An International Journal of Analytical Chemistry

ταλαντα

talanta

PERGAMON PRESS
LONDON NEW YORK PARIS LOS ANGELES

VOLUME I NUMBERS 1/2 JULY 1958

EDITOR-IN-CHIEF

Dr. C. L. Wilson; Department of Chemistry, The Queen's University, Belfast, Northern Ireland.

REGIONAL EDITORS

Professor L. Gordon; Department of Chemistry and Chemical Engineering, Case Institute of Technology, Cleveland 6, Ohio, U.S.A.

Dr. R. Přibil; Analytical Laboratory of ČSAV, Praha, I, Jilská 16, Czechoslovakia.

Professor T. Takahashi; 1051 Wadahon cho, Sugiyami ku, Tokyo, Japan.

ADVISORY BOARD

Professor F. E. Beamish—Toronto
Dr. R. Belcher—Birmingham (Chairman of the Board)
Professor H. Bode—Hanover
Professor C. Cimerman—Haifa
Dr. C. E. Crouthamel—Argonne, Illinois
Professor P. Delahay—Baton Rouge, Louisiana
Professor H. Diehl—Ames, Iowa
Dr. C. Drăgulescu—Timisoara
Professor L. Erdey—Budapest
Professor F. Feigl—Rio de Janeiro
Dr. H. Flaschka—Atlanta, Georgia
Professor W. Geilmann—Mainz
Dr. J. Hoste—Ghent
Mr. H. W. Kirby—Miamisburg, Ohio
Professor F. Lucena-Gonde—Salamanca
Dr. S. J. Lyle—Durham
Dr. R. J. Magee—Belfast
Dr. H. Malissa—Düsseldorf
Professor W. Wayne Meinke—Ann Arbor, Michigan
Dr. J. Minczewski—Warsaw
Dr. A. D. Mitchell—London
Dr. G. H. Morrison—Flushing, New York
Professor F. Nydahl—Uppsala
Dr. E. Rancke-Madsen—Copenhagen
Professor G. Gopala Rao—Waltair, S. India
Professor C. N. Reilley—Chapel Hill, N. Carolina
Dr. M. L. Salutsky—Baltimore, Maryland
Professor E. Schulek—Budapest
Professor G. Frederick Smith—Urbana, Illinois
Dr. T. B. Smith—Sheffield
Professor H. Specker—Dortmund-Aplerbeck
Professor P. S. Tutundžić—Belgrade
Professor F. L. Warren—Pietermaritzburg
Dr. H. Weisz—Vienna
Dr. T. S. West—Birmingham
Dr. James C. White—Oak Ridge, Tennessee
Professor H. H. Willard—Ann Arbor, Michigan
Mr. F. J. Woodman—Sellafield

Publishing Offices: 4 & 5 Fitzroy Square, London W.1. (EUS 4455)

Subscription (including postage): (A) *per volume* £6 (U.S.A. $17.00). (B) for subscribers certifying that the journal is for their own personal use—*per annum* £5 5s. ($15.00)

Payment must be made in advance

Copyright
©
1958
Pergamon Press Ltd.

Pergamon Press are also the publishers of the following journals:

Journal of Nuclear Energy (*including* The Soviet Journal of Atomic Energy *on behalf of Pergamon Institute, a non-profit-making foundation*)
Health Physics (*The official journal of the Health Physics Society*)
Tetrahedron (*The International Journal of Organic Chemistry*)
Journal of Inorganic and Nuclear Chemistry
International Journal of Applied Radiation and Isotopes
Biochemical Pharmacology (*An International Journal devoted to Research into the Development of Biologically Active Substances and their Mode of Action on the Biochemical and Sub-cellular Level*)
*Bulletin of the Academy of Sciences of the U.S.S.R., Geophysics Series
*Biophysics
*Journal of Microbiology, Epidemiology and Immunobiology
*Problems of Hematology and Blood Transfusion
*Problems of Oncology
*Problems of Virology
*Radio Engineering and Electronics
*Radio Engineering
*Telecommunications
*Electric Technology, U.S.S.R.
*Abstracts of Metallurgy
*The Physics of Metals and Metallography
Chemical Engineering Science
Journal of Atmospheric and Terrestrial Physics
Geochimica et Cosmochimica Acta
Bulletin Géodésique
Annals of the International Geophysical Year
Spectrochimica Acta
Acta Metallurgica (*for the Board of Governors of Acta Metallurgica*)
Journal of the Mechanics and Physics of Solids
International Journal of the Physics and Chemistry of Solids
Deep-Sea Research
Journal of Neurochemistry
Journal of Psychosomatic Research
Journal of Insect Physiology
Journal of Air Pollution
International Abstracts of Biological Sciences (*for Biological and Medical Abstracts Ltd.*)
Rheology Abstracts

* Translations of Russian Journals published on behalf of Pergamon Institute, a non-profit-making foundation.

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

F. E. Beamish
University of Toronto, Toronto, Ontario, Canada

(*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 0·2–0·5*N* 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 für 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 natürlichen Quellen werden nicht berücksichtigt, 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.

REFERENCES

[1] W. J. Allen and F. E. Beamish, *Analyt. Chem.*, 1952, **24,** 1608–12.
[2] *Idem, ibid.*, 1950, **22,** 451–4.
[3] C. J. Anderson and R. A. Keeler, *ibid.*, 1954, **26,** 213–4.
[4] U. Antony and A. Lucchesi, *Gazzeta*, 1896, **26,** 211.
[5] A. Atterburg, *Chem.-Ztg.*, 1898, **22,** 522, 538: *Chem. Zentr.*, 1898, **11,** 316, 604.
[6] G. Ayres and E. W. Berg, *Analyt. Chem.*, 1953, **25,** 980–1.
[7] R. R. Barefoot, W. J. McDonnell and F. E. Beamish, *ibid.*, 1951, **23,** 514–6.
[8] F. E. Beamish and J. Dale, *Ind. Eng. Chem. Anal.*, 1938, **10,** 697.
[9] F. E. Beamish and J. J. Russell, *ibid.*, 1936, **8,** 141.
[10] F. E. Beamish, J. J. Russell, and J. Seath *ibid.*, 1937, **9,** 174.
[11] F. E. Beamish and M. Scott, *ibid.*, 1937, **9,** 460–3.
[12] E. W. Berg and W. L. Senn, *Analyt. Chem.*, 1955, **27,** 1255.
[13] J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, 1826, **21,** 186.
[14] A. P. Blackmore, M. A. Marks, R. R. Barefoot and F. E. Beamish, *Analyt. Chem.*, 1952, **24,** 1815–9.
[15] H. Bode, *Z. analyt. Chem.*, 1951, **133,** 95–100.
[16] E. E. Bugbee, *Textbook of Fire Assaying*. New York, John Wiley and Sons, 1938, p. 258.
[17] F. Burriel and F. Pino Perez, *Anales Fis. Quim.*, 1951, **47B,** 653–6.
[18] P. Champ, P. Fauconnier and C. Duval, *Analyt. Chim. Acta*, 1952, **6,** 250–8.
[19] *Idem, ibid.*, 1954, **10,** 443.
[20] M. L. Cluett, S. S. Berman and W. A. E. McBryde, *Analyst*, 1955, **80,** 204.
[21] R. A. Cooper, *J. Chem. Met. Mining Soc. S. Africa*, 1924–5, **25,** 296–7.

[22] J. E, Currah, W. A. E. McBryde, A. J. Cruikshank and F. E. Beamish, *Ind. Eng. Chem. Anal.*, 1946, **18,** 120.

[23] P. R. Dasgupta, *J. Indian Chem. Soc.*, 1953, **30,** 761–4.

[24] S. K. Datta, *ibid.*, 1955, **32,** 785–90.

[25] C. W. Davis, *Bur. Mines Rept., Invest.*, 1922, 2351.

[26] R. Doht, *Z. analyt. Chem.*, 1924, **64,** 37.

[27] L. Duparc, *Compt. Rend. Soc. Phys. Hist. Nat., Genève*, 1912, **29,** 20.

[28] C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier Publishing Co., New York, 1953, p. 85.

[29] H. Erdmann and O. Makowka, *Bull. Soc. chim.*, 1905, (3), **34,** 572.

[30] *Idem, Z. analyt. Chem.*, 1907, **46,** 1251.

[31] F. Feigl, *ibid.*, 1924, **65,** 25: *Z. anorg. Chem.*, 1926, **157,** 269.

[32] J. F. Flagg, *Organic Reagents.* Interscience Publishers, New York, 1948.

[33] C. H. Fulton and W. J. Sharwood, *Manual of Fire Assaying.* McGraw-Hill Book Co., New York, 1929, p. 225.

[34] E. Gagliardi and R. Pietsch, *Monatsh*, 1951, **82,** 432–6.

[35] *Idem, ibid.*, 1951, 656–61.

[36] *Idem, ibid.*, 1952, **83,** 487–92.

[37] R. Gaze, *Analyst*, 1913, **38,** 173.

[38] R. Gilchrist, *Bur. Stand. Sci. Papers*, 1924, **19,** 325.

[39] *Idem, Bur. Stand. J. Res.*, 1929, **3,** 993–1004.

[40] *Idem, ibid.*, 1931, **6,** 421.

[41] *Idem, ibid.*, 1932, **9,** 547.

[42] *Idem, ibid.*, 1934, **12,** 291.

[43] R. Gilchrist and E. Wichers, *J. Amer. Chem. Soc.*, 1935, **57,** 2565–73.

[44] Z. E. Gol'Braikh, *J. Gen. Chem.*, (*U.S.S.R.*), 1944, **14,** 810–1.

[45] A. Gutbier and F. Falco, *Z. analyt. Chem.*, 1909, **48,** 555.

[46] *Idem, ibid.*, 1910, **49,** 287.

[47] A. Gutbier and C. Fellner, *ibid*, 1915, **54,** 205–8.

[48] A. Gutbier and L. V. Muller, *Ber.*, 1909, **42,** 2205.

[49] A. Gutbier and M. Riess, *ibid.*, 1437–41.

[50] R. L. Haines and D. E. Ryan, *Canad. J. Res.*, 1949, **27B,** 72–5.

[51] J. Hanus, J. Jilek and J. Lukas, *Chem. News*, 1925, **131,** 401–2; *ibid.*, 1926, **132,** 1–4.

[52] J. R. Hayes, *Univ. Microfilms*, Ann Arbor, Mich., Pub. No. 341, 1941, pp. 47.

[53] J. R. Hayes and G. C. Chandlee, *Ind. Eng. Chem. Anal.*, 1942, **14,** 491–3.

[54] M. A. Hill and F. E. Beamish, *Analyt. Chem.*, 1950, **22,** 590.

[55] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis,* John Wiley and Sons, New York, 1929.

[56] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis,* John Wiley and Sons, Inc., New York, 2nd Edn., 1953.

[57] I. Hoffman, J. E. Schweitzer, D. E. Ryan and F. E. Beamish, *Analyt. Chem.*, 1953, **25,** 1091–94.

[58] H. Holzer, *Z. analyt. Chem.*, 1933, **95,** 392.

[59] E. de Hovre, *Ing. chim.*, 1953, **35,** 83–7.

[60] V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, 1916, **48,** 527.

[61] D. S. Jackson and F. E. Beamish, *Analyt. Chem.*, 1950, **22,** 813–7.

[62] P. Jannasch and W. Bettges, *Bull. Soc. chim.*, 1905, (3), **34,** 570.

[63] P. Jannasch and L. Rostosky, *ibid.*, 571.

[64] N. F. Kember and R. A. Wells, *Analyst*, 1955, **80,** 735.

[65] M. R. Kennedy and J. J. Fitzgerald, *U.S. Atomic Energy Comm.*, KAPL-**1052,** 6 pp., 1954.

[66] I. M. Kolthoff and E. A. Pearson, *J. Phys. Chem.*, 1932, **36,** 549.

[67] E. Leidié and L. Quennessen, *Bull. Soc. chim.*, 1903, (3), **29,** 805.

[68] *Idem, Compt. rend.*, 1903, **136,** 1399.

[69] O. Makowka, *Z. analyt. Chem.*, 1907, **46,** 145–50.

[70] C. Mayr, *ibid.*, 1934, **98,** 402.

[71] C. Mayr and W. Prodinger, *ibid.*, 1939, **117,** 334.

[72] H. Mazourevitch, *Bull. Soc. chim.*, 1930, **47,** 1160.

[73] E. von Meyer, *J. prakt. Chem.*, 1877, **15,** 1, 123.

[74] A. Musil and R. Pietsch, *Z. analyt. chem.*, 1952, **137,** 321–4.
[75] T. Naito, *Bunseki to Shiyaku*, 1949, **3,** 84–5.
[76] T. Naito, Y. Y. Kinoshita and J. Hayoshi, *J. Pharm. Soc. Japan*, 1949, **69,** 361–3.
[77] S. C. Ogburn Jr., *J. Amer. Chem. Soc.*, 1926, **48,** 2507.
[78] S. C. Ogburn, Jr. and W. C. Brastow, *ibid.*, 1933, **55,** 1307.
[79] S. C. Obburn and L. F. Miller, *ibid.*, 1930, **52,** 42.
[80] S. C. Ogburn and A. H. Reismeyer, *ibid.*, 1928, **50,** 3018.
[81] C. Paal and C. Amberger, *Bull. Soc. chim.*, 1905, (3), **34,** 1277.
[82] *Idem, Ber.*, 1907, **40,** 1378.
[83] F. Pino Perez, and F. Burriel, *Anales Fís. Quím.*, 1951, **47B,** 657–8.
[84] E. S. Przhevals skii, V. I. Shlenskaya and N. F. Ogarkova, *Vestnik Moskov Univ.* 9, *No.* 10, *Ser. Fiz-Mat. i Estestven.*, 1954, **7,** 59–64.
[85] N. K. Pshenitsyn, *Izvest. Sektora Platiny i Drugikh Blagorodnykh Metal., Inst. Obshehei i Neorg. Khim. Akad. S.S.S.R.*, 1948, **22,** 16.
[86] N. K. Pshenitsyn and I. A. Fedorova, *ibid.*, 1948, 76–9.
[87] N. K. Pshenitsyn and G. A. Nekrasova, *ibid.*, 1955, **30,** 126–41.
[88] P. C. Ray, *Proc. Chem. Soc.*, 1914, **30,** 304.
[89] S. A. Reed and C. V. Banks, *Proc. Iowa Acad. Sci.*, 1948, **55,** 267–75.
[90] W. J. Rogers, F. E. Beamish and D. S. Russell, *Ind. Eng. Chem. Anal.*, 1940, **12,** 561.
[91] H. Rose, *Handb. der Anal. Chem.*, 6th edn., Vol. 2, p. 204.
[92] D. E. Ryan, *Analyst*, 1952, **77,** 46–8.
[93] *Idem, Canad. J. Chem.*, 1956, **34,** 1683–6.
[94] D. E. Ryan and P. Fainer, *Canad. J. Res.*, 1949, **27B,** 67–71.
[95] M. A. Sa, *Rev. Asoc. bioquím. argentina*, 1949, **16,** No. 64, 11–16.
[96] E. B. Sandell, *Ind. Eng. Chem. Anal.*, 1944, **16,** 342.
[97] W. Schmidt, *Z. anorg. Chem.*, 1913, **80,** 335.
[98] W. R. Schoeller, *Analyst*, 1926, **51,** 392–7.
[99] *Idem, ibid.*, 1930, **55,** 354.
[100] *Idem, ibid.*, 550.
[101] R. Schontal, *J. Chem. Soc.*, 1938, 1099; *Mikrochemie*, 1938, **24,** 20.
[102] W. W. Scott, *Standard Methods of Chemical Analysis*, 5th Edn., 1945, Vol. 1. D. Van Nostrand Co., New York.
[103] E. A. Smith, *Sampling and Assaying of the Precious Metals*, 2nd Edn. Griffin and Co., London, 1947.
[104] N. C. Sogani and S. C. Bhattacharya, *Analyt. Chem.*, 1956, **28,** 81–3.
[105] *Idem, ibid.*, 1616–8.
[106] P. C. Stevenson, A. A. Franke, R. Borg and W. Nervic, *J. Amer. Chem. Soc.*, 1953, **75,** 4876.
[107] E. H. Swift and E. A. Butler, *Analyt. Chem.*, 1956, **28,** 146–53.
[108] I. K. Taimni and G. B. S. Salaria, *Analyt. Chim. Acta*, 1954, **11,** 329–37.
[109] *Idem, ibid.*, 1955, **13,** 28.
[110] M. Tashiro, *J. Chem. Soc. Japan*, 1931, **52,** 232.
[111] R. Thiers, W. Graydon and F. E. Beamish, *Analyt. Chem.*, 1948, **20,** 831–7.
[112] S. O. Thompson, F. E. Beamish and M. Scott, *Ind. Eng. Chem. Anal.*, 1937, **9,** 420.
[113] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 9th Edn., Vol. 2, John Wiley and Sons, Inc., New York, 1942.
[114] L. Tshugaev and J. Benevolenski, *Z. anorg. Chem.*, 1913, **82,** 420.
[115] L. A. Tshugaev and W. Subbotin, *J. Chem. Soc.*, 1910, **98,** 354.
[116] I. Ubaldini, *Gazzetta*, 1948, **78,** 293–301.
[117] I. Ubaldini and L. Nebbie, *Ann. Chim. appl.*, 1948, **38,** 241–8.
[118] *Idem, Chimica e Industria*, Milan 1951, **33,** 360.
[119] J. Vorisek and Z. Vejdelek, *Chem. Listy*, 1943, **37,** 50–3, 65–70, 91–5.
[120] R. C. Voter, C. V. Banks and H. Diehl, *Analyt. Chem.*, 1948, **20,** 652–4.
[121] G. W. Watt, D. M. Sowards and R. E. McCarley, *ibid.*, 1956, **28,** 556.
[122] A. D. Westland and F. E. Beamish, *Amer. Min.*, Publication expected June 1958.
[123] *Idem, Analyt. Chem.*, 1954, **26,** 739.
[124] *Idem, Mikrochim. Acta*, 1956, 1474–9.

[125] *Idem*, *ibid.*, 1957, 625- 639.
[126] M. Wunder and V. Thuringer, *Ann. Chim. anal. et Chim. appl.*, 1912, **17**, 201-2.
[127] *Idem*, *Z. analyt. Chem.*, 1913, **52**, 101–4, 660–4, 737.
[128] *Idem*, *Compt. Rend. Soc. Phys. Hist. Nat. Genève*, 1913, **30**, 12.
[129] R. F. Wilson and L. E. Wilson, *Analyt. Chem.*, 1956, **28**, 93–6; *J. Amer. Chem. Soc.*, 1956, **78**, 2370–1.
[130] M. Ziegler and O. Glemser, *Z. analyt. Chem.*, 1956, **153**, 352–4.
[131] H. E. Zschiegner, *J. Ind. Eng. Chem.*, 1925, **17**, 294.

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

REACTIONS OF THIOACETAMIDE IN ALKALINE BUFFER SYSTEMS

DENNIS G. PETERS and ERNEST H. SWIFT
California Institute of Technology, Pasadena, California, U.S.A.

(*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.

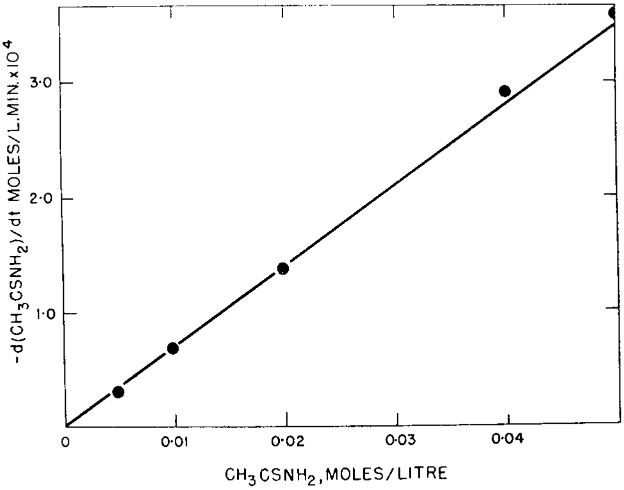


Fig. 1. Rate of disappearance of thioacetamide at 90° as a function of thioacetamide concentration.

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 0.35VF 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

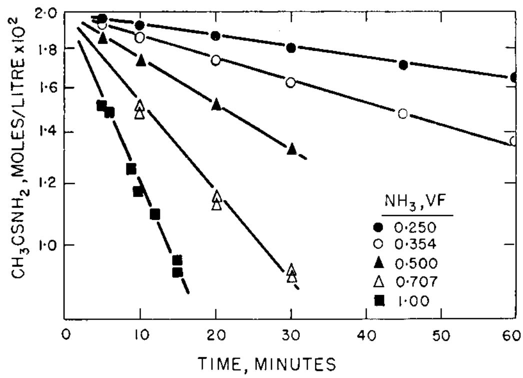


Fig. 2. Plot of thioacetamide concentration against time, showing second-order dependence of the rate of reaction on the ammonia concentration.

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

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

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

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°.

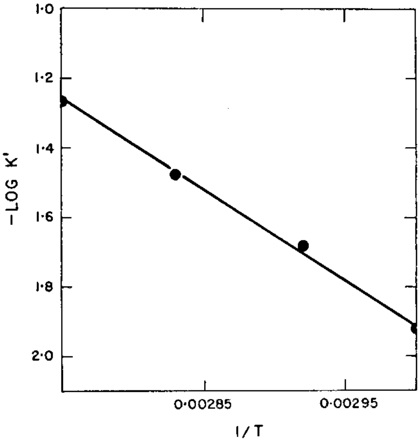
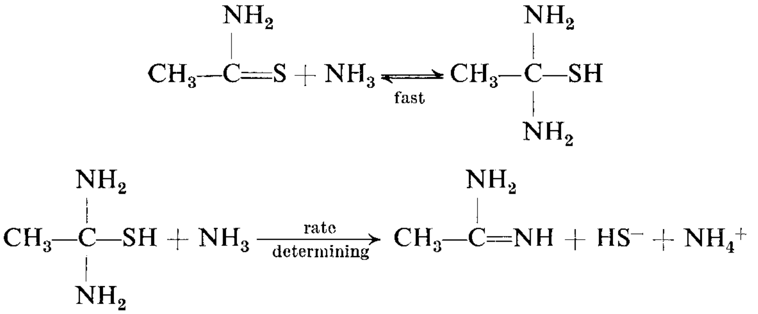


FIG. 3. Rate of the ammonia–thioacetamide reaction as a function of temperature.

