ce genre d'analyse sont discutées. On insiste particulièrement sur l'analyse des produits de réactions nucléaires par chromatographie sur papier et par spectrométrie à scintillation, et on décrit ces méthodes.

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PRELIMINARY COMMUNICATIONS

The determination of metals in organic compounds by the closed flask method

(*Received* 8 *October* 1958)

THE closed oxygen flask method has become widely used in recent years for the determination of sulphur and halogens in organic compounds.[1] It has lately been applied in the determination of phosphorus[2,3] and, since the present work was started, it has been extended to the determination of mercury.[4] It seemed possible that this simple means of decomposition might be applicable as a general procedure for the determination of many metals in organic compounds, hence a selected range of metal-containing organic compounds has been examined. The method was quite successful with certain metals but with others some difficulties were encountered. Silicon-containing compounds were not examined for obvious reasons, nor were compounds containing metals which give difficultly soluble oxides after ignition, *e.g.* aluminium and iron, nevertheless an examination of such compounds might repay investigation. It should be emphasised that only a few compounds of each type were examined. Further work is undoubtedly necessary to establish the most favourable conditions for the decomposition, absorption and titration of all types of compound containing a particular metal; and the purpose of this paper is to indicate the possibilities of the general technique. In order to make the procedures as general as possible, EDTA was used for the titration wherever applicable.

Zinc, cadmium and magnesium

Compounds containing these metals could be burnt without difficulty and the combustion products were absorbed in *N* hydrochloric acid solution. When nitrogenous compounds were analysed, nitrogen oxides, which interfered with the indicator used in the EDTA titration, were decomposed by warming with sulphamic acid. Typical results are shown in Table 1.

TABLE I

Compound	% Metal	
	Found	Theor.
Zinc benzoate	21·77 ± 0·1	21·58
Zinc lactate	22·44 ± 0·2	22·37*
Zinc dibenzyl dithiocarbamate	10·72 ± 0·28	10·71
Magnesium oxinate	6·85 ± 0·35	6·90
Cadmium oxinate	28·55 ± 0·2	28·1
Trifluoromethylphenyldiethylphosphine-cadmiumdiiodide	19·28 ± 0·4	18·99
Di-(trifluoromethylphenyldiethylphosphine)-cadmium tetraiodide	10·11 ± 0·4	10·24
Potassium tetraphenylboron (B determined)	2·99 ± 0·08	3·02
Sodium tetraphenylboron (B determined)	3·16 ± 0·07	3·20

* Determined by a standard method

Procedure: Weigh the sample (5–10 mg) on to filter paper and ignite in the oxygen flask (250-ml) in the usual way.[1,3] The absorption solution is 5 ml of 1*N* hydrochloric acid. Shake the flask thoroughly and allow to stand for at least 20–30 minutes. After having rinsed the stopper and platinum gauze with water, neutralise the solution approximately with ammonia and add 10 ml of

$0{\cdot}005M$ EDTA, 5 ml of buffer solution (67·5 g of ammonium chloride and 570 ml of concentrated ammonia diluted to 1 litre with water) and 2 drops of 0·5% ethanolic Solochrome Black 6B indicator solution. Titrate the excess of EDTA with a $0{\cdot}005M$ magnesium chloride solution to the first appearance of a red colour.

For nitrogen-containing compounds, after rinsing the gauze, suck the air from above the solution at the pump, add several crystals of sulphamic acid, bring just to the boil, cool, neutralise with ammonia, and proceed as above.

For iodine-containing compounds, remove the iodine from the solution by dropwise addition of 1% sodium bisulphite solution until a slight excess is present. Then add a slight excess of 10% formaldehyde solution before proceeding to the neutralisation.

In all determinations, blank tests were run.

Boron

Only two compounds containing boron were available and the amounts of boron present were small. The results were satisfactory at this level (Table 1) but compounds containing higher amounts of boron require testing. To avoid risk of contamination from the usual borosilicate flask, a soda-glass flask was used.