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:



$$CH_3-\overset{\overset{\displaystyle NH_2}{|}}{C}=S + NH_3 \xrightleftharpoons[\text{fast}]{} CH_3-\underset{\underset{\displaystyle NH_2}{|}}{\overset{\overset{\displaystyle NH_2}{|}}{C}}-SH$$

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

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.

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

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

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

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 wären.

In Lösungen mit Ammoniak und Ammonium-chlorid an pH 10 gepuffert, ist die Geschwindigkeit der Sulphid-Bildung erster Ordnung bezüglich des Thioacetamids und zweiter Ordnung bezüglich des Ammoniaks, die Dritte-Ordnung-Geschwindigkeits-Konstante war 0,055 L^2Mol^{-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 Primär-Ordnen in Abhangigkeit von Thioacetamid und Carbonat-Ion-Konzentrationen, aber von Wasserstoffcarbonat 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°.

REFERENCES

[1] D. F. Bowersox and E. H. Swift, *Analyt. Chem.*, 1958, in press.

[2] *Idem*, unpublished experiments.

[3] E. A. Butler, D. G. Peters and E. H. Swift, *Analyt. Chem.*, 1958, in press.

[4] J. C. Crocker and F. H. Lowe, *J. Chem. Soc.*, 1907, **91**, 952.

[5] E. H. Swift and E. A. Butler, *Analyt. Chem.*, 1956, **28**, 146.

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

Talanta, 1958, Vol. 1, pp. 39-40, Pergamon Press Ltd., London.

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

CARL E. CROUTHAMEL and CHRISTOPHER GATROUSIS
Argonne National Laboratory, Lemont, Illinois, U.S.A.

(*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 Salzsäure und Fluorwasserstoffsäure als Lösungsmittel wird beschrieben. Dieses Verfahren für Isolation von ^{210}Po aus Wismuth-Scheiben gibt in einer einzigen Operation reine Proben von 100 % Ausbeute. Die Lösungen von ^{210}Po in einem sehr kleinen Volum werden erhalten und sie waren für Hochauflösung-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.

REFERENCES

[1] W. J. Frierson and J. W. Jones, *Analyt. Chem.*, 1951, **23**, 1447.
[2] K. W. Bagnall, *Quart. Reviews*, 1957, **11**, 34.
[3] C. E. Crouthamel and A. J. Fudge, *J. Inorg. Nuclear Chem.*, 1958, **5**, 240.

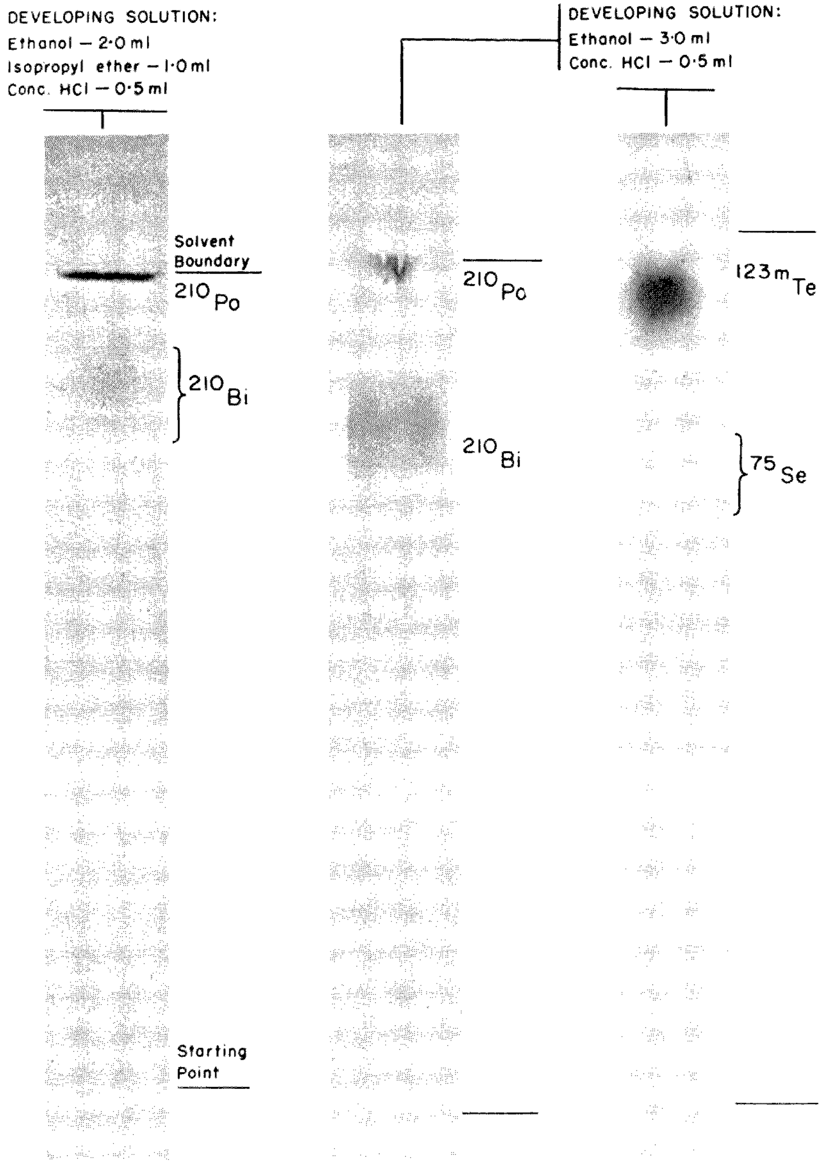


FIG. 1.—Chromatographic separation of polonium and bismuth, and selenium and tellurium.

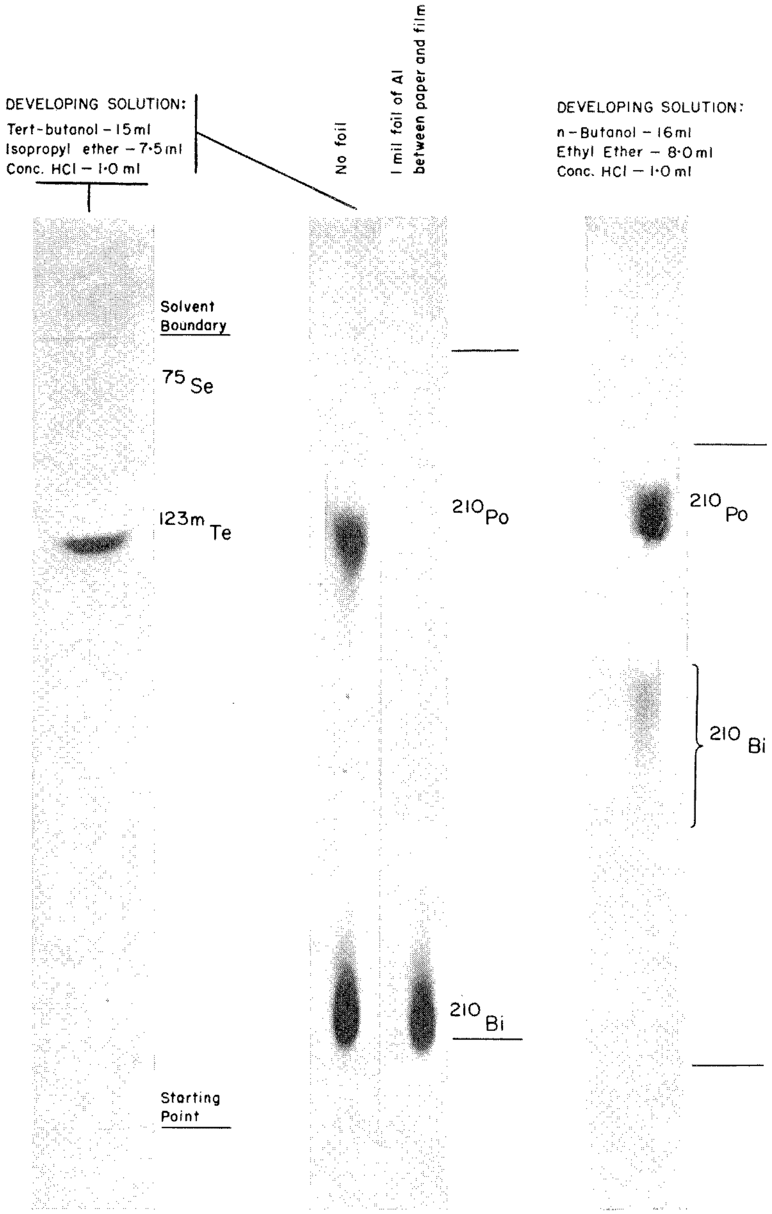


FIG. 2.—Chromatographic separation of selenium, tellurium, polonium and bismuth.

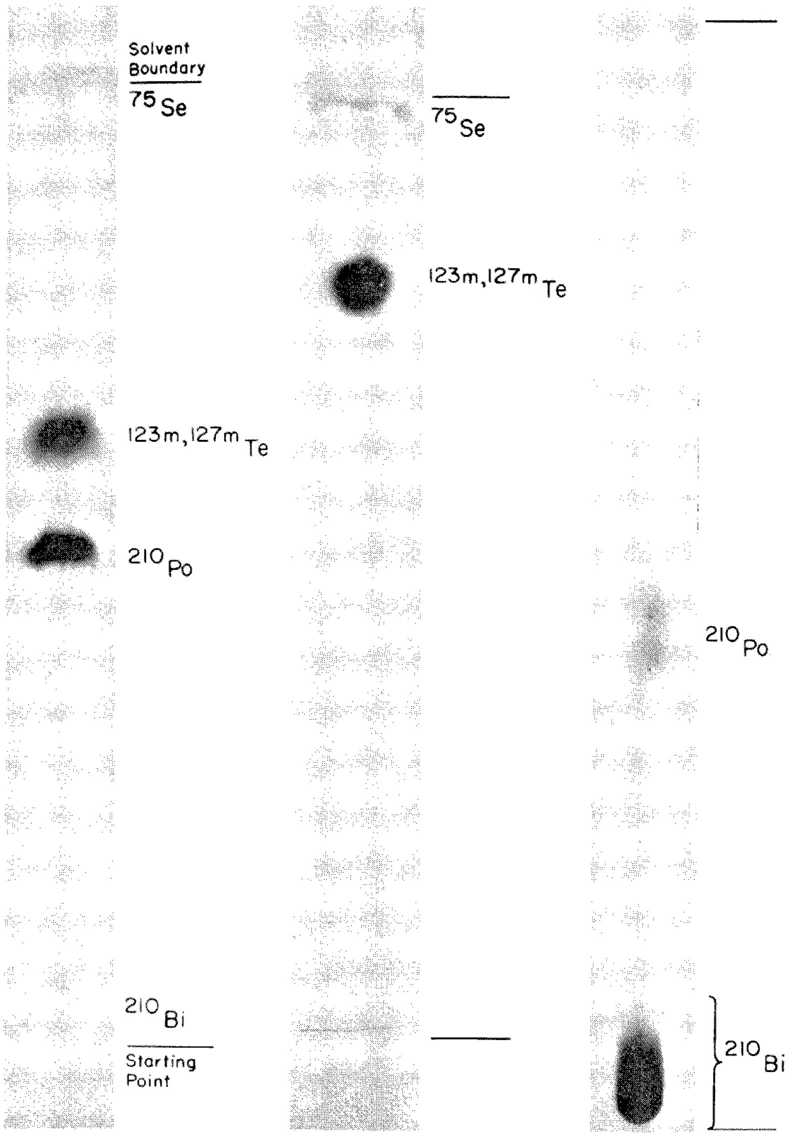


FIG. 3.—Chromatographic separation of tellurium and selenium, and polonium and bismuth. (Developing solution 60 g of 49% hydrofluoric acid per 100 ml methyl ethyl ketone.)

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

SODIUM HYDROGEN DIGLYCOLATE AS A REFERENCE BUFFER

DONALD A. KEYWORTH and RICHARD B. HAHN
Chemistry Department, Wayne State University, Detroit 2, Michigan, U.S.A.

(*Received* 20 *February* 1958)

Summary—A 0·2*M* 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 0·2*M* sodium hydrogen diglycolate solution has a high buffer capacity. The pH is not changed greatly by addition of salt up to a concentration of 0·05*M*. Dilution of the 0·2*M* 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 0·33*M* (saturated) to 0·001*M*. Table I shows the pH to be constant over a wide concentration range, with the value 3·40 ± 0·01 at 20° for a 0·2*M* 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

---

* 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

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

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

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

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. β_{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 $K_1 = 1{\cdot}1 \times 10^{-3}$, and[11] the ionisation constant $K_2 = 3{\cdot}7 \times 10^{-5}$. 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* Lösung von Natrium Wasserstoff-diglycolat hat pH 3,40 ± 0,02 und wird von dem allgemein erhältlichen Salz hergestellt. pH dieser Lösung ist über einem bruten Temperatur-Gebiet konstant und hat eine hohe Puffer-Kapazität. Der Zusatz von Salz bis Konzentration von 0,05*M* bringt keine grosse Änderung mit sich.

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

Durch diese Eigenschaften ist diese Verbindung anwendbar als Referenz-Puffer für 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.

REFERENCES

[1] G. Bates, *Analyt. Chem.*, 1957, **29,** 15A.
[2] *Idem.*, *Electrometric pH Determinations.* John Wiley and Sons, Inc., New York, 1954, p. 180.
[3] *Idem.*, *ibid.*, p. 93.
[4] *Idem.*, *ibid.*, p. 74.
[5] W. M. Brunner and L. T. Sherwood, *Ind. Eng. Chem.*, 1949, **41,** 1653.
[6] I. Feldman, *Analyt. Chem.*, 1956, **28,** 1859.
[7] W. J. Hammer and S. F. Acree, *J. Res. Nat. Bur. Stand.*, 1944, **32,** 215.
[8] D. A. Keyworth and R. B. Hahn, ACS National Meeting, September 1957; *Analyt. Chem.*, 1958, (In press).
[9] J. J. Lingane, *Analyt. Chem.*, 1947, **19,** 810.
[10] W. Ostwald, *Z. Phys. Chem.*, 1889, **3,** 186.
[11] R. Wegscheider, *Monatsh.*, 1902, **23,** 624.

Talanta, 1958, Vol. 1, pp. 46-54, Pergamon Press, Ltd. London.

PHOTOMETRIC TITRATION OF PHENOLS

ROBERT W. MCKINNEY and C. A. REYNOLDS
Department of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.

(*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 0.05M 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.

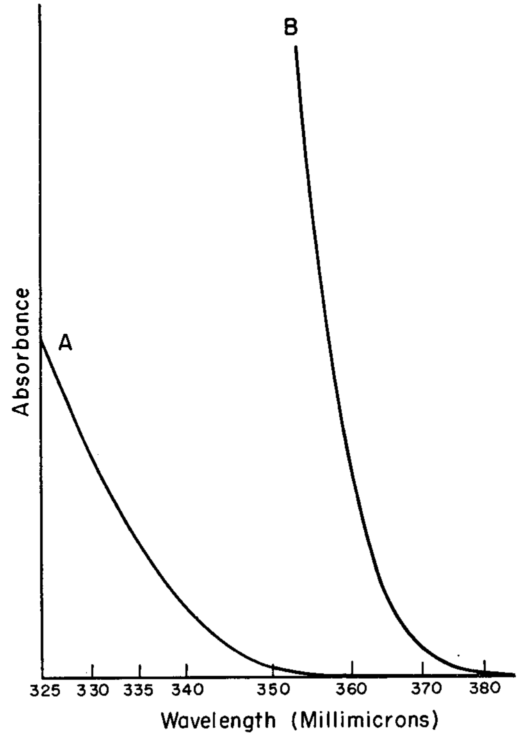


FIG. 1.—Absorption spectra of *p*-hydroxydiphenyl and its phenate anion.
A. *p*-hydroxydiphenyl B. *p*-hydroxydiphenyl anion

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 0·05N 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

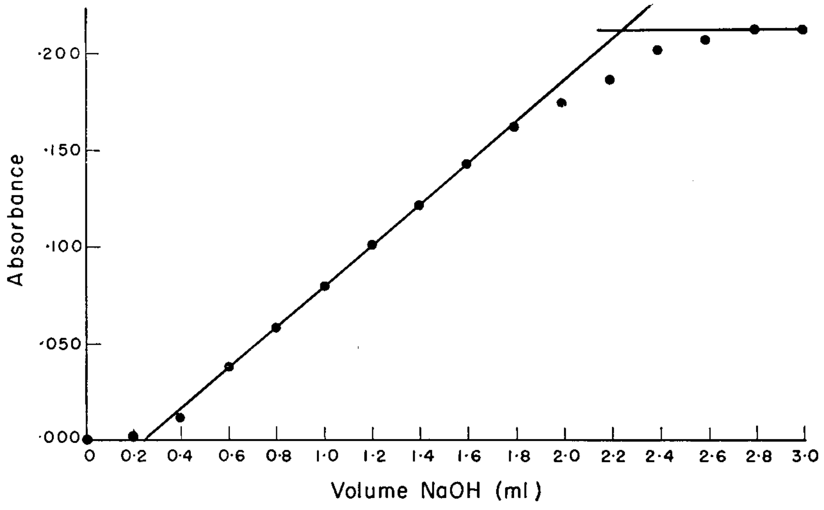


FIG. 2.—Photometric titration curve for p-hydroxydiphenyl.

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 0.001*M* were unsuccessful and invariably gave high results. Evidently most phenols are too weakly acidic to be titrated at concentrations less than 0.001*M* 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, 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.

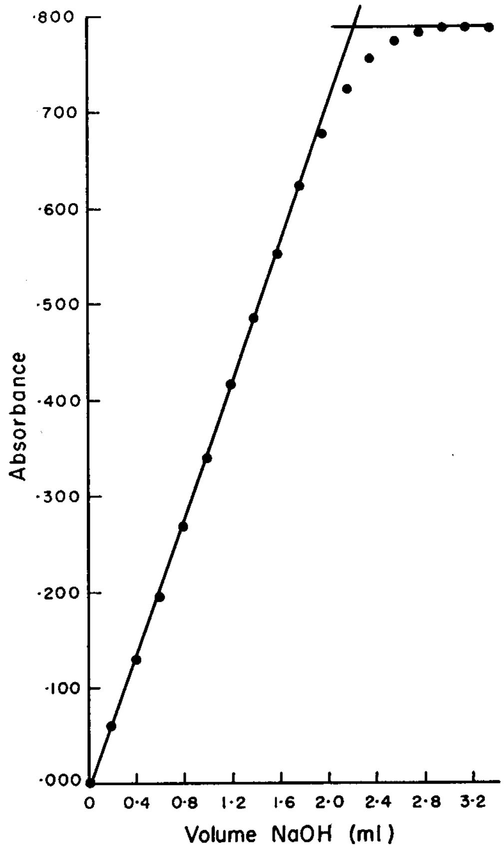


FIG. 3.—Photometric titration curve for 2:4-dibromophenol in the presence of phenol.

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.

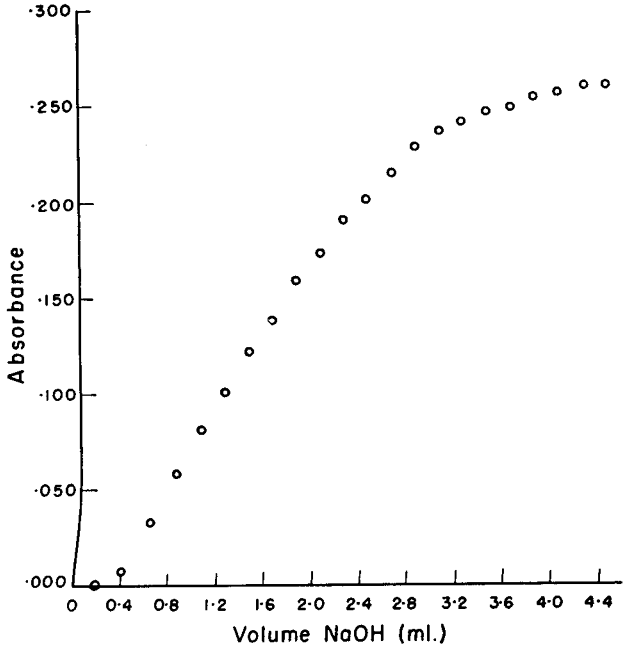


FIG. 4.—Photometric titration curve of a mixture of *p*-hydroxydiphenyl and 2:4-dimethylphenol.

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 (0.01*M* 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 für die Bestimmung von Phenolen entwickelt, das für eine Konzentration von $10^{-3}M$ oder mehr mit einer Durchschnitts-Abweichung von ungefähr 1 % verwendbar ist.

Man kann ohne Schwerigkeit Phenole mit pK_A-Werte im Wasser von 5 bis ungefähr 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.

REFERENCES

[1] E. J. Corey, *J. Amer. Chem. Soc.*, 1953, **75,** 1172.
[2] V. Z. Deal and G. E. A. Wyld, *Analyt. Chem.*, 1955, **27,** 47.
[3] J. S. Fritz and N. M. Lisicki, *ibid.*, 1951, **23,** 589.
[4] R. J. Goddu and D. N. Hume, *ibid.*, 1954, **26,** 1689.
[5] G. A. Harlow, C. M. Noble and G. E. A. Wyld, *ibid.*, 1956, **28,** 784.
[6] M. L. Mass, J. H. Elliott and R. T. Hall, *ibid.*, 1948, **20,** 784.

Talanta, 1958, Vol. 1, pp. 55–59, Pergamon Press Ltd., London.