Procedure: Burn the sample in a soda-glass flask containing 10 ml of water as absorbent. Complete the determination by acidimetric titration in the presence of mannitol.[5]

Arsenic

Some attention was given to the method of completion. The quinoline[3,6] method and the bromate method were preferable to various iodometric finishes. During the decomposition of the sample some arsenic was lost by alloying with platinum; this was proved by spectrographic analysis of used wires. Other materials were substituted for platinum; with glass, nickel, nichrome or inconel spirals, either the combustion was unsatisfactory or contamination of the wire still occurred. Platinum has a definite catalytic effect on the combustion and is therefore to be preferred. The formation of an arsenic-platinum alloy is usually assumed to occur only in a reducing atmosphere and this may have been present at the platinum surface at the moment of ignition. However, when the filter paper used to enwrap the sample was impregnated with potassium nitrate, bromate, persulphate or perchlorate, the arsenic recoveries were still slightly low although the combustion took place under stronger oxidising conditions. Of the various reagents tested, potassium nitrate was by far the most satisfactory; the ignition proceeded vigorously but safely and nitrate-impregnated paper might be satisfactory for general use with refractory materials.

Surprisingly, with the standard compound used, arsanilic acid, most of the arsenic was in the tervalent state after the ignition, hence the bromate titration was preferred after the reduction of the small amount of arsenic^{V}. Eventually it was concluded that the flask method for the determination of arsenic has no advantage over the method of Schulek and Villecz[7] and no further attempt was made to solve the problem of the alloy formation.

Antimony compounds were not examined because of the probability of similar behaviour. Again the method of Schulek and Villecz would seem preferable to the flask method.

Other metals

Lead and bismuth compounds were tested with an absorption solution of 3 ml of concentrated nitric acid. Both metals alloyed with platinum, the alloy formation being particularly evident in the case of lead. Further work is required to overcome these effects. In some instances, the alloy could probably be dissolved off the wire and the platinum^{IV} masked with cyanide before the titration.

Certain metals, *e.g.* nickel and gallium, formed insoluble oxides which could not be dissolved by solvents convenient for the subsequent EDTA titration.

Conclusion

Of the metals examined, zinc, cadmium, magnesium and boron offered no unusual difficulties over the range of organic materials available. For arsenic and antimony, the method seemed less advantageous than those already available. Alkali and alkaline earth metals were not examined but it seems likely that flame photometry would be suitable for their determination after the combustion. A silica flask would probably be necessary because of contamination from ordinary glass. Further investigations will fall into three categories: (1) the extension of the method to other metals and to a wider range of compounds; (2) the establishment of the optimum conditions for absorption of the combustion products; and (3) the resolution of the problem of alloy formation with platinum which is serious in some cases. In the meantime it can be concluded that the flask method is a promising means of decomposing some organo-metallic compounds although it cannot at present be considered generally applicable.

Acknowledgment—We wish to express our sincere thanks to Miss Marie Marks for her assistance in carrying our some of these experiments.

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The adherence to Beer's law of solutions of ammonium chloro-iridate and similar compounds

(*Received* 9 *October* 1958)

In 1956, Spitzy, Magee and Wilson[1] confirmed the formation of quinquevalent rhenium by reduction of perrhenate in sulphuric acid solution with bismuth amalgam, and applied this to the determination of rhenium. During the course of recent work in this laboratory in which quinquevalent rhenium was obtained by the above method, it was found that on standing the blue rhenium^{V} solution was transformed into a deep purple solution, with sedimentation of a black powder. The assumption that this change was due to disproportioning of the rhenium^{V} into 4- and 6-valent forms, with deposition of ReO_2 is being investigated polarographically, and the results will be reported later.

It was also observed, in the preparation of potassium perrhenate solutions in sulphuric acid for reduction, that if the concentration of the sulphuric acid was greater than 34*N*, potassium perrhenate (Specpure) dissolved, not with formation of a colourless solution (as in less strongly acid solutions) but with the formation of a solution identical in colour with the disproportioning quinquevalent solutions. The absorption spectra of both solutions were identical.

It is supposed, therefore, that in the solutions in concentrated sulphuric acid the SO_2 impurity reduces a small amount of potassium perrhenate to the 5-valent state, and that this in turn disproportions to rhenium^{IV} and rhenium^{VI} as before.