A NEW EXTRACTION METHOD FOR THE DETERMINATION OF COPPER

FEDIR JANČIK and JIŘÍ KÖRBL
Pharmaceutical and Biochemical Research Institute, Prague, Czechoslovakia

(*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$^{\mathrm{I}}$ *pyridinohalide complexes*

The most satisfactory reagent for reduction of copper$^{\mathrm{II}}$ 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$^{\mathrm{II}}$ 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 97·5[a]	58·0
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 $0{\cdot}05M$ Cu^{2+} AND 10 ml OF $0{\cdot}05M$ SOLUTIONS OF THE APPROPRIATE CATION)

Metal added	Found ml of $0{\cdot}05M$ 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)-pyridinohalogenid-Komplexe, besonders des Bromids und des Jodids, für die rasche Trennung des Kupfers von einer Reihe anderer Kationen benützt werden kann. Das Kupfer wird im Chloroformextrakt komplexometrisch bestimmt. Zink kann mit Iminodiessigsäure maskiert werden. Eine solche Tarnung ist jedoch für Cadmium und Quecksilber unbrauchbar, weil diese Elemente auch in der Anwesenheit der Iminodiessigsäure in die Chloroformschicht übergehen.

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.

REFERENCES

[1] T. S. West, *Metallurgia*, 1956, **53**, 91, 132, 185, 233, 240.
[2] *Idem, ibid.*, 91.
[3] I. P. Alimarin and V. V. Koreneva, *Zavodskaya Lab.*, 1956, **22**, 402.
[4] W. Lang, *Ber.*, 1888, **21**, 1578.
[5] R. Varet, *Compt. rend.*, 1891, **112**, 391.

[6] *Idem, ibid.*, 1897, **124**, 1156.
[7] *Idem, ibid.*, 1891, **112**, 622.
[8] R. L. Datta and J. N. Sen, *J. Amer. Chem. Soc.*, 1917, **39**, 750.
[9] J. A. Hunter and C. C. Miller, *Analyst*, 1956, **81**, 79.
[10] J. Körbl, E. Kraus and R. Přibil, *Chem. Listy*, 1957, **51**, 1809.
[11] J. Körbl, E. Kraus, F. Jančik and R. Přibil, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1416.
[12] J. Körbl, R. Přibil and A. Emr, *ibid.*, 1957, **22**, 961.
[13] J. Körbl and R. Přibil, *Chem.-Analyst*, 1956, **45**, 102.
[14] *Idem, Chem. Listy*, 1957, **51**, 1061.

Talanta, 1958, Vol. 1, pp. 60–75, Pergamon Press Ltd., London.

ZUR THEORIE DER VISUELLEN INDICATION UND SELECTIVITÄT KOMPLEXOMETRISCHER TITRATIONEN

H. FLASCHKA
Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.*

(*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 0,01M) 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

---

* Present address: Chemical Institute, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.

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 gemäss den jeweils herrschenden Titrationsbedingungen umzurechnen und zwar durch Berücksichtigung 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 Stabilitätskonstante 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 Stabilität 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 müssen

$$K_M = \frac{[MY]}{[M] . [Y]} \qquad (1)$$

$$C_M = [MY] + [M] \qquad (2)$$

$$C_Y = [MY] + [Y] \qquad (3)$$

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

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

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 $pM = -\log(a \,.\, C_M)$. 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 übrigen kann man die mit den a-Werten erhaltenen Kurven ohne weiters durch Addition der $\log \beta_A$-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 $C_M = 10^{-2}$ 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 $K_M > K_N$.

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

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

(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

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

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

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

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

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

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

$$z = \frac{C_N \,.\, K_N}{C_M \,.\, K_M \,.\, a} \,.\, 100 \tag{26}$$

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

Liegen die Konstanten verhältnismässig 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 für 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 natürlich 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 beschränkte Selectivität bestehen kann. Nur die stark bindenden Metalle wie etwa Fe-III, Th, In, Ga, Bi, Hg usw. können 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 angeführt. 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 ($K_{\text{abs}\cdot\text{Ca}} = 10^{10,7}$, $K_{\text{abs}\cdot\text{Mg}} = 10^{5,4}$) 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 für 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 völlig oder mit ausreichender Genauigkeit erfüllt 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 Stabilitätskonstante 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 spät 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

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

Daraus ergibt sich unter Berücksichtigung der entsprechenden Stabilitätskonstanten

$$\frac{[\mathrm{MY}] \,.\, [\mathrm{I}]}{[\mathrm{MI}] \,.\, [\mathrm{Y}]} = \frac{K_\mathrm{M}}{K_\mathrm{I}} \tag{28}$$

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

$$\frac{9 \,.\, C_\mathrm{M}}{C_\mathrm{Y} - C_\mathrm{M}} = \frac{K_\mathrm{M}}{K_\mathrm{I}} \tag{29}$$

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

$$z = \frac{K_\mathrm{I}}{K_\mathrm{M}} \,.\, 10^3 \tag{30}$$

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 lässt auch keine Aussage über die Güte des Endpunktes,

---

* Ausdrücke, 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 für das menschliche Auge nicht genügend unterschiedlich, d.h. komplementär sind. Zum anderen aber kann gemeint sein, dass der Farbwechsel nicht mit einem genügend kleinen Bruchteil an Titrationsmittel erreicht wird. So z.B. ist bei einer Säure-Basen-Titration Methylrot kontrastreicher als Methylorange. Ein bei der Titration einer starken Säure mit einer starken Base einwandfrei arbeitender Indicator hingegen wird bei der Titration einer schwachen Säure "schleppen". Die Ausarbeitung einer neuen Klassifikation von Indicatoren nach diesen Gesichtspunkten ist in Zusammenarbeit mit Dr. C. N. Reilley derzeit im Gange und wird später anderwärts veröffentlicht werden.

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

$$K_{\mathrm{M}} = \frac{[\mathrm{MY}]}{[\mathrm{M}]\,.\,[\mathrm{Y}]} \tag{31}$$

$$K_{\mathrm{I}} = \frac{[\mathrm{MI}]}{[\mathrm{M}]\,.\,[\mathrm{I}]} \tag{32}$$

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

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

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

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

$$K_{\mathrm{M}} = \frac{[\mathrm{MY}]}{(C_{\mathrm{M}} - [\mathrm{MY}] - [\mathrm{MI}])\,.\,(C_{\mathrm{Y}} - [\mathrm{MY}])} \tag{36}$$

$$K_{\mathrm{I}} = \frac{[\mathrm{MI}]}{(C_{\mathrm{M}} - [\mathrm{MY}] - [\mathrm{MI}])\,.\,(C_{\mathrm{I}} - [\mathrm{MI}])} \tag{37}$$

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

$$C_{\mathrm{Y}} = \left(C_{\mathrm{M}} - [\mathrm{MI}] - \frac{\mathrm{I}}{K_{\mathrm{I}}}\,.\,\frac{[\mathrm{MI}]}{C_{\mathrm{I}} - [\mathrm{MI}]}\right)\,.\,\left(\frac{C_{\mathrm{I}} - [\mathrm{MI}]}{[\mathrm{MI}]}\,.\,\frac{K_{\mathrm{I}}}{K_{\mathrm{M}}} + 1\right) \tag{38}$$

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

$$\varphi \equiv \frac{[\mathrm{MI}]}{C_{\mathrm{I}}} \tag{39}$$

wonach sich ergibt

$$C_{\mathrm{Y}} = \left(C_{\mathrm{M}} - \varphi\,.\,C_{\mathrm{I}} - \frac{1}{K_{\mathrm{I}}}\,.\,\frac{\varphi}{1-\varphi}\right)\,.\,\left(\frac{1-\varphi}{\varphi}\,.\,\frac{K_{\mathrm{I}}}{K_{\mathrm{M}}} + 1\right) \tag{40}$$

In Abb. 1 sind einige Kurven für verschiedene Werte der Parameter berechnet, wobei φ auf der Abszisse und, um die Kurven für verschiedene Konzentrationen beisammen zu haben, $C_{\mathrm{Y}}/C_{\mathrm{M}}$ 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 gemäss Punkt (*d*) im vorigen Abschnitt] und kombiniert mit (8) so errechnet sich der prozentuale Fehler zu

$$z = \frac{100}{C_{\mathrm{M}}}\,.\left[9\,.\,\frac{K_{\mathrm{I}}}{K_{\mathrm{M}}}\,.\,C_{\mathrm{M}} - 0{,}1\;C_{\mathrm{I}}\,.\left(1 + 9\,\frac{K_{\mathrm{I}}}{K_{\mathrm{M}}}\right) - \frac{1}{K_{\mathrm{M}}} - \frac{1}{9\,.\,K_{\mathrm{I}}}\right] \tag{41}$$

$1/K_{\mathrm{M}}$ ist so klein, dass es gegen das nächst grössere Glied vernachlässigt werden kann. Ferner ist $9\,.\,K_{\mathrm{I}}/K_{\mathrm{M}} \ll 1$ womit sich die Formel vereinfacht zu

$$z = \frac{100}{C_{\mathrm{M}}}\,.\left(9\,.\,\frac{K_{\mathrm{I}}}{K_{\mathrm{M}}}\,.\,C_{\mathrm{M}} - 0{,}1\,.\,C_{\mathrm{I}} - \frac{1}{9\,.\,K_{\mathrm{I}}}\right) \tag{42}$$

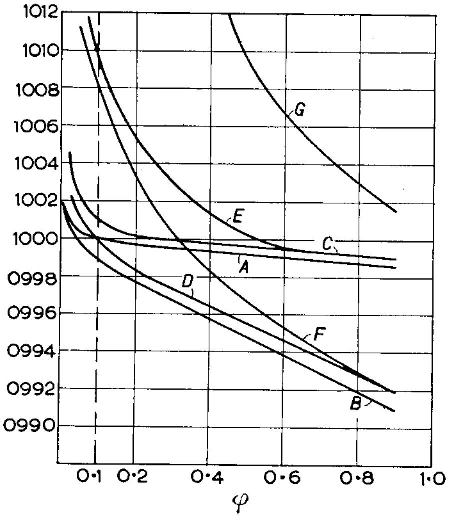


Abb. 1. Umschlagskurven für verschiedene Werte der Parameter in Formel (40). In allen Fällen ist $C_I = 10^{-5}$ und $K_I = 10^{11}$.

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 genügend 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 für K_I

Ist die Indicatorkonstante klein, dann wird durch Dissoziation frühzeitig Indicator in der freien Form erscheinen und der Endpunkt wird verfrüht sein und überdies schleppen. Nehmen wir zur Vereinfachung an, dass durch K_M und durch das Verhältnis K_I/K_M keine Komplikationen eingeführt 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

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

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 grössenordnungsmässiger 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

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

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 Güte des Endpunktes lässt sich nun bestimmen durch die Anzahl der Tropfen an Masslösung 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 für ΔC_Y

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

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

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

Aus diesem Ausdruck lässt sich die Güte des Endpunktes berechnen, indem man herausfindet, wieviele Tropfen oder Tropfenbruchteile zum Durchschreiten des Intervalles $\varphi = 0{,}2 \rightarrow \varphi = 0{,}1$ nötig sind. Ist die Indicatorkonstante sehr gross und das Konstantenverhältnis sehr klein, so haben wir den Idealfall vorliegen, wo tatsächlich 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 für 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 für die Zinkbestimmung 0,5 Tropfen. Dies ist durchaus in guter Übereinstimmung mit der praktischen Erfahrung, wenn man berücksichtigt, dass die Komplementäritat der Farben vernachlässigt wurde und die Annahme des Endpunktintervalles naturgemäss 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 Störmetall N und der Indicator I. Nur M bildet mit I einen Komplex. Würde auch N einen Indicatorkomplex bilden so wäre 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 für die Titration. Unter Einführung der entsprechenden Stabilitätskonstanten erhält man aus (47) sofort

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

In ähnlicher 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 grösser, 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

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

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

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

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

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

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

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

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

$$C_{\mathrm{Y}} = [\mathrm{MY}] + \frac{C_{\mathrm{N}} \dfrac{K_{\mathrm{N}}}{K_{\mathrm{M}}} \dfrac{[\mathrm{MY}]}{[\mathrm{M}]}}{\dfrac{K_{\mathrm{N}}}{K_{\mathrm{M}}} \dfrac{[\mathrm{MY}]}{[\mathrm{M}]} + 1} + \frac{[\mathrm{MY}]}{K_{\mathrm{M}} [\mathrm{M}]} \tag{57}$$

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

$$C_{\mathrm{Y}} = \frac{\left(C_{\mathrm{M}} - \varphi C_{\mathrm{I}} - \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_{\mathrm{I}}}\right) \left\{ \dfrac{K_{\mathrm{N}}}{K_{\mathrm{M}}} \left[\left(C_{\mathrm{M}} - \varphi C_{\mathrm{I}} - \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_{\mathrm{I}}}\right) \times \left(1 + \dfrac{1-\varphi}{\varphi} \dfrac{K_{\mathrm{I}}}{K_{\mathrm{M}}}\right) + C_{\mathrm{N}} \right] + \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_{\mathrm{I}}} \left(1 + \dfrac{1-\varphi}{\varphi} \dfrac{K_{\mathrm{I}}}{K_{\mathrm{M}}}\right) \right\}}{\dfrac{K_{\mathrm{N}}}{K_{\mathrm{M}}} \left(C_{\mathrm{M}} - \varphi C_{\mathrm{I}} - \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_{\mathrm{I}}}\right) + \dfrac{\varphi}{1-\varphi} \dfrac{1}{K_{\mathrm{I}}}} \tag{58}$$

Setzt man zur Kontrolle $C_{\mathrm{N}} = K_{\mathrm{N}} = 0$, 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 $C_{\mathrm{Y},0,1}$ bezeichnet, indem man $\varphi = 0{,}1$ einsetzt, wobei erlaubterweise $\dfrac{1-\varphi}{\varphi} \, . \, \dfrac{K_{\mathrm{I}}}{K_{\mathrm{M}}}$ gegen 1 vernachlässigt wurde, zu

$$C_{\mathrm{Y},0,1} = \frac{\left(C_{\mathrm{M}} - 0{,}1 C_{\mathrm{I}} - \dfrac{1}{9K_{\mathrm{I}}}\right) \left[\dfrac{K_{\mathrm{N}}}{K_{\mathrm{M}}} \left(C_{\mathrm{M}} - 0{,}1 C_{\mathrm{I}} - \dfrac{1}{9K_{\mathrm{I}}} + C_{\mathrm{N}}\right) + \dfrac{1}{9K_{\mathrm{I}}} \right]}{\dfrac{K_{\mathrm{N}}}{K_{\mathrm{M}}} \left(C_{\mathrm{M}} - 0{,}1 C_{\mathrm{I}} - \dfrac{1}{9K_{\mathrm{I}}}\right) + \dfrac{1}{9K_{\mathrm{I}}}} \tag{59}$$

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

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

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

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

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 obendreib 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 zweckmässig 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

---

* 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 Fälle, für die alle Daten aus der Literatur bekannt sind, zeigte, dass auch das erhältnis K_N/K_M für die Güte des Endpunktes massgeblich ist. Generelle Daten mitzuteilen ist aus bereits erwähnten Gründen unmöglich.

SELECTIVITÄT KOMPLEXOMETRISCHER TITRATIONEN

Die Ableitungen zeigen bereits zur genüge, 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 Selectivität besteht, wie schon oben näher ausgeführt wurde. Um die Selectivität zu steigern hat man nun verschiedene Mittel zur verfügung. Einmal kann in beschränktem Ausmasse durch Änderung der scheinbaren Stabilitätskonstanten über den pH-Einfluss eine Verbesserung erzielt werden. Diese Möglichkeiten sind genügend. bekannt und erschöpft, 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 müssen. 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 Stabilitätskonstanten führen, die in den Formeln ausschliesslich Verwendung finden. Es werden aber durch die komplexbildenden Maskierungsmittel nicht nur die Stabilitäten der Komplexe der Störmetalle 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 natürlich nicht den Ableitungen angelastet werden. Die in zahlreichen Laboratoriem laufenden Untersuchungen, die nötigen Konstanten zu bestimmen, geben jedoch gute Hoffnung, dass in absehbarer Zeit das nötige 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. für die Praxis der Titration, wenn sich das Gleichgewicht praktisch momentan oder zumindest doch genügend schnell einstellt. Wenn langsame Gleichgewichtseinstellung erfolgt, so liegen völlig anders geartete Verhältnisse vor. Es können dann "robuste" Komplexe auftreten, deren Konstante viel höher zu liegen scheint, als es tatsächlich der Fall ist. Solche Verzögerungen 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 0·01M) 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 0,01M) 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.

LITERATUR

[1] G. Schwarzenbach, *Die komplexometrische Titration.* F. Encke, Stuttgart, 1956.
[2] H. Flaschka und S. Khalafallah, *Z. analyt. Chem.*, 1957, **156,** 401.
[3] H. Flaschka und A. Soliman, *ibid.*, 1957, **158,** 254; *ibid.*, 1957, **159,** 30.
[4] R. W. Schmid und C. N. Reilley, *Analyt. Chem.*, 1957, **29,** 264.

Talanta, 1958, Vol. 1, pp. 76-79, Pergamon Press Ltd., London

DETERMINATION OF TRACES OF IRON IN METALLIC COPPER

HARVEY DIEHL and E. B. BUCHANAN, JR.
Department of Chemistry, Iowa State College, Ames, Iowa, U.S.A.

(*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.

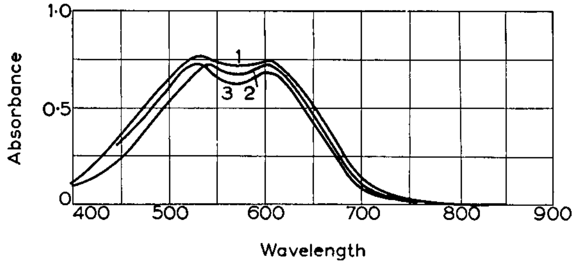


FIG. 1. Absorption spectrum of $Fe(4:7\text{-diphenyl-}1:10\text{-phenanthroline})_2(CN)_2$ in chloroform (Curve 1); $Fe(1:10\text{-phenanthroline})_2(CN)_2$ in chloroform (Curve 2); $Fe(1:10\text{-phenanthroline})_2(CN)_2$ in nitrobenzene (Curve 3).

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.

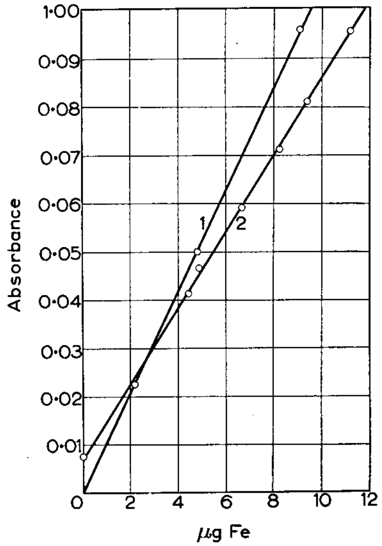


FIG. 2. Calibration curves, Fe(4:7-diphenyl-1:10-phenanthroline)$_2$(CN)$_2$ in chloroform. Curve 1, copper absent; curve 2, 1.0 g of copper present. Intercept of curve 2 presumably represents iron present in the "pure" copper used in making up the standards.

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 Lösung und bildet einen violett-gefärbten Komplex, Dicyano-*bis*-(4:7-Diphenyl-1:10-Phenanthrolin)-Eisen-II.

Der Gebrauch dieses Komplexes für die Bestimmung von Eisen in Kupfer wird beschrieben. Die Methode ist für 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.

REFERENCES

[1] D. Margerum and C. V. Banks, *Analyt. Chem.*, 1954, **26**, 200.
[2] A. A. Schilt, *J. Amer. Chem. Soc.*, 1957, **79**, 5421.
[3] S. E. Kreimer and N. V. Tuzhilina, *Zavodskaya Lab.*, 1957, **23**, 543; (*Analyt. Abstr.*, 1957, 3568).

Talanta, 1958, Vol. 1, pp. 80–87, Pergamon Press Ltd., London

APPLICATIONS OF PYROHYDROLYTIC CLEAVAGES IN SPOT TEST ANALYSIS

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

F. FEIGL, D. HAGENAUER-CASTRO and E. JUNGREIS
Laboratorio da Produção Mineral, Ministerio da Agricultura,
Rio de Janeiro, Brazil

(*Received* 20 *March* 1958)

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

---

* 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:

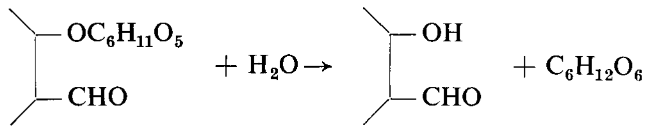
$$(CH_2COOH)_2 \rightarrow (CH_2CO)_2O + H_2O$$

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
25 μg adipic acid anilide
25 μg *p*-bromoacetanilide
25 μg propionanilide
10 μg formanilide
10 μg acetanilide
10 μg carbanilide
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

$$R(Ar)Hal + H_2O \rightarrow R(Ar)OH + H\,Hal$$

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

---

* 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).

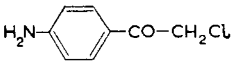
Among the aromatic halogen compounds tested were: 2-chloromandelic acid, 2-bromomandelic acid, 4-iodomandelic acid, *p*-chloroaniline, 7-iodo-8-hydroxyquinoline-5-sulphonic acid, 2-hydroxy-7-chloro-2-quinoline carboxylic acid, 4-bromobenzhydrol, 6:8-dichlorobenzoylenurea, 2:6-dichlorobenzylcyanide, 1:2:4:5-tetrachlorobenzene, 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.

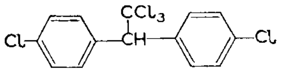
Detection of aromatic sulphonic acids

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

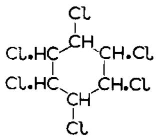
$$ArSO_3Na + NaOH \rightarrow ArOH + Na_2SO_3$$



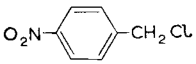
I



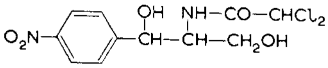
II



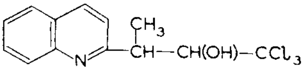
III



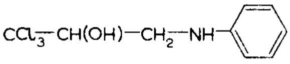
IV



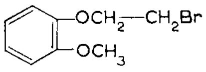
V



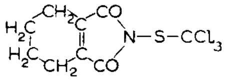
VI



VII



VIII



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.