At a recent extended discussion[2] concerning the existence of mixed valency states in the compound $(NH_4)_2IrCl_6$, it was stated[3] that the deep purple colour of that compound was evidence of the presence of mixed valencies. No-one present, however, was able to confirm that solutions of that compound obey Beer's law. As there appeared to be an obvious similarity between the ammonium chloro-iridate system and the rhenium system which we are investigating, it was considered useful to examine the adherence to Beer's Law of solutions of ammonium chloro-iridate and the rhenium system. Since it is not supposed that mixed valency states of ammonium metals and to a wider range of compounds; (2) the establishment of the optimum conditions for absorption of the combustion products; and (3) the resolution of the problem of alloy formation with platinum which is serious in some cases. In the meantime it can be concluded that the flask method is a promising means of decomposing some organo-metallic compounds although it cannot at present be considered generally applicable.

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It is supposed, therefore, that in the solutions in concentrated sulphuric acid the SO_2 impurity reduces a small amount of potassium perrhenate to the 5-valent state, and that this in turn disproportions to rhenium^{IV} and rhenium^{VI} as before.

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Ammonium chloro-iridate

An aqueous solution containing 0·03 g/100 ml of this compound was prepared, and the absorption spectrum was examined. Absorption maxima were found to occur at 305 mμ, 416 mμ, 435 mμ and 490 mμ. Measurements were carried out in subsequent work at 305 mμ, 435 mμ and 490 mμ.

A series of accurate dilutions of the original solution of ammonium chloro-iridate were prepared, and the spectral densities of the solutions at the above wavelengths were determined. The plot of extinction against dilution factor produced a curve showing marked deviations from Beer's law.

The rhenium system

To compare this system with the ammonium chloro-iridate, a solution containing 0·082 g/100 ml of potassium perrhenate in $36N\ H_2SO_4$ was prepared. The absorption spectrum of this solution has a marked maximum occurring at 513 mμ. Measurements were made at this wavelength.

A series of accurate dilutions of the original solution were prepared, and the plot of extinction against dilution factor produced a curve showing deviation from Beer's law.

Ammonium chloro-osmate

An aqueous solution of this compound containing 0·004 g/100 ml was prepared, and it was found that absorption maxima occur at 309 mμ, 425 mμ and 480 mμ. A series of dilutions of the original solution were prepared. The plot of extinction against dilution factor, in contrast to the other two systems, showed complete adherence to Beer's law.

Conclusion

The results obtained in the above investigations lend support to the view that mixed valencies occur in the ammonium chloro-iridate and the rhenium systems. It will be of interest to extend these investigations to related compounds, and to examine the results obtained from a complete polarographic study, from which indisputable evidence should be obtained.

The investigations described above will be reported in detail subsequently.

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Talanta, 1958, Vol. 1, pp. 412–413. Pergamon Press Ltd., London

BOOK REVIEWS

Radioisotope Laboratory Techniques. R. A. Faires and B. H. Parks. George Newnes Ltd., London, 1958. pp. xii + 244. 25s. net

The rapid proliferation of radiochemical techniques has made it difficult for the specialist to keep abreast of new developments in the field. For the neophyte, the task is virtually impossible. Specialised instrumentation for these techniques has developed along with the techniques themselves, and an entire new industry has sprung up to manufacture and sell the equipment which is essential to the modern radiochemical laboratory.

In many laboratories, the use of radioisotopes for analytical purposes has become almost routine. Biochemists, in particular, have seized on radioactive tracers with enthusiasm, so that many analyses which were either impossible or prohibitively time-consuming are now performed rapidly and with precision by laboratory technicians. Inorganic analysts have been somewhat slower to adopt radiochemical methods, preferring instead to use the more "classical" methods of gravimetry, titrimetry and spectroscopy.

To some extent, this reluctance is traceable to an exaggerated fear of the hazards attendant on the handling of radioactive materials. A more valid reason, however, lies in the substantial capital investment required to outfit a radiochemical laboratory. The radiochemical analyst needs not only the standard analytical equipment—balances, centrifuges, glassware, furnaces, etc.—which must be kept separate from similar equipment for non-radioactive work, but he must also have electronic measuring and recording equipment which may rival a mass spectrometer in cost and complexity. In addition, the radiochemical analyst requires an isolated laboratory to guard against the spread of contamination. He must have special waste-disposal and personnel-monitoring facilities for control of radiation hazard. If the radiochemist is not himself well versed in electronic equipment maintenance, he must either have available the services of specialists or learn to do a substantial amount of maintenance and trouble-shooting himself.

The analytical chemist or laboratory director charged with the responsibility of initiating a radiochemistry programme is certainly entitled to sympathy, at the very least, if he has qualms as he approaches the task of justifying such a programme.