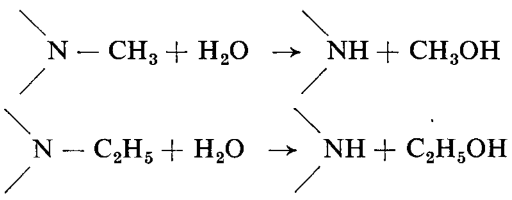
Reagent. 0·08 g anhydrous ferric chloride and 0·1 g potassium ferricyanide are dissolved in 100 ml of water.

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. Bernsteinsäure oder Phthalsäure in Kontakt mit organischen Verbindungen erhitzt, so können durch das im Temperaturbereich 100–230° abgespaltene Wasser Hydrolysen bewirkt werden, die mit kochendem Wasser nicht eintreten. Für derartige, nur bei höherer Temperatur realisierbare Hydrolysen wird die Bezeichnung Pyrohydrolyse vorgeschlagen.

Analytische Anwendungen von Pyrohydrolysen sind möglich, wenn bei kurzer Erhitzung mit geeigneten Wasserdonors Spaltprodukte entstehen, die in ihrer Gasphase empfindlich nachweisbar sind. Hierfür werden folgende Beispiele angeführt:

Nachweis von Helicin durch Abspaltung von Salicylaldehyd
Nachweis von Aniliden alifatischer Carbonsäuren durch Abspaltung von Anilin
Nachweis von o-Acetylverbindungen durch Abspaltung von Essigsäure
Nachweis von alifatisch gebundenem Halogen durch Abspaltung von Halogenwasserstoff.
Nachweis von-aromatischen Sulfosäuren durch Abspaltung von Schwefeldioxyd.
Nachweis von N-methyl u. N-äthylgruppen durch Abspaltung von Formaldehyd bzw. Acetaldehyd.

Sämtliche Nachweise können in der Arbeitsweise der Tüpfelanalyse 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.

REFERENCES

[1] F. Feigl, E. Jungreis and C. Stark-Mayer, *Analyt. Chim. Acta*, in press.
[2] F. Feigl, *Angew. Chem.*, 1958, **70**, 166.
[3] F. Feigl and R. Moscovici, *Analyst*, 1955, **80**, 803.
[4] F. Feigl, *Spot Tests in Organic Analysis*. Elsevier Publishing Co., New York, 5th Ed., 1956, p. 376.
[5] S. N. Chakravarti and M. B. Roy, *Analyst*, 1937, **62**, 603.
[6] W. H. Rauscher, *Ind. Eng. Chem. Anal.*, 1937, **9**, 296.
[7] F. Feigl, *Laboratory Manual of Spot Tests*. Elsevier Publishing Co., New York, 1943, p. 110.
[8] G. B. Heisig and A. Lerner, *Ind. Eng. Chem. Anal.*, 1941, **13**, 843.
[9] L. Lewin, *Ber.*, 1899, **32**, 3388.

Talanta, 1958, Vol. 1, pp. 88–104, Pergamon Press Ltd., London.

ANALYTICAL CHEMISTRY OF COBALT

WILLIAM J. WILLIAMS
Royal Holloway College, Englefield Green, Surrey, England

(*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 Rüdisüle.[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.

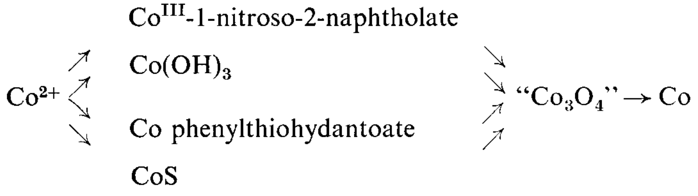
Benzoquinaldinic acid as a reagent for cobalt estimation was suggested by Majumdar and De[97] in 1953, the complex $Co(C_{14}H_8NO_2)_2{\cdot}2H_2O$ being weighed after drying at 110°–115°, or the anhydrous form after drying at 150°–155°. They used 10-mg quantities of cobalt only in assessing the method,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



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

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

iodine
bromine
sodium perborate
or *hydrogen peroxide*

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:

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

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

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

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 4*N* 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

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

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

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 $\mathrm{Co^{II}}$ 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 $\mathrm{Co^{II}}$ 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:

$$2Co^{2+} + 10NH_3 + I_3^- \rightarrow 2Co(NH_3)_5 I^{2+} + I^-$$

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 ursprünglicheren Methoden für die Nachweis und die Bestimmung von Kobalt, mit insbesonders Nachdrock über Entwicklungen während 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.

REFERENCES

[1] H. E. Affsprung, N. A. Barnes and H. A. Potratz, *Analyt. Chem.*, 1951, **23,** 1680.
[2] H. Almond, *ibid.*, 1953, **25,** 1830.
[3] B. Bagshaw and J. D. Hobson, *Analyst*, 1948, **73,** 152.
[4] L. C. W. Baker and T. P. McCutcheon, *Analyt. Chem.*, 1950, **22,** 944.
[5] *Idem, ibid.*, 1955, **27,** 1625.
[6] H. Baron, *Z. analyt. Chem.*, 1953, **140,** 173.
[7] K. C. Beeson and R. L. Gregory, *J. Assoc. Off. Agric. Chem.*, 1950, **33,** 409.
[8] R. Berg, *Z. analyt. Chem.*, 1929, **76,** 191.
[9] N. J. Blay and L. A. Warren, *Analyst*, 1951, **76,** 115.
[10] M. Bobtelsky and E. Jungreis, *Analyt. Chim. Acta*, 1956, **12,** 248.
[11] M. Bobtelsky and C. Heitner, *Bull. Soc. chim. Fr.*, 1951, **18,** 502.
[12] H. Bode, *Z. analyt. Chem.*, 1955, **144,** 165.
[13] G. Brandt, *Acta Soc. Uppsala*, 1742, **5,** 33.
[14] D. H. Brophy, *Ind. Eng. Chem. Anal.*, 1931, **3,** 363.
[15] B. D. Brummet and R. M. Hollweg, *Analyt. Chem.*, 1956, **28,** 448.
[16] F. Buscaróns and J. Artigas, *Anales Fis Quím.*, 1952, **48B,** 140.
[17] C. Calzolari and A. Donda, *Ann. Chim. Roma*, 1954, **44,** 280.
[18] W. A. C. Campen and H. Geerling, *Chem. Weekblad*, 1952, **78,** 193.
[19] F. Cassy, *Chem. and Ind.*, 1956, 305.
[20] Chancell, *Précis d'analyse chimique*, Paris, 1862.
[21] K. L. Cheng and P. F. Lott, *Analyt. Chem.*, 1956, **28,** 462.
[22] K. L. Cheng and R. H. Bray, *ibid.*, 1955, **27,** 782.
[23] J. M. Chilton, *ibid.*, 1953, **25,** 1274.
[24] *Idem, ibid.*, 1954, **26,** 940.
[25] R. C. Chirnside, H. J. Cluley and P. M. C. Proffitt, *Analyst*, 1947, **72,** 351.
[26] A. Claassen and W. Westerveld, *Rec. Trav. Chim. Pays-Bas*, 1948, **67,** 720.
[27] J. Clarke, *Chem. News*, 1884, **48,** 262.
[28] J. F. Coetzee, *J. Chem. Soc.*, 1951, 997.
[29] L. A. Congdon and T. H. Chen, *Chem. News*, 1924, **128,** 132.
[30] C. F. Cumbers and J. B. M. Coppock, *J. Soc. Chem. Ind.*, 1937, **56T,** 405.
[31] F. Čůta and K. Rauscher, *Coll. Czech. Chem. Comm.*, 1955, **20,** 180.
[32] V. Cuvelier, *Natuurwet. Tijdschr.*, 1929, **11,** 131.
[33] H. D. Dakin, *Z. analyt. Chem.*, 1902, **41,** 279.
[34] H. Debray, *Ann. Chim. Phys.*, 1860, **61,** 438.
[35] E. Deltombe and M. Pourbaix M., *International Committee of Electrochem. Thermodynamics & Kinetics, Proc. 6th meeting.* Poitiers, 1954, 153.
[36] A. de Sousa, *Mikrochem. Mikrochim. Acta*, 1952–53, **40,** 352.
[37] J. Dick, *Z. analyt. Chem.*, 1930, **82,** 406.
[38] P. Dickens and G. Maassen, *Mitt. K. Wilh.-Inst. Eisenforsch*, 1935, **17,** 191.
[39] H. Diehl and J. P. Butler, *Analyt. Chem.*, 1955, **27,** 777.
[40] P. Dirvell, *Compt. rend.*, 1879, **89,** 903.
[41] J. T. Dobbins and J. P. Sanders, *Ind. Eng. Chem. Anal.*, 1934, **6,** 459.

[42] L. Dufty, *J. Iron Steel Inst.*, 1914, **90,** 52.

[43] C. Duval, *Analyt. Chim. Acta,* 1951, **5,** 84; *Inorganic Thermogravimetric Analysis.* Elsevier, Amsterdam, 1953.

[44] A. Eder, *Chem.-Ztg.*, 1922, **46,** 430.

[45] K. W. Ellis and N. A. Gibson, *Analyt. Chim. Acta,* 1953, **9,** 275.

[46] W. D. Engle and R. G. Gustavson, *Ind. Eng. Chem.*, 1916, **8,** 901.

[47] B. S. Evans, *Analyst,* 1937, **62,** 363.

[48] P. V. Faleev, *Gorno-obogat. Dyelo.*, 1932, **10,** 53.

[49] F. Feigl and D. Goldstein, *Analyst,* 1956, **81,** 709.

[50] D. N. Finkel'shtein, *Zavodskaya Lab.*, 1956, **22,** 648.

[51] N. W. Fischer, *Pogg. Ann.*, 1847, **72,** 477.

[52] H. Flaschka and H. Abdine, *Chem.-Analyst,* 1955, **44,** 30.

[53] *Idem, ibid.*, 1956, **45,** 2.

[54] H. Flaschka, *Mikrochem. Mikrochim. Acta,* 1952, **39,** 38.

[55] H. R. Fleck and A. M. Ward, *Analyst,* 1933, **58,** 388.

[56] A. G. Foster and W. J. Williams, Unpublished work.

[57] N. S. Fortunatov, V. I. Mikhaǐlovskaya and Yu. P. Nazarenko, *Ukrain. Chem. J.*, 1956. **22,** 536.

[58] C. R. Fresenius, *Quantitative Analysis,* Vol. 1, London, 1876, p. 210.

[59] H. Fritzche, *Brennstoff-Chem.*, 1954, **35,** 49.

[60] Y. Fujita, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1954, **75,** 1235.

[61] H. Funk and M. Ditt, *Z. analyt. Chem.*, 1933, **93,** 241.

[62] J. Gagnon, *Chem.-Analyst,* 1954, **43,** 15.

[63] J. Garrido, *Anales Fis. Quím.*, 1947, **43,** 1195.

[64] S. P. Ghosh and H. M. Ghose, *J. Indian Chem. Soc.*, 1956, **33,** 899.

[65] J. Gillis, J. Hoste and J. Pijck, *Mikrochim. Acta,* 1953, 244.

[66] S. Glasstone and J. C. Speakman, *Analyst,* 1930, **55,** 93.

[67] G. S. Goldberg, *Zhur. anal. Khim.*, 1954, **9,** 56.

[68] R. B. Golubstova, *ibid.*, 1956, **11,** 694.

[69] H. Goto, *J. Chem. Soc. Japan,* 1934, **55,** 1156.

[70] R. Hara and P. W. West, *Analyt. Chim. Acta,* 1955, **12,** 72.

[71] H. B. Harris, *J. Amer. Chem. Soc.*, 1898, **20,** 173.

[72] W. F. Harris, *Diss. Abs.*, 1956, **16,** 441.

[73] W. E. Harris and T. R. Sweet, *Analyt. Chem.*, 1954, **26,** 1648.

[74] H. L. Helwig, J. K. Ashikawa and E. R. Smith, *U.S. Atomic Energy Comm.* UCRL-2655.

[75] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorg. Analysis.* Wiley, New York, 1929.

[76] F. Holmes, K. G. Reed and W. R. C. Crimmin, *Analyt. Chim. Acta,* 1956, **15,** 312.

[77] S. Ikeda, Japan, *Analyst,* 1953, **3,** 218.

[78] M. Ilinski and G. von Knorre, *Ber.*, 1885, **18,** 699.

[79] M. Jean, *Analyt. Chim. Acta,* 1952, **6,** 278.

[80] *Idem, ibid.*, 1954, **11,** 451.

[81] D. Jentzsch and I. Frotscher, *Z. analyt. Chem.*, 1955, **144,** 17.

[82] S. Kallman, *Analyt. Chem.*, 1950, **22,** 1519.

[83] W. J. Karslake, *J. anal. chem.*, 1892, **6,** 469.

[84] K. Kawagaki, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1956, **77,** 1461.

[85] J. Kinnunen and B. Wennerstrand *Chem. Analyst,* 1955, **44,** 33.

[86] A. G. Kniga and V. I. Ustinskaya, *Tr. Leningr. Tekhnol. In-ta Pischevoǐ Prom-sti,* 1953, **3,** 154.

[87] I. M. Kolthoff and A. Langer, *J. Amer. Chem. Soc.*, 1940, **62,** 3172.

[88] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis,* 3rd Edn. Macmillan, London, 1952, p. 352.

[89] M. Kopanica and J. Doležal, *Chem. Listy,* 1956, **50,** 1225.

[90] I. M. Korenman, I. M. Sheyanova and M. N. Baryshnikova, *Zh. obshchei. Khim.*, 1956, **26,** 365.

[91] H. Kraus, *Z. analyt. Chem.*, 1948, **128,** 241.

[92] H. A. Laitinen and L. W. Burdett, *Analyt. Chem.*, 1951, **23,** 1268.

[93] J. Lamure, *Bull. Soc. chim., France,* 1946, **13,** 661.

[94] G. E. F. Lundell and J. I. Hoffmann, *J. Ind. Eng. Chem.*, 1921, **13,** 541.

[95] R. Lundquist, G. E. Markle and D. F. Boltz, *Analyt. Chem.*, 1955, **27**, 1731.
[96] E. Lyons, *ibid.*, 1813.
[97] A. Majumdar and A. K. *J.* De, *Ind. Chem. Soc.*, 1953, **30**, 123.
[98] M. Malát, V. Suk and A. Jeničková, *Chem. Listy*, 1954, **48**, 663.
[99] F. B. Martínez and A. P. Bouzo, *Informac. Quím. anal.*, 1955, **9**, 86.
[100] J. Martinek and V. Hovorka, *Chem. Listy*, 1956, **50**, 1450.
[101] T. Matsuo, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, 1951, **54**, 707.
[102] C. Mayr and F. Feigl, *Z. analyt. Chem.*, 1932, **90**, 15.
[103] J. P. Mehlig and G. J. Zeagas, *Chemist-Analyst*, 1951, **40**, 76.
[104] J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, London, 1935, Vol. XIV, 765.
[105] J. Mermillod, *Metal Abstr.*, 1951, **19**, 215.
[106] A. Metzl, *Z. analyt. Chem.*, 1914, **53**, 537.
[107] J. Michal and J. Dolezal, *Chem. Listy*, 1956, **50**, 911.
[108] R. R. Miller and W. W. Brandt, *Analyt. Chem.*, 1954, **26**, 1968.
[109] M. Mori and M. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1954, **75**, 1044.
[110] A. K. Mukherjee and B. Banerjee, *Naturwiss.*, 1955, **42**, 416.
[111] K. A. Nenadkevich and V. S. Saltykova, *Zhur. anal. Khim.*, 1946, **1**, 123.
[112] G. D. Nessonova and E. K. Pogosyants, *ibid.*, 1956, **11**, 754.
[113] W. Nielsch and G. Boltz, *Z. analyt. chem.*, 1954, **142**, 329.
[114] C. N. Nikolow, *Przemysl Chem.*, 1933, **17**, 46.
[115] Oi Nobuichi, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1955, **76**, 413.
[116] Y. Oka and M. Miyamoto, *Japan Anal.*, 1953, **2**, 322.
[117] W. R. Orndorff and M. L. Nichols, *J. Amer. Chem. Soc.*, 1923, **45**, 1439.
[118] S. M. Peach, *Analyst*, 1956, **81**, 371.
[119] E. Yu. Perel'man, *Vestnik Khim. Obshch. im. D. I. Mendeleeva Chkalovskoe Otd.*, 1954, [5], 31.
[120] A. T. Pilinenko and N. V. Vl'ko, *Zhur. anal. Khim.*, 1955, **10**, 299.
[121] D. Pirtea, G. Dumitrescu and N. Melencu, *Stud. Cercet. Chim. Bucharest*, 1955, **3**, 237.
[122] F. H. Pollard, J. F. W. McOmie and A. J. Banister, *Chem. and Ind.*, 1955, 1598.
[123] R. Přibil, *Coll. Czech. Chem. Comm.*, 1949, **14**, 320.
[124] *Idem*, *Chem. Listy.*, 1954, **48**, 825.
[125] R. Přibil, J. Jeník and M. Kobrová, *ibid.*, 1952, **46**, 603.
[126] R. Přibil and V. Malicky, *Coll. Czech. Chem. Comm.*, 1949, **14**, 413.
[127] K. Protiva, *Chem. Listy.*, 1954, **48**, 778.
[128] A. Rüdisüle, *Nachweis, Bestimmung und Trennung der chemischen Elemente.* Bühler and Werder Bern, 1918, Band V.
[129] E. Rupp and F. Pfenning, *Chem.-Ztg.*, 1910, **34**, 322.
[130] D. Salyer and T. R. Sweet, *Analyt. Chem.*, 1956, **28**, 61.
[131] L. Sarver, *Ind. Eng. Chem. Anal.*, 1933, **5**, 275.
[132] A. Schleicher, *Z. Erzbergbau u. Metallhüttenw.*, 1949, **2**, 210.
[133] W. R. Schoeller, *Analyst*, 1944, **69**, 8.
[134] W. R. Schoeller and A. R. Powell, *ibid.*, 1916, **41**, 124.
[135] W. W. Scott and N. H. Furman, *Standard Methods of Chemical Analysis.* The Technical Press Ltd., London, 1954, Vol. 1., 315.
[136] I. G. Shafran and R. I. Gordeeva, *Trudy vsesoyuz. nauch. Inst. Khim. Reactivov*, 1956, [21], 26.
[137] G. B. Shakhtakhtinskiǐ and M. L. Turchinskiǐ, *Trud. Azerbaidzh. Ind. Inst.*, 1955, [11], 70.
[138] R. J. Shennan, *J. Soc. Chem. Ind.*, 1942, **61**, 164.
[139] R. J. Shennan, J. H. F. Smith and A. M. Ward, *Analyst*, 1936, **61**, 395.
[140] M. Shinagawa, H. Matsuo and R. Kohara, *Japan Anal.*, 1956, **5**, 29.
[141] W. H. Shipman and J. R. Lai, *Analyt. Chem.*, 1956, **28**, 1151.
[142] S. K. Siddhanta and S. N. Bannerjee, *Sci. and Culture (India)*, 1954, **19**, 573.
[143] F. Sierra and F. Cárceles, *Anales Fis Quim.*, 1951, **47B**, 281.
[144] *Idem*, *ibid.*, 341.
[145] *Idem*, *ibid.*, 811.
[146] B. Singh and S. Singh, *Analyt. Chim. Acta*, 1955, **13**, 405.

[147] P. Slawik, *Chem-Ztg.*, 1914, **38,** 514.
[148] G. Spacu and J. Dick, *Z. analyt. Chem.*, 1927, **71,** 97.
[149] G. Spacu and M. Kuraš, *Bull. Soc. Stiinte cluj.*, 1934, **1,** 377.
[150] G. Spacu and M. Schiau, *Stud. Cercet. Chim. Bucharest*, 1955, **3,** 167.
[151] G. W. Standen, *Ind. Eng. Chem. Anal.*, 1944, **16,** 675.
[152] J. E. Strassner, *Diss. Abs.*, 1955, **15,** 1309.
[153] V. Suk, M. Malát and A. Jeníčková, *Coll. Czech. Chem. Comm.*, 1956, **21,** 418.
[154] S. Takamoto, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1955, **76,** 1339.
[155] A. Taurins, *Z. analyt. Chem.*, 1935, **101,** 357.
[156] G. Telep and D. F. Boltz, *Analyt. Chem.*, 1952, **24,** 945.
[157] S. N. Tewari, *Kolloid. Z.*, 1954, **133,** 178.
[158] O. Tomicek and K. Komarek, *Z. analyt. Chem.*, 1932, **91,** 90.
[159] O. Tomicek and F. Freiberger, *J. Amer. Chem. Soc.*, 1935, **57,** 801.
[160] S. Torrance, *Analyst*, 1939, **64,** 109.
[161] T. Torii, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1955, **76,** 328.
[162] E. P. Treadwell and W. T. Hall, *Analytical Chemistry*, Wiley, New York, 1935, Vol. II, 143.
[163] P. S. Tutundžić and D. Stojković, *Analyt. Chim. Acta*, 1955, **11,** 580.
[164] A. A. Vassiliev, *Z. anal. Chem.*, 1929, **78,** 439.
[165] G. Venturello and A. M. Ghe, *Ann. Chim. Rome*, 1953, **43,** 267.
[166] K. Wagenmann, *Metall. u. Erz*, 1921, **18,** 447.
[167] H. Weisz, *Mirkochim. Acta*, 1954, 376.
[168] P. W. West and L. A. Longacre, *Analyt. Chim. Acta*, 1952, **6,** 485.
[169] R. D. Whealy and S. O. Colgate, *Analyt. Chem.*, 1956, **28,** 1897.
[170] D. H. Wilkins and G. F. Smith, *Analyt. Chim. Acta*, 1953, **9,** 338.
[171] H. H. Willard and R. D. Fowler, *J. Amer. Chem. Soc.*, 1932, **54,** 509.
[172] H. H. Willard and D. Hall, *ibid.*, 1922, **44,** 2226, 2237.
[173] W. M. Wise and W. W. Brandt, *Analyt. Chem.*, 1954, **26,** 693.
[174] R. G. Yalman, *ibid.*, 1956, **28,** 91.
[175] J. T. Yardley, *Analyst*, 1950, **75,** 156.
[176] S. K. Yasuda and J. L. Lambert, *J. Chem. Educ.*, 1954, **31,** 572.
[177] R. S. Young, and A. J. Hall *Ind. Eng. Chem. Anal.*, 1946, **18,** 262.
[178] A. C. Zettermoyer and W. C. Walker, *Amer. Ink Maker*, 1950, **28,** 69.
[179] M. Ziegler and O. Glemser, *Z. analyt. Chem.*, 1956, **152,** 241.
[180] M. Ziegler, O. Glemser and E. Preisler, *Angew. Chem.*, 1956, **68,** 436.