There are many excellent books which deal with the theory of radiochemistry and nuclear physics. Others discuss, in considerable detail, the various experimental applications of radiochemistry in analysis. There are relatively few comprehensive sources, however, which deal with the practical problems of setting up a radiochemical laboratory and putting it to use. The authors, in this book, have made a useful contribution to this problem. In twenty well-edited chapters, they have covered virtually the entire range of subject matter which should be of interest to the beginning radiochemist or to the general analytical chemist who wishes to broaden his professional background.

The first three chapters deal with elementary nuclear physics and radiochemical concepts, giving the reader sufficient background information for his intelligent use of the remainder of the book. Chapter titles include: Introduction to Health Physics; The Laboratory; Decontamination and the Disposal of Waste; Particle Detectors and Their Use; The Statistics of Counting; The Choice of Counting Equipment; and Some Chemical Applications. None of the chapters is definitive; one cannot, for example, read the four chapters on electronic techniques and equipment, and feel equipped to do battle with a 100-channel pulse-height analyser. On the other hand, the authors describe in detail exactly how to prepare a zinc sulphide screen for alpha scintillation counting and name specific sources of supply in Great Britain.

One of the more useful qualities of the book is the recognition by the authors that certain laboratory practices, which are peculiar to radiochemistry and not readily learned except through experience, have not been adequately described. Thus, for example, they devote several paragraphs to the important, though apparently trivial, matter of the proper procedure for putting on and removing a pair of rubber gloves.

The chapter on "Feasibility" will be of particular interest to those who are uncertain as to the possible usefulness of radiochemistry in the solution of their own problems. Several examples are given of feasibility calculations, including one which shows that it would be impractical to label golf balls with cobalt-60 in order to locate them with a Geiger counter.

Both of the authors are associated with the Isotope School at Harwell, and the pedagogical approach, devoid of pedantry, makes for a book of welcome clarity and considerable value.

H. W. KIRBY

Differential Thermal Analysis. W. J. SMOTHERS and Y. CHIANG. Chemical Publishing Co., New York, 1958. pp. 444. $16.00.

THIS book is a comprehensive review of the literature on differential thermal analysis (D.T.A.) covering the period from 1877 to 1957, and contains a directory giving details of differential thermal analysis equipment, the names of the users, and notes of the applications in various laboratories throughout the world.

The text, which occupies only about one third of the work, opens with an historical introduction and goes on in Chapter 1 to describe the development of early forms of D.T.A. apparatus used in the study of clays and in metallurgy. Chapter 2 deals fully with the various items of equipment under the headings of: sample holders, thermocouples, furnaces, rate controllers and recorders; and ends with a description of the special equipments which have been used for high temperature work and for work in controlled atmospheres including vacuum. Also included is a reprint of the A.S.T.M.'s specification E14-51T. Next, there follows a discussion of the factors involved in the qualitative use of the technique and this is illustrated in Chapter 4 by a description of some selected applications of it to the analysis of mixtures, phase studies, the sorption of ions and the transformation of clays. This section concludes with a consideration of the use of other qualitative techniques such as X-ray and chemical analysis, dilatometry, microscopy and weight loss, which may be used to assist in the interpretation of D.T.A. results. Quantitative aspects are introduced in Chapter 5 (by N. F. Tsang) which deals with the various mathematical treatments which have been applied to account for the form of the D.T.A. curve. The simple theories of Speil and Vold are described first, followed by an account of conduction theory and the equivalent system, the latter being illustrated by some numerical examples. Chapter 6 then goes on to consider the methods used by various workers to obtain quantitative data from experimental D.T.A. records. Finally, some further applications of the technique in the study of radiation damage and in geology, chemistry and ceramics are outlined, and the text closes with a chapter on more recent developments and applications.

In view of the large number of references which are given it is not surprising that little attempt has been made by the authors to provide a critical appraisal of the published work. It is without doubt the most compendious reference work on this subject which has appeared to date, and should prove invaluable to most workers in D.T.A. The appendices on the operators of D.T.A. equipment are most useful and, very important in a review of this kind, the applications of D.T.A. to specific substances are indexed with their appropriate literature references.

For the most part the book is well written, although the small size of type used for the subscripts in the mathematical sections occasionally leads to difficulties, and some typographical errors of punctuation make a few sentences read a little strangely. These, however, are minor defects and the authors are to be congratulated on the successful presentation of a very large quantity of data. Whilst the book sets out to review the applications of D.T.A. in the whole field of chemistry and chemical technology, it is clear that by far the greater proportion of work using the technique has so far been concentrated in mineralogy and in ceramics. Nevertheless, the book makes it equally clear that the method has wide scope and it is to be hoped that the authors' efforts will stimulate increased effort in those areas where hitherto it has received little attention.

C. P. CONDUIT

paragraphs to the important, though apparently trivial, matter of the proper procedure for putting on and removing a pair of rubber gloves.

The chapter on "Feasibility" will be of particular interest to those who are uncertain as to the possible usefulness of radiochemistry in the solution of their own problems. Several examples are given of feasibility calculations, including one which shows that it would be impractical to label golf balls with cobalt-60 in order to locate them with a Geiger counter.

Both of the authors are associated with the Isotope School at Harwell, and the pedagogical approach, devoid of pedantry, makes for a book of welcome clarity and considerable value.

H. W. KIRBY

Differential Thermal Analysis. W. J. SMOTHERS and Y. CHIANG. Chemical Publishing Co., New York, 1958. pp. 444. $16.00.

THIS book is a comprehensive review of the literature on differential thermal analysis (D.T.A.) covering the period from 1877 to 1957, and contains a directory giving details of differential thermal analysis equipment, the names of the users, and notes of the applications in various laboratories throughout the world.

The text, which occupies only about one third of the work, opens with an historical introduction and goes on in Chapter 1 to describe the development of early forms of D.T.A. apparatus used in the study of clays and in metallurgy. Chapter 2 deals fully with the various items of equipment under the headings of: sample holders, thermocouples, furnaces, rate controllers and recorders; and ends with a description of the special equipments which have been used for high temperature work and for work in controlled atmospheres including vacuum. Also included is a reprint of the A.S.T.M.'s specification E14-51T. Next, there follows a discussion of the factors involved in the qualitative use of the technique and this is illustrated in Chapter 4 by a description of some selected applications of it to the analysis of mixtures, phase studies, the sorption of ions and the transformation of clays. This section concludes with a consideration of the use of other qualitative techniques such as X-ray and chemical analysis, dilatometry, microscopy and weight loss, which may be used to assist in the interpretation of D.T.A. results. Quantitative aspects are introduced in Chapter 5 (by N. F. Tsang) which deals with the various mathematical treatments which have been applied to account for the form of the D.T.A. curve. The simple theories of Speil and Vold are described first, followed by an account of conduction theory and the equivalent system, the latter being illustrated by some numerical examples. Chapter 6 then goes on to consider the methods used by various workers to obtain quantitative data from experimental D.T.A. records. Finally, some further applications of the technique in the study of radiation damage and in geology, chemistry and ceramics are outlined, and the text closes with a chapter on more recent developments and applications.

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For the most part the book is well written, although the small size of type used for the subscripts in the mathematical sections occasionally leads to difficulties, and some typographical errors of punctuation make a few sentences read a little strangely. These, however, are minor defects and the authors are to be congratulated on the successful presentation of a very large quantity of data. Whilst the book sets out to review the applications of D.T.A. in the whole field of chemistry and chemical technology, it is clear that by far the greater proportion of work using the technique has so far been concentrated in mineralogy and in ceramics. Nevertheless, the book makes it equally clear that the method has wide scope and it is to be hoped that the authors' efforts will stimulate increased effort in those areas where hitherto it has received little attention.

C. P. CONDUIT

NOTICES

The following meetings have been arranged:

Tuesday 25 *November* 1958: **Society for Analytical Chemistry,** Physical Methods Group: Annual General Meeting followed by a meeting on *Modern Methods of Purification*: *Preparative Scale Gas Chromatography*: Dr. C. R. PATRICK, A.R.I.C. *Some Aspects of the practice of Zone Refining*: Dr. C. R. VEALE, A.R.I.C. Chemical Society Meeting Room, Burlington House, London, W.1. 6.30 p.m.

Thursday 27 *November* 1958: **Chemical Society,** Northern Ireland Area: **Royal Institute of Chemistry,** Northern Ireland Section: **Society of Chemical Industry,** Northern Ireland Section. *Analytical Applications of Co-ordination Compounds:* Dr. T. S. WEST. The Queen's University, Belfast. 7.45 p.m.