Talanta, 1958, Vol. 1, pp. 105–109, Pergamon Press Ltd., London.

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

JOSEPH GAYNOR* and SELBY M. SKINNER
Department of Chemistry and Chemical Engineering, Case Institute of Technology
Cleveland 6, Ohio, U.S.A.

(*Received* 17 *February* 1958)

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.

---

* Now with the General Electric Company, Schenectady, N.Y.

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.

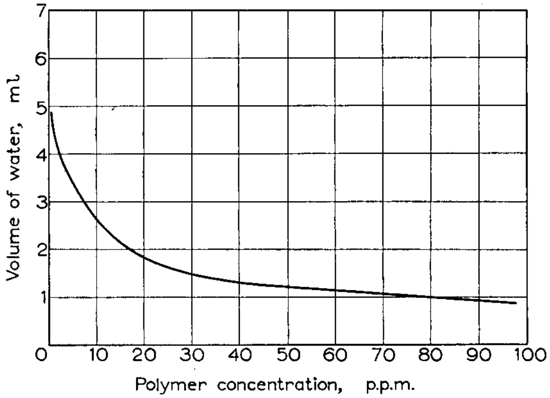


FIG. 1. Calibration curve for poly(methylmethacrylate). Plot of volume of water (ml) vs. polymer concentration in benzene (p.p.m.). Temperature = 72°F.

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.

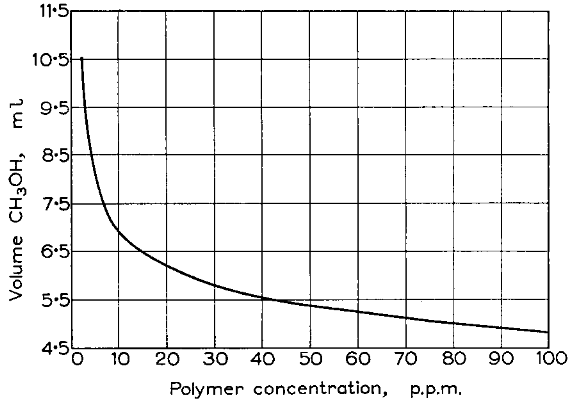


FIG. 2. Calibration curve for polystyrene. Plot of CH_3OH (ml) vs. concentration of polymer in benzene (p.p.m.). Temperature = 73°F.

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.

REFERENCES

[1] E. Jenckel and B. Rumbach, *Z. Elektrochem.*, 1951, **55,** 612.

[2] S. G. Weissberg, R. Simha and S. Rothman, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 298.

[3] D. J. Streeter and R. F. Boyer, *J. Polymer Sci.*, 1954, **14,** 5.

[4] R. F. Boyer and R. S. Spencer, *ibid.*, 1950, **5,** 375.

[5] P. M. Doty and R. F. Steiner, *ibid.*, 383.

[6] M. C. Schroeder, *Prediction of the Storage Stability of Alkyd Resin Enamels*, Ph.D. thesis. Case Institute of Technology, 1951.

[7] H. Staudinger, *Die Hochmolekularen Organischen Verbindungen.* J. Springer, Berlin, 1932.

[8] P. J. Flory, *Principles of Polymer Chemistry.* Cornell University Press, Ithaca, New York, 1953, Chap. XIII.

[9] A. Münster in *Fester Zustand der Hochpolymeren Substanzen,* edited by F. H. Müller. Dietrich Steinkopf, Darmstadt, 1951, pp. 141–159.

[10] R. L. Scott, *J. Chem. Phys.*, 1949, **17,** 268.

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

COULOMETRIC TITRATION OF DYESTUFFS WITH ELECTROLYTICALLY GENERATED DITHIONITE

MAKOTO MUNEMORI
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture,
Mozuhigashinocho, Sakai, Japan

(*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 $0{\cdot}01M$. 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 $\text{titanium}^{\text{III}}$[3] and $\text{uranium}^{\text{V}}$[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,

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

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 0·1M 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.

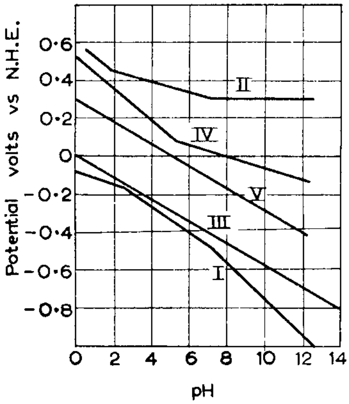


FIG. 1. Potential–pH diagram. (I): dithionite–sulphite system. (II): sulphite–sulphate or –dithionate system. (III): hydrogen–hydrogen ion system. (IV): leuco–methylene blue–methylene blue system. (V): leuco–indigo carmine–indigo carmine system.

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 cm^2. 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 1M 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^{II} sulphate solution[13], using a potentiometric method.

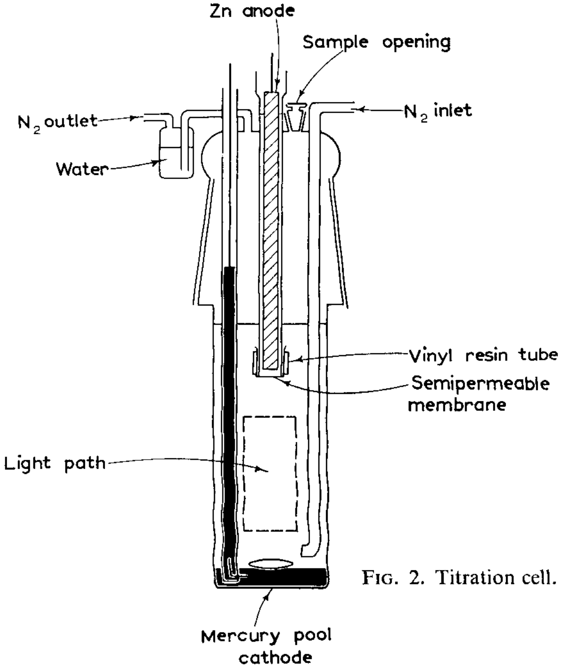


FIG. 2. Titration cell.

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.

---

* 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.

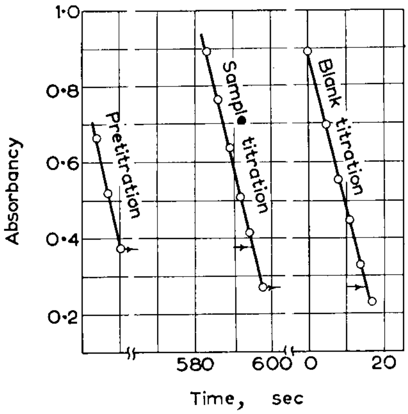


FIG. 3. Titration graph for 5·69 mg of methylene blue. The concentration of bisulphite was 0·01M and the pH was 4·0.

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 Gefäss entwickelt. Dieser Substanz wird erfolgreich benutzt um Methylenblau und Indigocarmin zu titern. Durch Titrage bei gewöhnlicher Temperatur wird Gleichgewicht schnell erreicht, und der End-punkt wird photometrisch bestimmt.

Das optimale Gebiet der Titrage behäuft 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%.

REFERENCES

[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry.* Longmans, Green, London, 1933. Vol. X, p. 166.
[2] T. Murooka, *Bull. Inst. Phys. Chem. Res., Tokyo,* 1935, **14,** 1091.
[3] J. J. Lingane and J. H. Kennedy, *Analyt. Chim. Acta,* 1956, **15,** 465.
[4] K. W. Edwards and D. M. Kern, *Analyt. Chem.,* 1956, **28,** 1876.
[5] W. M. Latimer, *Oxidation Potentials.* Prentice–Hall, Inc., New York, 1952, p. 76.
[6] *Idem, ibid.,* p. 74.
[7] G. Charlot, *Bull. Soc. chim. France,* 1943, **10,** 339.
[8] G. Charlot and R. Gauguin, *Les Méthodes d'Analyse des Réactions en Solution.* Masson et Cie, Paris, 1951, p. 278.
[9] J. A. V. Butler, *Chemical Thermodynamics.* Macmillan and Co., London, 1951, p. 175.
[10] J. J. Lingane and R. T. Iwamoto, *Analyt. Chim. Acta,* 1955, **13,** 464.
[11] R. T. Myers and E. H. Swift, *J. Amer. Chem. Soc.,* 1948, **70,** 1047.
[12] A. Bolliger, *Analyst,* 1939, **64,** 416.
[13] J. J. Lingane and R. L. Pecsok, *Analyt. Chem.,* 1948, **20,** 425.
[14] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.,* 1941, **63,** 2818.
[15] J. S. Parsons and W. Seaman, *Analyt. Chem.,* 1955, **27,** 210.

Talanta, 1958, Vol. 1, pp. 117–126, Pergamon Press Ltd., London.

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

JAMES B. HEADRIDGE* and ROBERT J. MAGEE
Department of Chemistry, The Queen's University, Belfast, N. Ireland

(*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 $0{\cdot}5 \mu M$ 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-6*N* 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.

---

* Present address: The Chemistry Department, The University, Sheffield, England.

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] p*K* 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

$10^{4\cdot5-5\cdot5}$ 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. $K_I(Mg)$ is taken as $10^{5\cdot0}$.

TABLE I. STABILITY CONSTANTS OF ALKALINE EARTH COMPLEXES

Cation	K_c	$K_c/K_I(Mg)$
Mg	$10^{8\cdot2}$	$10^{3\cdot2}$
Ca	$10^{10\cdot1}$	$10^{5\cdot1}$
Sr	$10^{8\cdot2}$	$10^{3\cdot2}$
Ba	$10^{7\cdot3}$	$10^{2\cdot3}$

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.

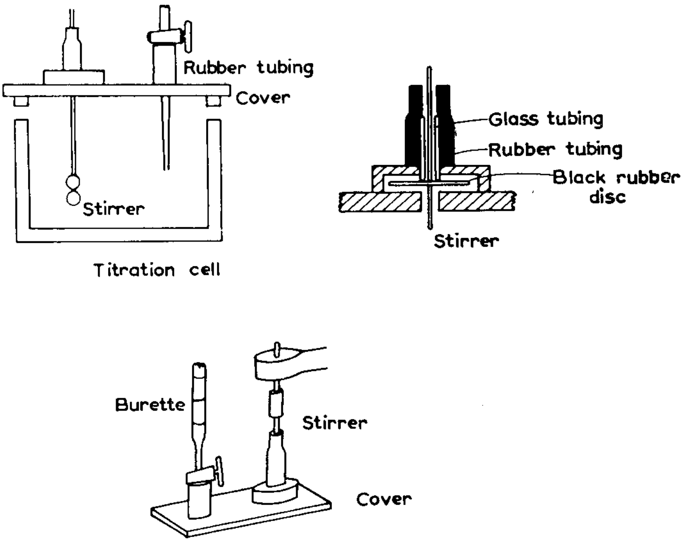


FIG. 1.

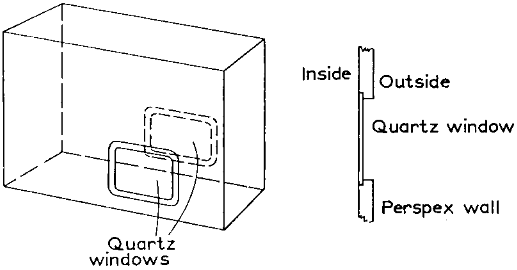


FIG. 2.

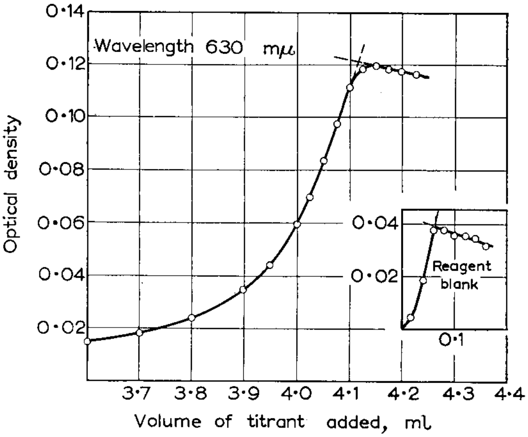


FIG. 3.

TITRATIONS IN SIMPLE BUFFERED SOLUTIONS

Approximately 0·0025M 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 0·05N 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 0·05N 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 $2{\cdot}4 \times 10^{-3}M$ 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 0·0025M 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 0·0025M 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

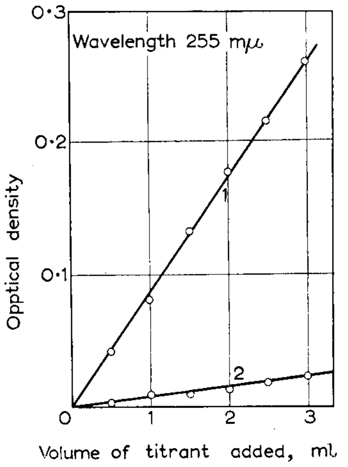


FIG. 4.

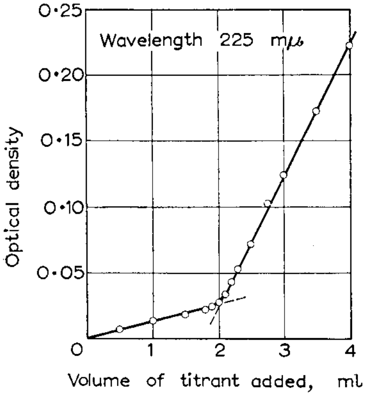


FIG. 5.

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 0·001*M* 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.*

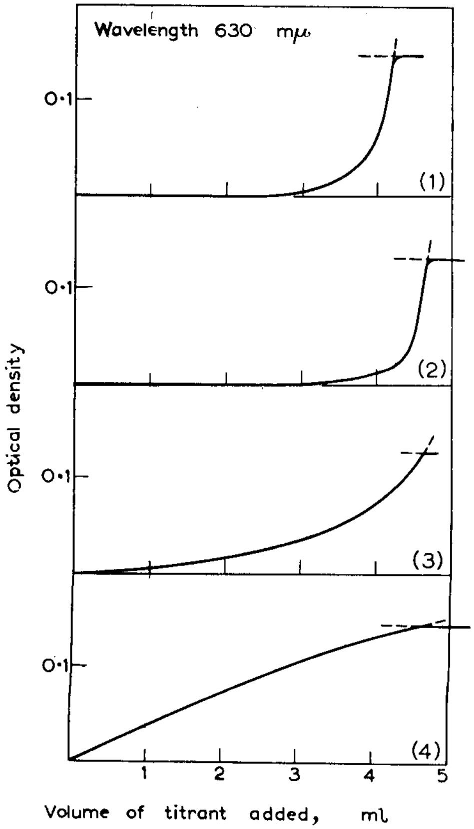


FIG. 6. (1) 10 μM magnesium chloride + reagent blank; (2) 10 μM calcium chloride + 1 μM strontium chloride + 1 μM magnesium chloride + reagent blank; (4) 10 μM barium chloride + 1 μM magnesium chloride + reagent blank.

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 ±0·20 μM.

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 für 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.

REFERENCES

[1] C. C. Miller and R. J. Magee, *J. Chem. Soc.*, 1951, 3183.
[2] H. Seiler, E. Sorkin and H. Erlenmeyer, *Helv. Chim. Acta*, 1952, **35**, 2483.
[3] D. R. Tristram and C. S. G. Phillips, *J. Chem. Soc.*, 1955, 580.
[4] F. H. Pollard, J. F. W. McOmie and J. V. Martin, *Analyst*, 1956, **81**, 353.
[5] R. J. Magee and J. B. Headridge, *ibid.*, 1955, **80**, 785.
[6] G. Schwarzenbach and H. Ackerman, *Helv. Chim. Acta*, 1947, **30**, 1798.
[6] W. Biedermann and G. Schwarzenbach, *Chimia*, 1948, **2**, 56.
[8] G. Schwarzenbach, W. Biedermann and F. Bangerter, *Helv. Chim. Acta*, 1946, **29**, 811.
[9] G. Schwarzenbach and H. Gysling, *ibid.*, 1949, **32**, 1314.
[0] J. R. Munger, R. W. Nippler and R. S. Ingols, *Analyt. Chem.*, 1950, **22**, 1455.
[11] T. J. Manns, M. U. Reschovsky and A. J. Certa, *ibid.*, 1952, **24**, 908.
[12] R. Sijderius, *Analyt. Chim. Acta*, 1954, **10**, 517.
[13] P. B. Sweetser and C. E. Bricker, *Analyt. Chem.* ,1953, **25**, 253.
[14] P. Karsten, H. L. Kies, H. Th. J. von Engelen and P. de Hoog, *Analyt. Chim. Acta*, 1955, **12**, 64.
[15] J. M. H. Fortuin, P. Karsten and H. L. Kies, *ibid.*, 1954, **10**, 356.
[16] J. A. Hunter and C. C. Miller, *ibid.*, 1956, **81**, 79.
[17] P. B. Sweetser and C. E. Bricker, *Analyt. Chem.*, 1954, **26**, 195.
[18] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffmann, *Applied Inorganic Analysis*, Wiley and Sons, Inc., New York, 2nd Edn. 1953, p. 618.
[19] B. Sunners, Unpublished work.

Talanta, 1958, Vol. 1, pp. 127–137. Pergamon Press Ltd., London.

SELECTIVE POTENTIOMETRIC TITRATION OF METAL IONS WITH TRIETHYLENETETRAMINE*

CHARLES N. REILLEY and MARY V. SHELDON
University of North Carolina, Chapel Hill, N.C., U.S.A.

(*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

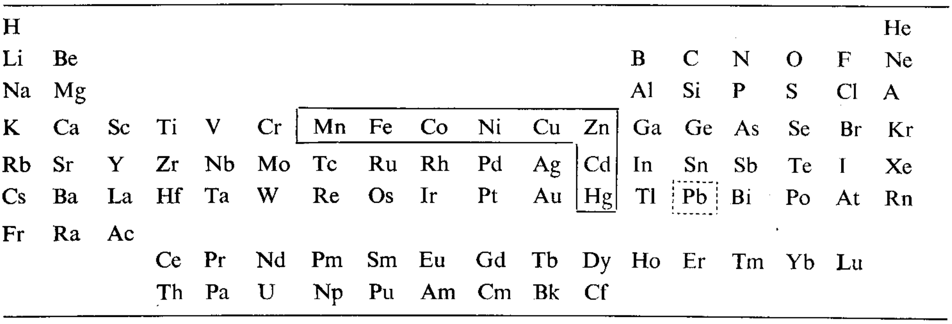
CERTAIN metal ions (such as cobalt, nickel, copper, zinc, cadmium, and mercury) form more stable co-ordination bonds with nitrogen than with oxygen.[13] In ammoniacal solutions such metal ions form stable ammine complexes. In contrast, other metal ions (such as alkaline and rare earths, aluminium, bismuth, 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						

---

* 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°.

$$\begin{array}{ccccc}
\multicolumn{2}{c}{\underbrace{\qquad\qquad M \qquad\qquad}} & + & Y \longrightarrow MY & \\
+ & + & & + & \\
xOH^- & yZ & & nH^+ & (1) \\
\downarrow & \downarrow & & \downarrow & \\
M(OH)_x & MZ_y & & H_nY & \\
(\textit{Hydrolysis Effect}) & (\textit{Complex Effect}) & & (\textit{pH Effect}) &
\end{array}$$

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

$$\alpha = 1 + \frac{[\mathrm{H}^+]}{K_n} + \frac{[\mathrm{H}^+]^2}{K_n \cdot K_{n-1}} + \cdots + \frac{[\mathrm{H}^+]^n}{K_n \cdot K_{n-1} \cdot \cdot K} \tag{3}$$

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 $\alpha =$ 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 $\alpha = 1.2$, 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.

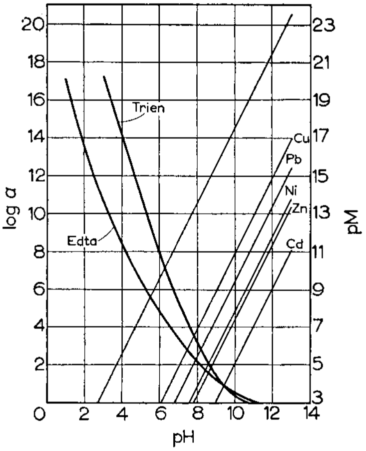


FIG. 1. Hydrolysis and pH effects for EDTA and trien and several metal ions.

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:

$$\mathrm{Hg} \mid \mathrm{Hg\ Trien,\ M\text{-}Trien}^{n+},\ \mathrm{M}^{n+}$$

A combination of the Nernst equation for a mercury electrode

$$E = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log [\mathrm{Hg}^{2+}]$$

with the equations for the stability constants of the 1:1 mercury trien complex

$$K_{\mathrm{HgZ}} = \frac{[\mathrm{HgZ}^{2+}]}{[\mathrm{Hg}^{2+}][\mathrm{Z}]}$$

and a 1:1 metal (Me^{n+}) trien complex

$$K_{\mathrm{MeZ}} = \frac{[\mathrm{MeZ}^{n+}]}{[\mathrm{Me}^{n+}][\mathrm{Z}]}$$

gives at 25°

$$E_{\mathrm{Hg}} = E^{\circ}_{\mathrm{Hg}} + 0.0296 \log \frac{[\mathrm{Me}^{n+}][\mathrm{HgZ}^{2+}]}{[\mathrm{MeZ}^{n+}]\,K_{\mathrm{HgZ}}} + 0.0296 \log K_{\mathrm{MeZ}} \qquad (7)$$

the potential is directly proportional to log $[\mathrm{M}^{n+}]$ 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

$$E = E^\circ_{\mathrm{Hg}} + 0.0296 \log \frac{[\mathrm{HgZ}^{2+}]\,\alpha}{[\mathrm{Z}]_t K_{\mathrm{HgZ}}} \tag{8}$$

where $[\mathrm{Z}]_t$ 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.