Thursday 27 *November* 1958: **Chemical Society,** Sheffield Area, **Royal Institute of Chemistry,** Sheffield, South Yorkshire and North Midlands Section: **Sheffield University Chemical Society.** *Organic Complexing Agents in Analytical Chemistry*: Dr. H. M. N. H. IRVING, F.R.I.C., Chemistry Department, The University, Sheffield. 7.30 p.m.

Wednesday 3 *December* 1958: **Society for Analytical Chemistry.** *Food Analysis*: Symposium. The Wellcome Building, Euston Road, London, N.W.1. 3.0 p.m.

Thursday 4 *December* 1958: **Society for Analytical Chemistry,** North of England Section: **Royal Institute of Chemistry,** North Lancashire Section. *Some Recent Advances in Polarography and Other Electrical Methods:* G. F. REYNOLDS, M.Sc., F.R.I.C. Storey Institute, Lancaster. 7.30 p.m.

Tuesday 9 *December* 1958: **Society for Analytical Chemistry,** Midlands Section. *The Analysis of Tar Acids:* H. G. WILLCOCK. Gas Showrooms, Nottingham. 7.0 p.m.

Tuesday 9 *December* 1958: **Society for Analytical Chemistry,** Biological Methods Group. Annual General Meeting followed by a Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 10 *December* 1958: **Society for Analytical Chemistry,** Microchemistry Group: London Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 17 *December* 1958: **Society for Analytical Chemistry,** Midlands Section. Discussion on *Flame Photometry*, to be opened by L. BREALEY, B.Sc. The University, Edgbaston, Birmingham 15.

Friday 19 *December* 1958: **Society for Analytical Chemistry,** Western Section: **Royal Institute of Chemistry,** Cardiff and District Section. *New Techniques in Qualitative Analysis:* D. W. WILSON, M.Sc., F.R.I.C. Cardiff.

Wednesday 7 *January* 1959: **Royal Institute of Chemistry,** Bristol and District Section. Christmas Lecture: *Chromatography:* Dr. F. H. POLLARD. Royal Fort, Bristol, 8.

Tuesday 13 *January* 1959: **Society for Analytical Chemistry,** Midlands Section. Discussion on *The Analytical Chemistry of Cobalt and Nickel*, to be opened by A. J. BROOKES. The University, Edgbaston, Birmingham 15.

Hilger Journal, Vol. V, No. 1 for August 1958 (Hilger and Watts, Ltd., 98 St. Pancras Way, Camden Road, London, N.W.1., England) contains articles dealing with automatic typewriter attachments for recording of spectrographic results, with statistical procedure in relation to spectrochemical analysis, and with atomic-absorpion spectroscopy using the UVISPEK spectrophotometer.

A Bibliography has been prepared (Development Division, the Geigy Company Ltd., Rhodes, Middleton, Manchester, England) dealing with the analytical uses of ethylenediaminetetra-acetic acid. The nine sections of the Bibliography contain more than a thousand references and a comprehensive subject index is provided.

The earliest ten volumes of *The Analyst*, for the years 1876–1885, have been re-published in facsimile form by W. Heffer & Sons Ltd., of Cambridge, who are currently publishers of that journal on behalf of **The Society for Analytical Chemistry.** Each volume is available separately from any bookseller or direct from the publishers at 6 gns. nett, bound in cloth boards in the style of the original. Publication in America is through the Johnson Reprint Corporation.

Talanta, 1958, Vol. 1, p. 415. Pergamon Press Ltd., London.

BOOK RECEIVED

Advanced Analytical Chemistry. LOUIS MEITES and HENRY C. THOMAS. McGraw-Hill Book Company Inc., New York: McGraw-Hill Publishing Company, Ltd., London, 1958. pp. xi + 540. $8.90. 69s.

PAPERS RECEIVED

Ferrous Iron-Sulphuric Acid Reagent for the Determination of Pure Oestrogens. EMMANUEL EPSTEIN WILLIAM O. MADDOCK and A. J. BOYLE. (26 *August* 1958.)

Photometric Determination of Gallium Using Malachite Green. J. JANKOVSKY. (17 *September* 1958.)

Direct Thermometric Titration of Boric Acid. F. J. MILLER and P. F. THOMASON. (19 *September* 1958.)