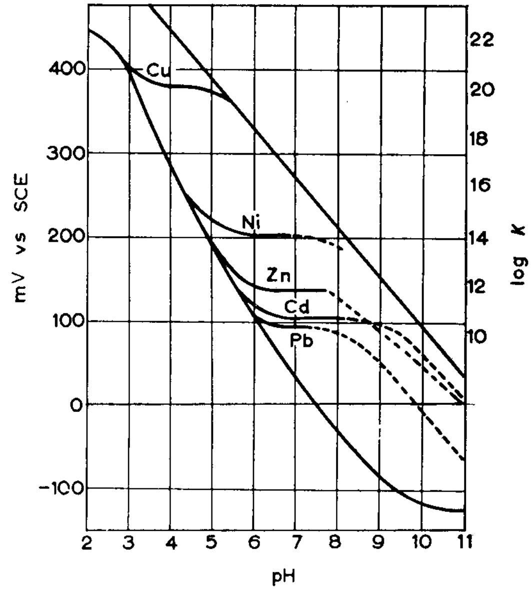


FIG. 2. Potential–pH diagram for metal trien complexes. 25° and ionic strength of 0.1 (KNO_3). I. 0.001M HgZ^{2+} + 0.001 Z. II. Calculated (3) potential for $Hg + 2\,OH^- \rightarrow HgO + H_2O + 2\,e^-$. Other lines, 0.001$M$ HgZ^{2+} + 0.001M MeZ^{2+} + 0.001M Me^{2+}. Note: line I is obtained in 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.

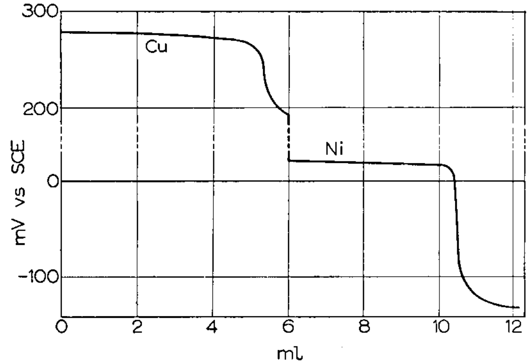


FIG. 3. Titration of copper–nickel mixture.

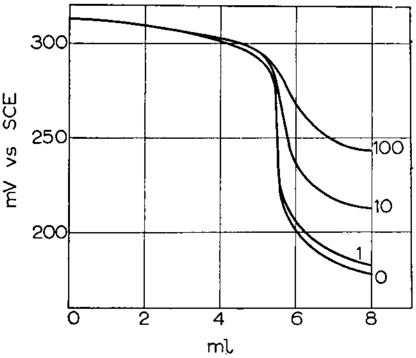


FIG. 4. Titration of copper in the presence of 0-, 1-, 10-, and 100-fold excess of nickel.

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 $0.1M$ EDTA	M moles of metal ion in 5.0 ml solution determined by titration with $0.1M$ N_4	Error in M moles	%Error	M moles of metal ion in 0.5 ml solution determined by titration with $0.01M$ 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 $0.1M$ N_4	Error in M moles	% error	M moles of metal ion in 0.5 ml solution determined by titration with $0.01M$ 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 für die potentiometrische Titration der Metall-Ionen mit Triäthylenetetramin („Trien"), und für die selektive Titrationen der Ionen-Gemengen mit diesem Reagens, allein oder zusammen mit ÄDTA wichtig sind, erortet.

Es wird bewiesen, dass es möglich ist, Bedingungen die für selektive Titrationen geeignet sind zu wählen, und dies wird durch Titrationen von Cu, Zn, Ni, Cd und Hg, allein und in 2-Bestandteil-Gemengen illustriert.

Die alkalinischen Erden stören 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.

REFERENCES

[1] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, (Compilers), *Stability Constants of Metal-Ion Complexes*, Part I. The Chemical Society, London, Special Publ. No. 6, 1957.
[2] H. Flaschka and A. Soliman, *Z. analyt. Chem.*, 1957, **158,** 254.
[3] W. M. Latimer, *Oxidation Potentials.* Prentice Hall, Inc., New York, N.Y., 1952.
[4] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, 1950, **33,** 963, 974, 985, 995.
[5] C. N. Reilley and J. H. Holloway, *J. Amer. Chem. Soc.*, 1958, in press.
[6] C. N. Reilley and W. W. Porterfield, *Analyt. Chem.*, 1956, **28,** 443.
[7] C. N. Reilley and R. W. Schmid, *ibid.*, 1958, **30,** 947.
[8] *Idem.*, *J. Elisha Mitchell Sci. Soc.*, 1957, **73,** 279.
[9] C. N. Reilley and M. V. Sheldon, *Chem.-Analyst.*, 1957, **46,** 59.
[10] R. W. Schmid and C. N. Reilley, *Analyt. Chem.*, 1957, **29,** 264.
[11] *Idem.*, *J. Amer. Chem. Soc.*, 1956, **78,** 5513.
[12] G. Schwarzenbach, *Analyst*, 1955, **80,** 713.
[13] N. V. Sidgwick, *J. Chem. Soc.*, 1941, 443.

Talanta, 1958, Vol. 1, pp. 138-141, Pergamon Press Ltd., London

BEITRAG ZUR CHARAKTERISIERUNG DES FLUORESCEINKOMPLEXONS

J. Körbl, F. Vydra und R. Přibil
Forschungsinstitut für Pharmazie und Biochemie, und Analytisches Laboratorium der Tschechoslowakischen Akademie der Wissenschaften, Prag, Czechoslovakia

(*Received* 27 *February* 1958)

Zusammenfassung—Es wurde gezeigt, dass das reine Fluoresceinkomplexon im Gegenteil zu dem kommerziellen Calcein in der alkalischen Lösung 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 Calciumüberschuss. Dies könnte zu den Fehlschlüssen bei der Beurteilung der Fluorescenzeigenschaften von verschiedenen Calcein-Präparaten führen.

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 löscht in alkalischem Medium, oberhalb der Laugenkonzentration von 0,025*N*. Die Erdalkaliionen, auch das Magnesium, rufen in solchen Lösungen eine gelbgrüne Fluorescenz hervor. Der Störeffekt des Magnesiums wird bei einer höheren Laugenkonzentration stark herabgesetzt, sodass es in 0,1*N* KOH-Lösung möglich ist, die Calciumbestimmung auch neben kleineren Mengen (bis 30 mg) Magnesium durchzuführen.[1,4] Das Fluoresceinkomplexon wurde vor kurzer Zeit auch für 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, ähnlich wie unser Präparat, als ein metallofluorescenter Indikator verhält. Das Auslöschen 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 durchgeführt. Als Quelle der Excitationsstrahlung wurde Philora "Philips" benutzt mit blauem Filter. Die Intensität der Emission wurde als Fotostrom der Selenzelle mittels eines empfindlichen Galvanometers gemessen. Die Messungen wurden in Quarzküvetten zylindrischer Form immer mit 25 ml Lösung durchgeführt. Alle Ergebnisse der Messungen wurden in Prozenten der Fluorescenz einer $6 \cdot 10^{-6} M$ Fluoresceinlösung ausgedrückt.

Zu den optischen Messungen wurde das Universalspektrofotometer Zeiss in Zürichtung für das Messen im Sichtbaren benützt. Die Messschicht betrug 0,5 cm.

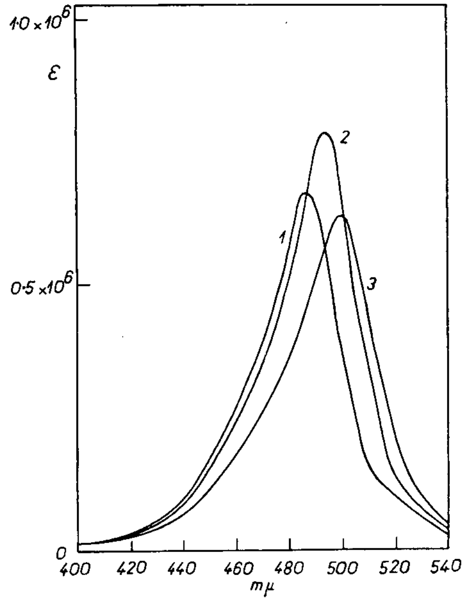


ABB. 1. Extinktionskurven von Fluorescein 1, Calcein 2 und Fluoresceinkomplexon 3 in 0,1*N* KOH

Reagenzien

Standardpräparat von Fluorescein (freie Säure) p.a.

Standardpräparat von Fluoresceinkomplexon. Für $C_{30}H_{26}N_2O_{13}$ (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 Vorratslösungen wurden in 0,1*N* KOH zubereitet, das auf 1 l. immer 5 ml 0,05*M* Dinatriumsalz der ÄDTA zur Bindung eventueller Spuren von Kationen enthielt.

0,5*M* $CaCl_2$ wurde aus einem p.a. Präparat vorbereitet.

Lichtabsorption von Fluoresceinkomplexon und Calcein

Die Messungen wurden in $3 \cdot 10^{-5} M$ Lösungen durchgeführt. Als Molekulargewicht des Calceins wurde das Gewicht des reinen Fluoresceinkomplexons genommen (622,5). Die Extinktionskurven der beiden Präparate wurden mit der Kurve des Fluoresceins verglichen, die in einer Lösung 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 kürzesten Wellenlänge (487 mμ), Fluoresceinkomplexon (Kurve 3) bei der längsten (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 Erhöhung des Extinktionskoeffizientes führt. Anderseits kann diese Erhöhung zur Beurteilung der Reinheit des Präparates dienen.

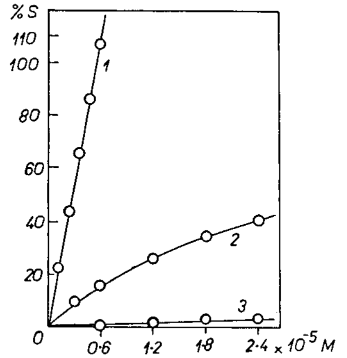


ABB. 2. Relative Intensität der Fluorescenz von Fluorescein 1, Calcein 2 und Fluoresceinkomplexon 3 in der Abhängigkeit von der Konzentration, in 0,1*N* KOH

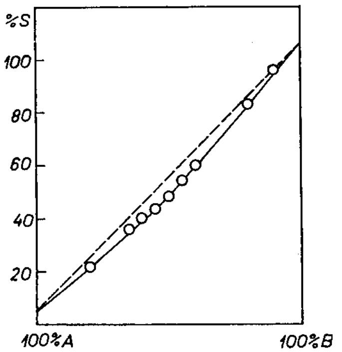


ABB. 3. Relative Fluorescenz der isomolaren Gemischen von Fluoresceinkomplexon und Fluorescein in 0,1*N* KOH (A = 6 . $10^{-6}M$ Fluoresceinkomplexon; B = 6 . $10^{-6}M$ Fluorescein)

Fluorescenzeigenschaften von Fluoresceinkomplexon und Calcein.

Die Restfluorescenz der beiden Präparate wurde bei ihren steigenden Konzentrationen in 0,1*N* 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 beträchtlich. Wenn auch im Vergleich mit dem linearen Verlauf der Fluorescenz des Fluoresceins in der Abhängigkeit von der Konzentration, die Werte der Restfluorescenz des Calceins viel niedriger sind, ist in diesem Falle die Linearität nicht erfüllt. Deshalb könnten wir zu irrtümlichen Schlüssen gelangen, wenn wir die Restfluorescenz bei verschiedenen Konzentrationen beurteilen würden. Es kommt hier offensichtlich eine Selbstabsorption der Fluorescenz zum Vorschein. Ähnlicher Selbstabsorption begegnen wir auch beim Mischen des Fluoresceinkomplexons mit Fluorescein, wie aus der nächsten Abbildung hervorgeht. In der Abb. 3 ist die Abweichung von der Additivität in den isomolaren Gemischen von Fluorescein und Fluoresceinkomplexon gegeben. Solche Abweichung wurde nicht in der Anwesenheit des Calciumüberschusses beobachtet (Abb. 4). Daraus folgt, dass wir bei höheren Konzentrationen eines durch Fluorescein verunreinigten Fluoresceinkomplexons, bei der Reaktion mit Erdalkaliionen eine grössere Fluorescenzausbeute erwarten können als bei einem reinen Präparat. Bei niedrigen Konzentrationen, bei denen die Selbstabsorption vernachlässigt 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 Calciumüberschusses wiedergegeben. Die Einwagen der beiden Stoffe wurden so gewählt, dass die Höhen ihre Lichtabsorptionsmaxima genau gleich sind. Die Fluorescenzen dieser Lösungen sind wieder mit der Fluorescenz des Fluoresceins verglichen. Dieser Versuch erlaubt uns auch, die Verunreinigung des Calceins abzuschätzen. Dies ist allerdings nur als eine Fluoresceinbeimengung ausdrückbar, 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.

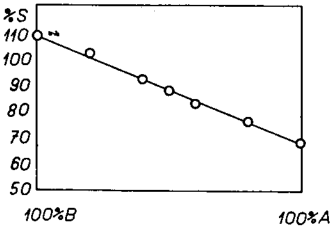


Abb. 4. Relative Fluorescenz der isomolaren Gemischen von Fluoresceinkomplexon und Fluorescein in 0,1N KOH und $10^{-2}M$ $CaCl_2$ Lösung; 0,5 ml 0,5M $CaCl_2$ in 25 ml der Messlösung (A = 6 . $10^{-6}M$ Fluoresceinkomplexon; B = 6 . $10^{-6}M$ Fluorescein)

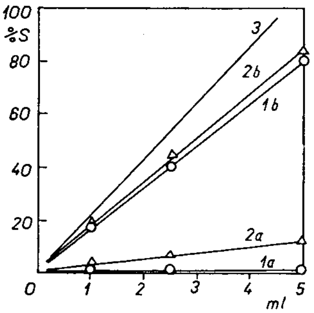


Abb. 5. Relative Fluorescenz von Fluoresceinkomplexon und Calcein in 0,1N KOH vor (1*a* und 2*a*) und nach (1*b* und 2*b*) der Zugabe des Calciumüberschusses, im Vergleich mit dem Fluorescein (3). (20 mg Fluoresceinkomplexon, resp. 17 mg Calcein, resp. 10 mg Fluorescein in 1 L der Vorratslösung. Die auf der Abscisenaxe angegebenen Mengen der Vorratslösungen wurden auf 25 ml verdünnt, eventuell nach der Zugabe von 0,5 ml 0,5M $CaCl_2$)

Le maximum d'absorption de la calcéine se situe entre ceux de la fluorescéine et du complexon-fluorescéine.

LITERATUR

[1] H. Diehl and J. L. Ellingboe, *Analyt. Chem.*, 1956, **28,** 882.
[2] G. Anderegg, H. Flaschka, R. Sallmann and G. Schwarzenbach, *Helv. Chim. Acta*, 1954, **37,** 113.
[3] B. M. Tucker, *Analyst*, 1957, **82,** 284.
[4] J. Körbl and F. Vydra, *Chem. Listy*, 1957, **51,** 1457.
[5] R. O. Ashby and M. Roberts, *J. Lab. Clin. Med.*, 1957, **49,** 958.
[6] M. Effenberger, *Chem. Listy*, 1958, **52,** im Drucke.
[7] J. Körbl, *ibid.*, im Drucke.

Talanta, 1958, Vol. 1, pp. 142–146, Pergamon Press Ltd., London.

A METHOD FOR THE DETERMINATION OF MILLIGRAM AMOUNTS OF SULPHUR WITH 4-AMINO-4′-CHLORODIPHENYL

M. N. Ahmed and G. J. Lawson
Mining Department, The University, Edgbaston, Birmingham 15, England

(*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.

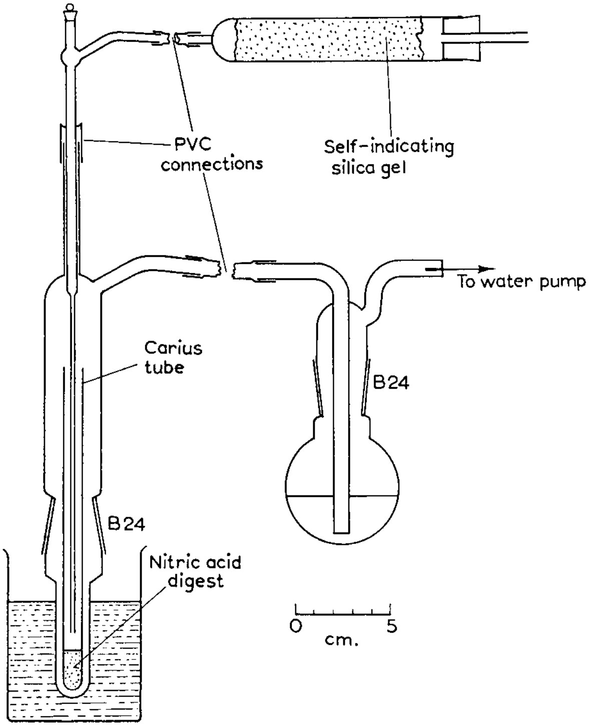


FIG. 1.—Apparatus for evaporation of digests

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 für die Bestimmung kleiner Mengen von Schwefel beschrieben, vorin 4-Amino-4′-Chlorodiphenyl benutzt wird, um das Sulphat, das von vorläufiger Zersetzung der organischen Proben mit Salpetersäure resultiert, niederzuschlagen. Der Verbrauch des Reagens wird durch spektrophotometrische Messung des zurückbleibenden Überschuss in Lösung bestimmt.

Die Methode wird zur Analyse von Steinkohlen und Humus-säuren 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.

REFERENCES

[1] R. Belcher, A. J. Nutten, E. Parry and W. I. Stephen, *Analyst*, 1956, **81**, 4.
[2] A. S. Jones and D. S. Letham, *ibid.*, 15.
[3] R. Belcher, A. J. Nutten and W. I. Stephen, *J. Chem. Soc.*, 1953, 1334.

Talanta, 1958, Vol. 1, pp. 147–152, Pergamon Press Ltd., London.

SUBSTITUTIVE HALOGENATION OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTIONS BY INTERHALOIDS—I

HALOGENATING EFFECT OF IODINE MONOCHLORIDE, IODINE MONOBROMIDE AND BROMINE MONOCHLORIDE

E. Schulek and K. Burger
Institute of Inorganic and Analytical Chemistry, L. Eötvös University,
Budapest, Hungary

(*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 0·1*N* iodine monobromide solution prepared in this way was about 0·5*N* 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 0·1*N* solution of antipyrine with 20 ml of 0·1*N* 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.

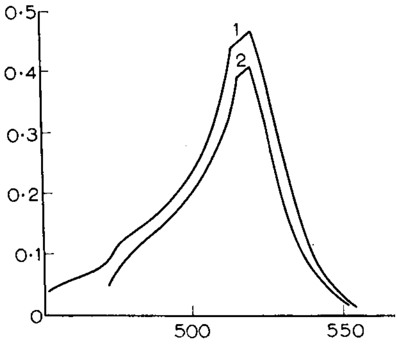


FIG. 1. Absorption spectra of eosin. Curve 1. Absorption spectrum of product obtained with bromine monochloride. Curve 2. Absorption spectrum of product obtained by direct bromination.

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 ünd Brom-chlorid mit gewissen aromatischen Verbindungen in wässerigen Lösungen 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 wässeriger bromidhaltiger Lösung.

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.

LITERATURE

[1] J. F. Brown, *Annalen.*, 1854, **92,** 321; *Phil. Mag.*, 1854, **8,** 201.

[2] P. Schützenberger, *Jahresber*, 1862, 251, 413; *ibid.*, 1861, 349; *Bull. Soc. chim. France*, 1865, [2] **4,** 102.

[3] J. Stenhouse, *J. Chem. Soc.*, 1864, **17,** 327, 366.

[4] A. Michael and L. M. Norton, *Ber.*, 1878, **11,** 107.

[5] C. Wilgerodt and E. Arnold, *ibid.*, 1901, **34,** 3343.

[6] A. E. Bradfield, K. J. P. Orton and J. C. Roberts, *J. Chem. Soc.*, 1928, 782.
[7] B. Blocke and G. Powell, *J. Amer. Chem. Soc.*, 1943, **65,** 143.
[8] A. M. Gandbhir, A. L. Fonseca, F. Rebello, A. N. Kothase and V. V. Nadkarny, *Current Sci. (India)*, 1950, **19,** 380.
[9] B. Jones and E. N. Richardson, *J. Chem. Soc.*, 1953, 713.
[10] E. Berliner, *J. Amer. Chem. Soc.*, 1956, **78,** 3632.
[11] F. W. Bennett and A. G. Sharpe, *J. Chem. Soc.*, 1950, 1383.
[12] L. I. Lambourne and P. W. Robertson, *ibid.*, 1947, 1167.
[13] E. D. Hughes and C. K. Ingold, *ibid.*, 1935, 244.
[14] W. A. Waters, *ibid.*, 1942, 153.
[15] C. Sandonnini and N. Borghello, *Atti. R. Acad. Lincei*, 1937, **25,** 46.
[16] L. Bruner and A. Galecki, *Z. Phys. Chem.*, 1913, **84,** 513.
[17] A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.*, 1929, **124A,** 610; *ibid.*, 1931, **132A,** 154.
[18] T. Erdey Gruz and G. Schay, *Elméleti fizikai kémia, Tankönyvkiadó*, 1952, 207.
[19] J. H. Foull, *J. Amer. Chem. Soc.*, 1934, **56,** 522.
[20] A. I. Gengrinovich, F. E. Kogan and Ja. A. Fialkov, *Trudi Komisszii Analiticseszkoj Chimii*, 1954, **5,** 237.
[21] A. I. Gengrinovich, *Farmac.*, 1946, **6,** 5.
[22] Ja. A. Fialkov and F. E. Kogan, *Ukrain. Khim. Zhur.*, 1952, **18,** 64.
[23] A. I. Gengrinovich and M. Sz. Baron, *Aptyecsnoje gyelo*, 1952, **4,** 27.
[24] A. I. Gengrinovich and Ja. K. Kadirov, *ibid.*, 1952, **1,** 46.
[25] A. I. Gengrinovich and Sc. Sach, *Med. Prom.*, 1948, **3,** 37.
[26] *Idem*, *Ucsenyije Zapiszki Kiev*, 1950, **1,** 79.
[27] W. Militzer, *J. Amer. Chem. Soc.*, 1938, **60,** 256.
[28] A. G. Sharpe, *J. Chem. Soc.*, 1953, 3713.
[29] D. E. Pearson and C. J. Ross, *J. Amer. Chem. Soc.*, 1952, **74,** 2933.
[30] E. Schulek, *Z. analyt. Chem.*, 1923, **62,** 337.
[31] *Idem*, *ibid.*, 1924, **65,** 352.
[32] *Idem*, *Analyt. Chim. Acta*, 1948, **2,** 74.
[33] E. Schulek and E. Körös, *Magy. Kém. Foly.*, 1950, **56,** 367, 421.
[34] E. Schulek and E. Pungor, *Analyt. Chim. Acta*, 1951, **5,** 137.
[35] E. Schulek and P. Endröi, *ibid.*, 1951, 245, 368.
[36] E. Schulek and E. Pungor, *ibid.*, 1952, **7,** 402.
[37] E. Schulek and K. Burger, *Acta Pharmac. Hung.*, 1957, **27,** 8.

Talanta, 1958, Vol. 1, pp. 153-158, Pergamon Press Ltd., London.

ULTRAVIOLET SPECTROPHOTOMETRIC PROPERTIES OF FERRIC COMPLEXES OF 2:2′-DIPYRIDINES IN GLACIAL ACETIC ACID

WM. M. BANICK, JR. and G. FREDERICK SMITH
William Albert Noyes Laboratory, Department of Chemistry, University of Illinois,
Urbana, Illinois, U.S.A.

(*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.* 0.010*F* 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 0.0020*F* and 0.0010*F* 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 0.0020*F* 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.

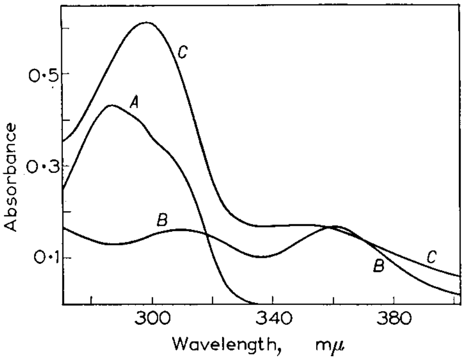


Fig. 1. A—0.50 ml of 0.00200*F* 2:2′-dipyridine (*a*) diluted to 25 ml; B—0.50 ml of 0.00200*F* ferric chloride (*b*) diluted to 25 ml; C—0.50 ml of (*a*) and 0.50 ml of (*b*) diluted to 25 ml.

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.

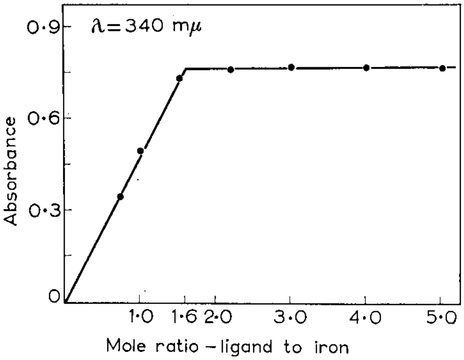


FIG. 2. Mole ratio plot.

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)$_2Cl_6$—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

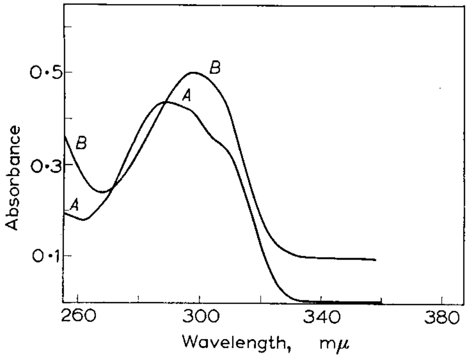


FIG. 3. A—2:2′-dipyridine; B—2:2′dipyridine–iron$^{\text{III}}$ complex.

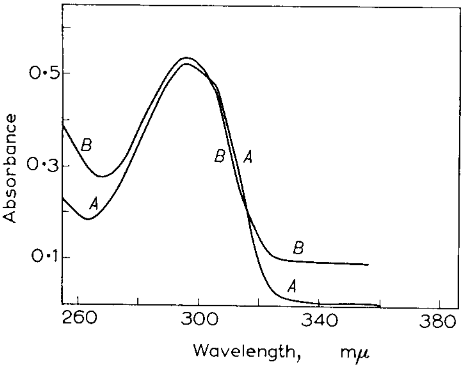


FIG. 4. A—4:4′-diethyl-2:2′-dipyridine; B—4:4′-diethyl-2:2′-dipyridine–iron$^{\text{III}}$ complex.

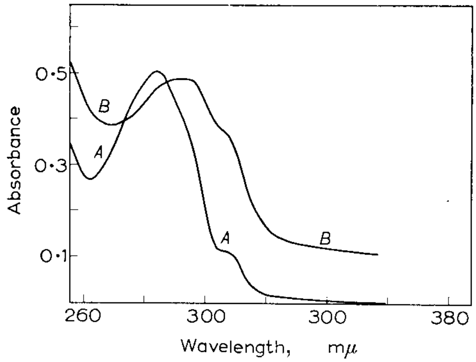


FIG. 5. A—4:4′-dibromo 2:2′ dipyridine; B—4:4′-dibromo-2:2′-dipyridine–iron$^{\text{III}}$ complex.

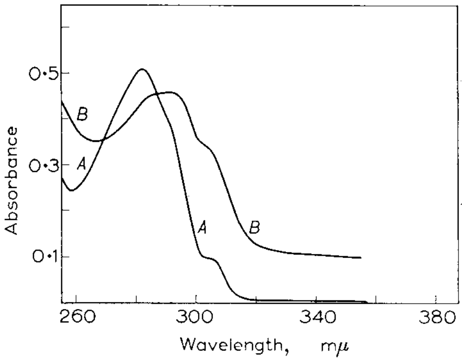


FIG. 6. A—4:4′-dichloro-2:2′-dipyridine; B—4:4′-dichloro-2:2′-dipyridine–iron$^{\text{III}}$ complex.

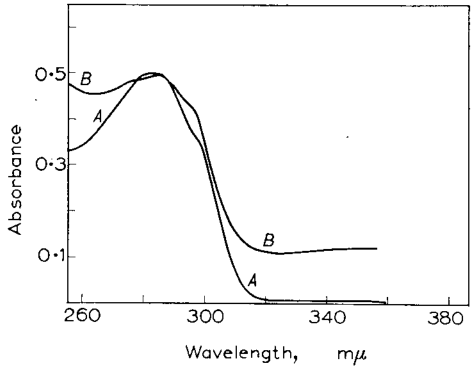


FIG. 7. A—4:4′-diethoxy-2:2′-dipyridine; B—4:4′-diethoxy-2:2′-dipyridine–iron$^{\text{III}}$ complex.

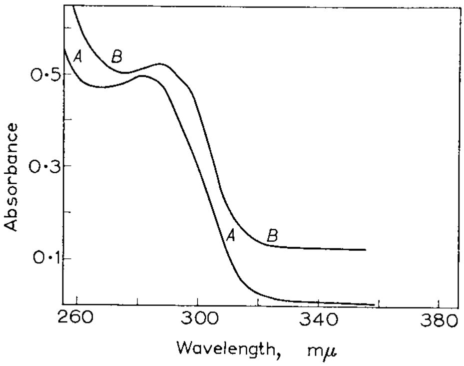


FIG. 8. A—4:4′-diphenoxy-2:2′-dipyridine; B—4:4′-diphenoxy-2:2′-dipyridine–iron$^{\text{III}}$ complex.

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.

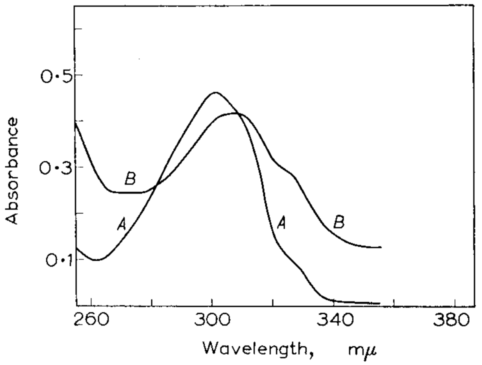


FIG. 9. A—4:4′-dicarbethoxy-2:2′-dipyridine; B—4:4′-dicarbethoxy-2:2′-dipyridine-iron^{III} complex.

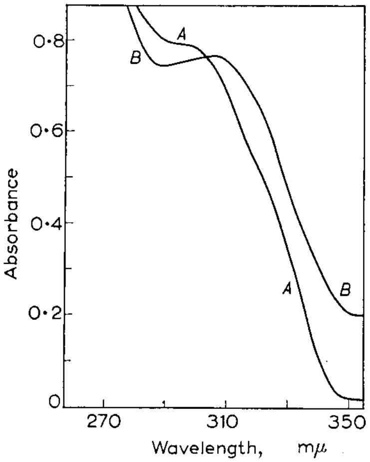


FIG. 10. A—4:4′-diphenyl-2:2′-dipyridine B—4,4′diphenyl-2,2′-dipyridine–iron^{III} complex.

Zusammenfassung—2:2′-Dipyridin bildet mit Eisen-III in Eisessig einen stabilen gelb-grünen 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-grünen Komplex. Lösungen 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 grösste Molabsorptivität 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 350mμ. 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.

REFERENCES

[1] D. L. Manning and A. E. Harvey, Jr., *J. Amer. Chem. Soc.*, 1952, **74**, 4744.
[2] W. W, Brandt and W. B. Howsman, Jr., *ibid.*, 1954, **76**, 6319.
[3] Frederick G. Smith and Wm. M. Banick, Jr., *Analyt. Chim. Acta*, in press.
[4] Wm. M. Banick, Jr., and G. Frederick Smith, *ibid.*, in press.
[5] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal.*, 1944, **16**, 11.

Talanta, 1958, Vol. 1, pp. 159–168, Pergamon Press Ltd., London.

STUDIEN ÜBER DIE POTENTIOMETRISCHE GOLDBESTIMMUNG DURCH ASCORBINSÄURE

L. Erdey und G. Rády
Institut für Allgemeine Chemie der Technischen Universität,
Budapest, Hungary

(*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 bewährte 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 Verdünnung 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 Verdünnung 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 Verdünnung 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 verläuft, 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.).

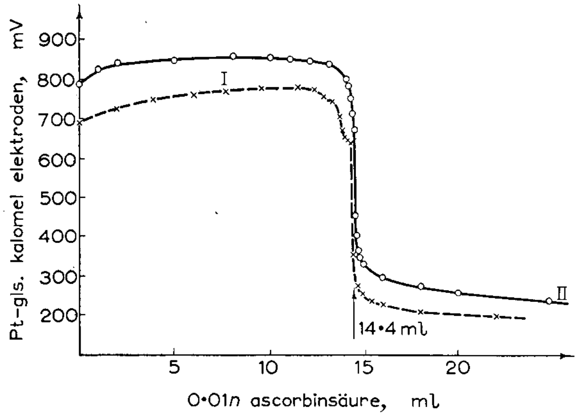


ABB. 1. 14,14 ml 0,01N Au-III-lösung + 85 ml Wasser, titriert. I. bei 20°, II. bei 50°.

Bei Zimmertemperatur verlief die Reaktion langsam, man muss ziemlich viel warten, bis sich die Potentialwerte einstellten. In warmer Lösung 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 Dehydroascorbinsäure zu verschreiben sei. Dies zu klären unternahmen wir folgende Versuche: 15 ml 0,01N Gold-III-lösung wurden mit Wasser auf 100 ml verdünnt, dazu 15 ml 0,01N Dehydroascorbinsäurelösung gesetzt und die Lösung während 30 Minuten bei 50, 60, 70 und 100° gehalten, und dann bei 50° mit 0,01N Ascorbinsäurelösung titriert. Die Ergebnisse zeigten, dass bei 50° keine Reduktionstattfand, [Abb. 2, Kurve 1.] über 70° jedoch die Dehydroascorbinsäure schon eine beträchtliche Menge der Gold-III-Ionen [ungefähr 50%] reduzierte [Kurve 2.], bei 100° schon während des Kochens das kolloidale Gold erschien. Die ascorbinometrische Goldtitration darf man folglich nicht über 60° durchführen. Es empfiehlt sich die Titration bei 50–55° vorzunehmen und die im Laufe der Titration abgekühlte Lösung beim ersten Erscheinen des Kolloidgolds neuerlich zu erwärmen. Die weiteren Versuche wurden stets derart unternommen.

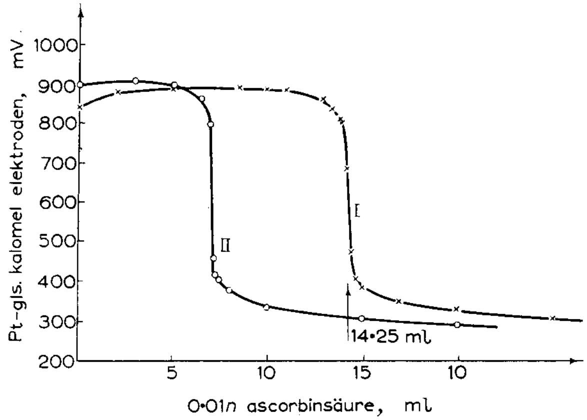


ABB. 2. 14,14 ml 0,01N Au-III-lösung + 15 ml 0,01N Dehydroascorbinsäurelösung + 70 ml Wasser, titriert. I. vorangehend während 30 Minuten bei 50°, II. vorangehend während 30 Minuten bei 70° gehalten.

Einfluss des pH

Zu je 15 ml der 0,01N Gold-III-lösung setzte man soviel 2N Salzsäure, dass 100 ml Anfangsvolumen der zu titrierenden Lösung auf Säure 2N, 1N, 0,5N, 0,1N und 0,01N wurde, mit Kaliumdihydrogensphosphat und Dinatriumhydrogenphosphat Puffergemische stellte man das pH weiterer Lösungen auf die Werte 3,4, 4,6 und 6 ein. Die so bereiteten Lösungen titrierte man dann mit 0,01N Ascorbinsäurelösung potentiometrisch. Die in Abb. 3 graphisch dargestellten Ergebnisse zeigen, dass in 2N und 1N salzsauren Lösungen die Reaktionsgeschwindigkeit der Reduktion des Gold-III-s zu metallischem Gold vernachlässigt werden kann. [Kurve 1, 2.] Die geringe Potentialzunahme und die Entfärbung der Lösung 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 Potentialänderung eintritt. In 0,5N saurer Lösung tritt eine auswertbare Potentialänderung auch nur erst bei einer 20%igen Übertitration ein. In 0,1N saurer Lösung 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 über pH 4,6 kann man die Titration praktisch nicht mehr ausführen.

Die Versuchsdaten zeigen, dass nicht nur im Ablauf der potentiometrischen Kurven sich eine beträchtliche Abweichung gestaltet, sondern auch schon bei den anfänglichen Potentialwerten. Diese erreichen im weiten nicht die theoretischen Potentialwerte des Systems Au^{3+}–Au. Diese Erscheinung ist aber verständlich. In der Lösung ist Chlorid anwesend, folglich bestimmen hier die damit entstehenden Komplexionen das Potential. Das Tetrachloroaureat-III-dissociiert in salzsäurer Lösung 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 Lösung niedriger als es der Einwaage entspräche, demzufolge der Elektrodenpotentialwert der Lösung der Nernstschen Gleichung gemäss sich ebenfalls wesentlich niedriger gestaltet. Die Dissociation der Komplexsäure wird durch die Wasserstoffionenkonzentration der Lösung, die des Komplexions durch die Chloridkonzentration beeinflusst.

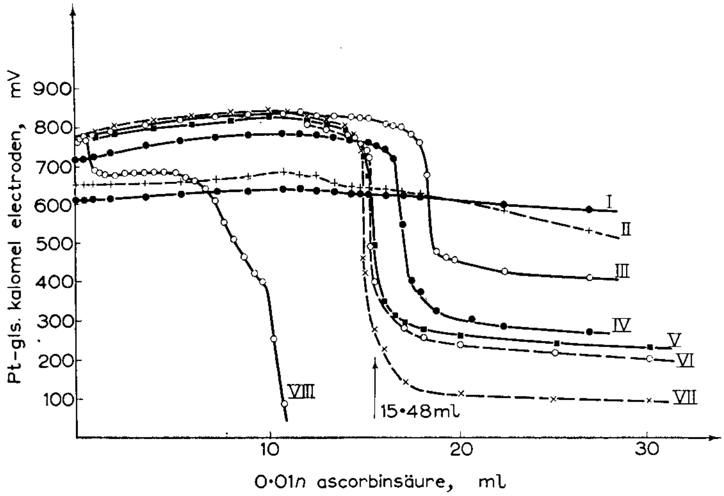


Abb. 3. 15,52 ml 0,01*N* Au-III-lösung + verschiedene Mengen Säure- bzw. Pufferlösungen auf 100 ml ergänzt und bei 50° titriert in folgenden medien. I. 2*N* Salzsäure, II. 1*N* Salzsäure, III. 2*N* Schwefelsäure, IV. 0,5*N* Salzsäure, V. 0,1*N* Salzsäure [pH = 1,4], VI. 0,01*N* Salzsäure [pH = 2,3], VII. Essigsäure-Natrium-acetat Puffer [pH = 3,6], VIII. Phosphatpuffer [pH = 6]

Die Reduktion des Gold-III-s durch Ascorbinsäure verläuft folglich in Übereinstimmung mit unseren Erfahrungen gemäss den verschiedenen Media veränderlich. 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 ausgeübte Einwirkung der Wasserstoffionen-, der Chloridionen- und der Salzsäurekonzentration abgesondert zahlenmässig untersucht.

15,52 ml 0,01*N* Gold-III-Lösung wurden mit 85 ml Wasser versetzt und das Potential zwischen einer vergoldeten Platinelektrode und einer gesättigten Kalomelelektrode bestimmt, dann zu einer Versuchsserie 8*N* Schwefelsäure [Abb. 4, Kurve 1.], zu einer anderen 6*N* Kaliumchloridlösung [Kurve 2.] und zu einer dritten 6*N* Salzsäure [Kurve 3.] in verschiedenen Mengen zugefügt. Wie aus

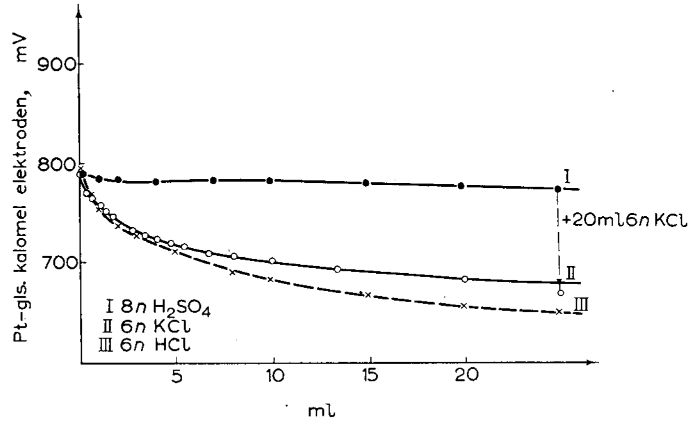


Abb. 4. 15,52 ml 0,01*N* Au-III-lösung + 85 ml Wasser versetzt mit, I. 8*N* Schwefelsäure, II. 6*N* Kaliumchloridlösung, III. 6*N* Salzsäure.

Abb. 4 ersichtlich beeinflusst die Zunahme der Wasserstoffionenkonzentration die Redoxpotentialwerte nicht, die Zunahme der Chlorid- und Salzsäurekonzentration erniedrigt sie dagegen beträchtlich. Die in salzsaurer Lösung gefundenen Potentialwerte stimmen übrigens gut mit den Literaturdaten[1,5] überein. Die Versuche begründen gut die Redoxpotentialwerte der in Abb. 3 dargestellten Titrationskurven und innerhalb dieser auch den Befund, dass in 2*N* Salzsäure der anfängliche Potentialwert 610 mV, in 2*N* Schwefelsäure jedoch 780 mV betrug.

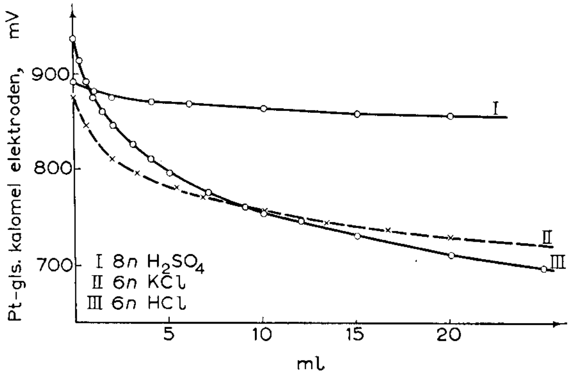


ABB. 5. 15,52 ml 0,01*N* Au-III-lösung + 10,34 ml 0,01*N* Ascorbinsäurelösung + 75 ml Wasser versetzt mit I. 8*N* Schwefelsäure, II. 6*N* Kaliumchloridlösung, III. 6*N* Salzsäure.