Studies on Materials Containing Uronic Acid—I: An Apparatus for Routine Semi-Micro Determinations of Uronic Acid Content: D. M. W. ANDERSON. (17 *September* 1958.)

The Determination of Aluminium, Titanium and Nickel in Their Alloys. LOUIS E. HIBBS and DONALD H. WILKINS. (22 *September* 1958.)

The Determination of Aluminium in Thorium Oxide, and a Separation Scheme for Interfering Ions. GERALD GOLDSTEIN, D. L. MANNING and OSCAR MENIS. (22 *September* 1958.)

Visual EGTA Titration of Calcium in the Presence of Magnesium. FAWZY S. SADEK, R. W. SCHMID and CHARLES N. REILLEY. (27 *September* 1958.)

Titrimetric Determination of Manganese following Nitric Acid Oxidation in the Presence of Pyrophosphate. C. OLIVER INGAMELLS. (3 *October* 1958).

The Determination of Copper with Triethylenetetramine using a Metalfluorechromic Indicator. DONALD H. WILKINS and LOUIS E. HIBBS. (3 *October* 1958).

Activation Analysis of Tungsten in High Alloy Steels. G. LELIAERT, J. HOSTE and Z. EECKHAUT (6 *October* 1958.)

Titrimetric Determination of Tetraphenylboron by Thallium$^{\mathrm{I}}$. BHARAT R. SANT and ANIL K. MUKHERJI. (13 *October* 1958).

New Chelons Based on Pyridine. DAVE C. PRIEST, FAWZY S. SADEK, J. F. BUNNETT and CHARLES N. REILLEY. (20 *October* 1958).

Determination of Protactinium-233 by Gamma Spectroscopy. E. I. WYATT and R. R. RICKARD. (22 *October* 1958).

The Use of EDTA to Eliminate Interference in the Zinc-Ferrocyanide Titration. DONALD G. DAVIS and HENRY T. MCLENDON. (23 *October* 1958).

A New Spot Test for the Determination of Fluoride Ion. R. BELCHER, M. A. LEONARD and T. S. WEST. (29 *October* 1958).

EDITORIAL NOTE

The editors and publishers are grateful for the patience of those authors who submitted material when *Talanta* was first projected, and who, because of the large number of papers submitted, have had to await publication until this issue.

It is hoped normally to offer the following schedule: short communications and preliminary communications (particularly if they do not involve illustrations) should be published within 30 to 60 days, and longer communications within 3 to 4 months of acceptance for publication.

Single issues of *Talanta* will normally consist of approximately 80 pages, and the Volume as a whole will contain 4 issues. The next issue, which will be Number 1 of Volume 2, is planned for publication in two months' time.

Talanta, 1958, Vol. 1, p. 416, Pergamon Press Ltd., London.

ERRATA

Page 121, *line* 17: *for* M^{2-} *read* M^{2+}

Page 122, *Fig.* 4 (*upper graph*): *for* 255 mμ *read* 225 mμ. *Transpose Curves* 1 *and* 2.

Page 123, *Fig.* 6. *Replace legend by the following:*

(1) 10 μM magnesium chloride + reagent blank; (2) 10 μM calcium chloride + 1 μM magnesium chloride + reagent blank; (3) 10 μM strontium chloride + 1 μM magnesium chloride + reagent blank; (4) 10 μM barium chloride + 1 μM magnesium chloride + reagent blank.

Page 124, *Table* III. *Error column should read as follows:*

Cation	Error (μM)	Cation	Error (μM)
Magnesium	−0·20 0 +0.04 −0·15	Strontium	−0·14 +0·02 0 +0·07
Calcium	−0·05 +0·20 −0·20 −0·02	Barium	+0·10 +0·14 +0·08 +0·09

Page 126. *Ref.* 16 *should read: Analyst.* 1956, **81,** 79.

Page 180. *Replace existing Fig.* 4 *by*

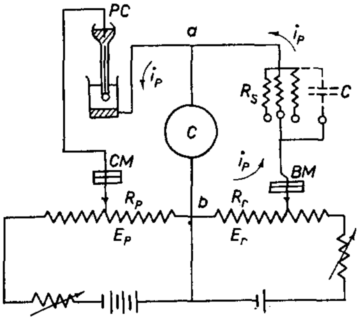

FIG. 4. Compensating bridge circuit.

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