In folgenden wurden zu 15,52 ml 0,01*N* Gold-III-lösung 10,34 ml 0,01*N* Ascorbinsäurelösung gefügt, mit Wasser auf 100 ml ergänzt und das Redoxpotential der so erzeugten Gold-I-lösungen zwischen den gleichen Elektroden gemessen indem zu den Lösungen in einer Probe 8*N* Schwefelsäure [Abb. 5, Kurve 1.], in einer anderen Probe 6*N* Kaliumchloridlösung [Kurve 2.] und in einer dritten Lösung 6*N* Salzsäure [Kurve 3.] gegeben wurde. Aus Abb. 5 ist es ersichtlich, dass die Änderung der Wasserstoffionenkonzentration die Potentialwerte des Systems Au^+–Au in messbarem Masse beeinträchtigt, dass die Zunahme der Chloridkonzentration eine bedeutende Abnahme des Potentialwertes verursacht und dass ein Salzsäurezusatz die Werte wie erwartbar in noch beträchtlicherer Weise ändert. Die Messergebnisse bezeugen folglich, dass man auch in 2*N* Schwefelsäurelösung über den Äquivalenzpunkt titrieren muss um eine ermittelbare Potentialänderung zu erhalten [Abb. 3, Kurve 3.], da die Zunahme der Wasserstoffionenkonzentration die Au^+–Au Reduktion beeinträchtigt. Laut der gemessenen Redoxpotentialwerte müsste jedoch theoretisch die ascorbinometrische Reduktion der Gold-III-ionen in stark saurer und sogar in chloridhaltiger Lösung glatt ablaufen. Der Grund, dass dies doch nicht in allen Fällen eintritt, ist wahrscheinlich in der Kinetik der Reduktion des Gold-I-chlorids zu suchen. Laut Abb. 3 verlief unter allen Umständen die Reduktion des Gold-III-s zu Gold-I. Dies wird durch die Entfärbung der ursprünglich gelben Lösung, weiterhin durch die Zunahme des Potentialwertes bezeugt. Die Reduktion des Gold-I-s verläuft dagegen nicht immer mit genügender Geschwindigkeit. Vergleicht man die Redoxnormalpotentialwerte der verschiedenen Goldchloridkomplexe,[3] so kommt man zur Folgerung, dass die entstehenden Gold-I-ionen eigentlich eine Disproportionierung gemäss $3\,Au^+ \rightleftharpoons Au^{3+} + 2\,Au$ erleiden müssten.

$$AuCl_4^- + 3\,e^- \rightleftharpoons Au + 4\,Cl^- \qquad E_0 = 0{,}99\ V$$

$$AuCl_4^- + 2\,e^- \rightleftharpoons AuCl_2^- + 2\,Cl^- \qquad E_0 = 0{,}95\ V$$

$$AuCl_2^- + e^- \rightleftharpoons Au + 2\,Cl^- \qquad E_0 = 1{,}13\ V$$

Gemass diesen Daten müsste man eigentlich am Anfang der Titration schon eine kolloidale Goldausscheidung beobachten. Da dies jedoch unterbleibt muss unter gegebenen Umständen die Geschwindigkeit der Disproportionierung sehr gering sein. Sogar die ascorbinometrische Reduktion der im Laufe der Titration entstandenen Gold-I-ionen verläuft trotz des positiveren Normalpotentials langsamer als die der Gold-III-ionen. Ein jeder weiterer Masslösungszusatz reduziert nämlich immer Gold-III-ionen anstatt der gleichzeitig anwesenden Gold-I-ionen.

Die Zunahme der Chloridkonzentration und Abnahme des pH-wertes der Lösung verlangsamt noch weiter die ursprünglich sowieso langame Reduktion der Gold-I-ionen zu Gold. Dies bezeugt, dass in $2N$ salzsaurem Medium die Lösung sich entfärbt, jedoch auf Einwirkung einer weiteren Masslösungszugabe weder eine bedeutende Potentialänderung noch Ausscheidung von Goldkolloid zu beobachten ist. Wird aber letztere Lösung für 24 Stunden bei seitegestellt, so tritt Goldausscheidung ein. Auch in $0{,}5N$ salzsauren Lösungen kann man den Fehler ermindern, wenn man im theoretischen Äquivalenzpunkt die Lösung für 30–50 Minuten bei 55° hält. All dies deutet auf einelang same Reaktionsgeschwindigkeit.

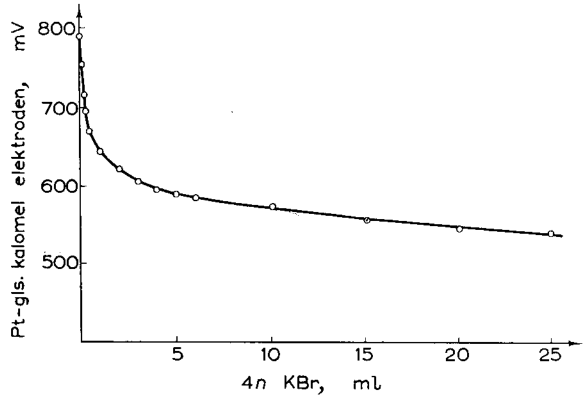


ABB. 6. 15,52 ml $0{,}01N$ Au-III-lösung + 85 ml Wasser versetzt mit $4N$ Kaliumbromidlösung.

Ausser den bisher erwähnten Faktoren muss man noch in Betracht nehmen, dass der Redoxpotentialwert des Systems Ascorbinsäure-Dehydroascorbinsäure ebenfalls vom pH abhängig ist.[12] Zunehmende Säurekonzentration erniedrigt die Reduktionsfähigkeit. In stark saurer Lösung nimmt also die Distanz der Redoxpotentialwerte der zwei Systeme beträchtlich ab, das ebenfalls den Ablauf der Reduktion beeinflusst.

Als Ergebnis der vielen Versuche können wir feststellen, dass eine Gold-III-chloridlösung in 0,01 bzw. $0{,}001N$ Mass mit Ascorbinsäuremasslösung neben potentiometrischer Endpunktsindication ausgezeichnet titriert werden kann, falls der pH-Wert der Lösung sich zwischen 1,5–3 befindet und die Chloridkonzentration nicht das $1N$ Mass übertrifft. Man soll bei 50–60° titrieren. Der Fehler beträgt unter diesen Umständen ungefähr 1 %.

Einfluss verschiedener Anionen

Alle diejenigen Anionen stören, die geschilderte Goldbestimmung, die mit Gold-III-bzw. Gold-I-ionen den Chloriden ähnlich stabile oder noch stabilere Komplexverbindungen bilden. So stören z.B. Bromid, Cyanid und Rhodanid. Aus der Reihe dieser Anionen bildet das Bromid die lockersten

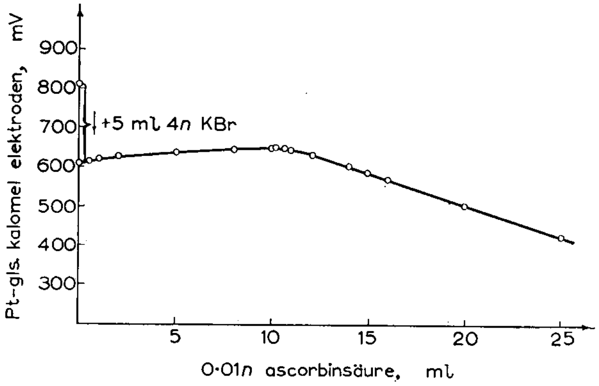


ABB. 7. 15,52 ml $0{,}01N$ Au-III-lösung + 80 ml Wasser + 5 ml $4N$ Kaliumbromidlösung titriert mit $0{,}01N$ Ascorbinsäure bei 50°.

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 könnte [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.

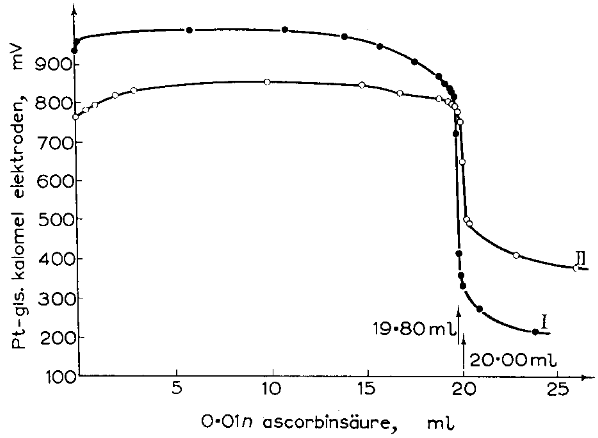


ABB. 8. I. 19,75 ml 0,01N Au-III-lösung + 80 ml Wasser II. 19,75 ml 0,01N Au-III-lösung + 80 ml Wasser + 1 g $HgCl_2$ titriert mit 0,01N Ascorbinsäure bei 50°.

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

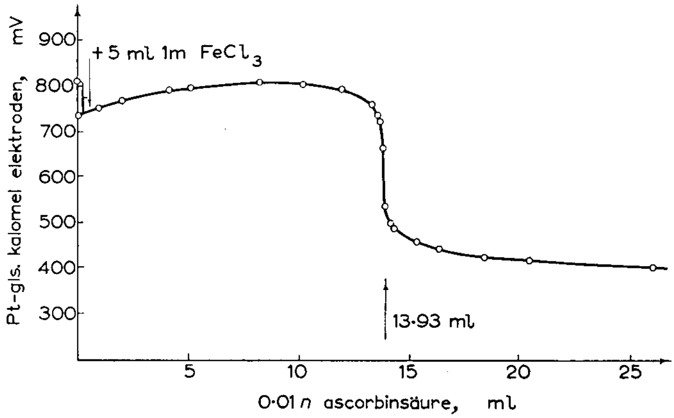


ABB. 9. 14,14 ml 0,01N Au-III-lösung + 5 ml 1M Fe-III-lösung + 1 ml konz. H_3PO_4 + 80 ml Wasser titriert mit 0,01N Ascorbinsäure bei 50°.

Ascorbinsäure nicht. Quecksilber-II-ionen in 120-facher Menge [Abb. 8.] und Kupfer-II-ionen in 50-facher Menge stören die Bestimmung nicht. Bei einer 10-fachen Menge von Eisen-III kann man die Bestimmung in Anwesenheit von 1 ml Phosphorsäure [sp.G. 1,74] noch gut ausführen [Abb. 9.]. Die Genauigkeit der Bestimmung beträgt in Gegenwart dieser Ionen ±1–3%.

Endpunktsindication ohne Salzbrücke

Zwecks Beseitigung der Kalomelelektrode führten 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 bewährte sich zur Endpunktsbestimmung, es hat jedoch den Nachteil, dass nach 3–4 Titrationen eine neue Silberchloridelektrode zu bereiten ist.

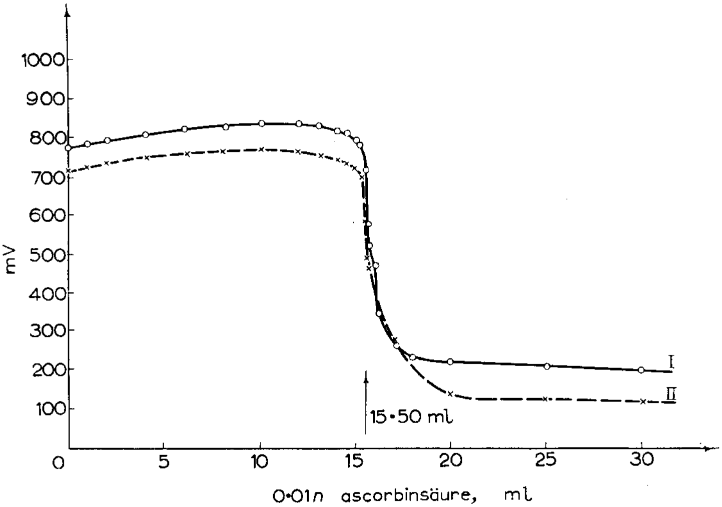


Abb. 10. 15,52 ml 0,01N Au-III-lösung + 80 ml Wasser titriert mit 0,01N Ascorbinsäure bei 50° I. zwischen einem Platin- Glaselektrodenpaar, II. Platin–Ag–AgCl Elektrodenpaar.

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.

LITERATUR

[1] N. Bjerrum und A. Kirschner, *Kgl. Danske Videnskab.-Selsk.*, 1918, **1**, 1.
[2] H. Brintzinger, *Kolloid Z.*, 1937, **78**, 22.
[3] G. R. Charlot und R. Gaugin, *Les methodes d'analyse des Reaction en Solution.* Masson et Cie, Paris, 1951, p. 317.

[4] N. K. Pchenitsy *et al.*, *Chim. analyt.*, 1956, **38**, 138.
[5] C. Drucker, *Messungen elektromotorischer Kräfte galvanischer Ketten mit wässrigen Elektrolyten-II.* Ergänzungsheft, Berlin, 1929, p. 152.
[6] L. Erdey, *Magyar. Kém. Folyóirat*, 1950, **56**, 262.
[7] L. Erdey und E. Bodor, *Analyt. Chem.*, 1952, **24**, 418.
[8] *Idem, Magyar. Kém. Folyóirat*, 1952, **58**, 295.
[9] *Idem, Z. analyt. Chem.*, 1953, **137**, 410.
[10] L. Erdey und H. Buzás, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 195.
[11] *Idem, ibid.*, 1955, **8**, 263.
[12] L. Erdey und G. Svehla, *Z. analyt. Chem.*, 1956, **150**, 407.
[13] C. del Ferno, E. Mairlot, *Z. anorg. Chem.*, 1933, **214**, 73.
[14] H. Frenck, *Mining Eng. World*, 1912, **37**, 853.
[15] V. E. Herschlag, *Ind. Eng. Chem. Anal.*, 1941, **13**, 561.
[16] H. F. Jüptner, *Österr. Berghüttenwesen*, 1880, 182.
[17] V. Lenher, *J. Amer. Chem. Soc.*, 1913, **35**, 735.
[18] G. Milazzo, *Analyt. Chim. Acta*, 1949, **3**, 126.
[19] E. Müller, *Z. analyt. Chem.*, 1926, **69**, 167.
[20] E. Müller und R. Bennewitz, *Z. anorg. Chem.*, 1929, **179**, 113.
[21] E. Müller und W. Stein, *Z. Elektrochem.*, 1930, **36**, 376.
[22] E. Müller und K. Tänzler, *Z. analyt. Chem.*, 1932, **89**, 339.
[23] E. Müller und F. Weisbrod, *Z. anorg. Chem.*, 1926, **156**, 17; 1928, **169**, 394.
[24] N. K. Pchenitsyn und S. I. Ginzbourg, *Izv. Sekt. Platiny*, 1955, **30**, 171.
[25] N. K. Pchenitsyn und J. V. Prokofjewa, *ibid.*, 176.
[26] H. Peterson, *Z. anorg. Chem.*, 1899, **19**, 59.
[27] W. B. Pollard, *Bull. Inst. Min. Met.*, 1932, 23.
[28] W. B. Pollard, *Analyst*, 1937, **62**, 597.
[29] E. Rupp, *Ber.*, 1902, **35**, 2011.
[30] D. J. Ryatchikov und G. V. Knyazheva, *Chem. Abs.*, 1940, **34**, 4011.
[31] K. Someya, *Sci. Reports Tohoku Univ.*, 1930, **19**, 124.
[32] E. C. Stathis und H. C. Gatos, *Analyt. Chem.*, 1946, **18**, 801.
[33] L. Szebellédy und B. Viczián, *Österr. Chem.-Ztg.*, 1938, **41**, 431.
[34] L. Vanino und L. Seeman, *Ber.*, 1899, **32**, 1968.
[35] E. Zintl, G. Rienäcker und F. Schloffer, *Z. anorg. Chem.*, 1927, **168**, 97.
[36] E. Zintl und A. Rauch, *ibid.*, 1925, **147**, 256; *Z. Elektrochem.*, 1925, **31**, 428.

Talanta, 1958, Vol. 1, pp. 169–176, Pergamon Press Ltd., London.

ANALYTICAL APPLICATIONS OF CACOTHELINE—I

COLORIMETRIC DETECTION AND DETERMINATION OF IRON^{II} AND IRON^{III}

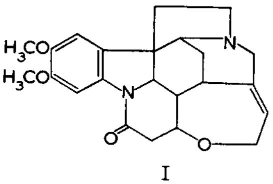
G. GOPALA RAO and V. NARAYANA RAO
Andhra University, Waltair, S. India

(*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.

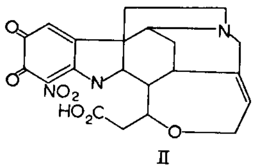
CACOTHELINE is a yellow crystalline substance, obtained by the action of hot 5*N* nitric acid on the alkaloid brucine. This substance appears to have been prepared by Gerhardt (1847), Strecker (1854), Moufang and Tafel[1] (1899) and later by Leuchs and Leuchs[2] (1910). It is sparingly soluble in water 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

$$Fe^{2+} \leftrightharpoons Fe^{3+} + e^-$$

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 (0·1*M*) + 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.

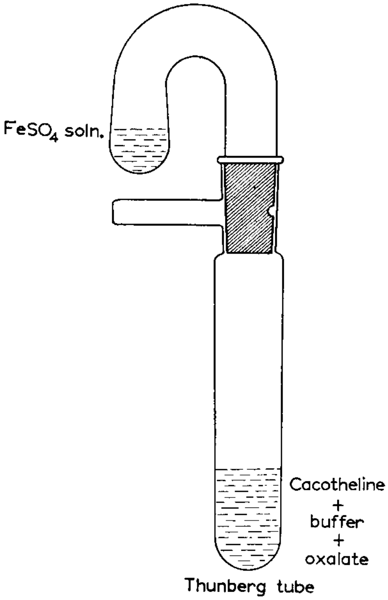


FIG. 1

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 *µ*g to 80 *µ*g 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 *µ*g to 80 *µ*g 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, Ferrosälze 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.

Ferrisälze 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.

REFERENCES

[1] N. Maufang and J. Tafel, *Annalen*, 1899, **304,** 24.
[2] H. Leuchs and F. Leuchs, *Ber.*, 1910, **43B,** 1042.
[3] N. Moufang and J. Tafel, *Annalen*, 1899, **304,** 24.
[4] F. J. Welcher, *Organic Analytical Reagents*, 1948, Vol. 4, p. 217.
[5] F. Feigl, *Qualitative Analysis by Spot Tests*, 1946, p. 187.
[6] I. Mellan, *Organic Reagents in Inorganic Analysis*, 1942, Vol. I, p. 60.
[7] R. H. F. Manske and H. L. Holmes, *The Alkaloids*, 1950, Vol. 1, p. 421.
[8] H. Leuchs, H. Seeger and K. Jaeger, *Ber.*, 1938, **71B,** 2023.
[9] E. Spath and H. Bretschneider, *ibid.*, 1938, **71,** 1023.
[10] H. L. Holmes, H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 1946, 908.
[11] H. Leuchs, F. Osterburg and H. Kaehrn, *Ber.*, **55B,** 1922, 564.
[12] H. Leuchs and F. Leuchs, *ibid.*, 1910, **43B,** 1042.
[13] H. Leuchs and H. Kaehrn, *ibid.*, 1922, **55B,** 724.
[14] H. Leuchs, F. Leuchs and B. Winkler, *ibid.*, 1922, **55B,** 3936.
[15] G. Gutzeit, *Helv. Chim. Acta*, 1929, **12,** 720.
[16] F. Feigl, *Qualitative Analysis by Spot Tests*, 1946, p. 87.
[17] I. L. Newell, J. B. Ficklen and L. S. Maxfield, *Ind. Eng. Chem. Anal.*, 1935, **7,** 26.
[18] G. Beck, *Mikrochim Acta*, 1937, **2,** 288.
[19] *Idem.*, *ibid.*, 1938, **3,** 141.
[20] L. Rosenthaler, *ibid.*, 1938, **3,** 190.
[20a] F. Feigl, *Qualitative Analysis by Spot Tests*, 1946, p. 99.
[21] F. Feigl and P. W. West, *Nad. producao mineral lab producao mineral biol.*, 1946, **24,** 13.
[22] L. Michaelis and E. Friedheim, *J. Biol. Chem.*, 1931, **91,** 343.
[23] R. Belcher and T. S. West, *Analyt. Chim. Acta*, 1951, **5,** 368.
[24] G. Gopala Rao, V. Narayana Rao, G. Somidevamma and K. Lalitha, *ibid.*, 1955, **12,** 271.
[25] G. Gopala Rao and V. Madhusudana Rao, *Proc. Nat. Inst. Sci. India*, 1946, **12,** 217.

Talanta, 1958, Vol. 1, pp. 177–183, Pergamon Press Ltd., London.

SOME DEVELOPMENTS IN RECORDING POLAROGRAPHY

TAKEO TAKAHASHI and EIJI NIKI
Institute of Industrial Science, University of Tokyo, Japan

(*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.

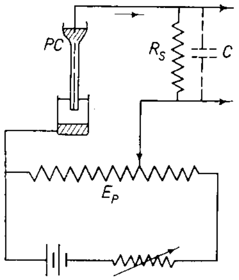


FIG. 1. Ammeter-type polarograph.

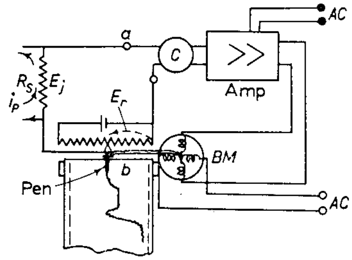


FIG. 2. Automatic balancing potentiometer type polarograph. BM = two-phase balancing motor; C = a.c. converter.

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_SI_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 $R_SI_p = E_j$ 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:—

$$I_p = E_r/R_s \tag{1}$$

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.

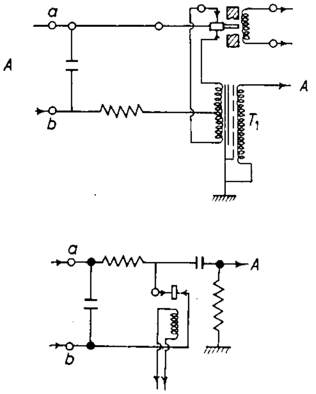


FIG. 3. Converter circuit using a vibrator.

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 photo-pen 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

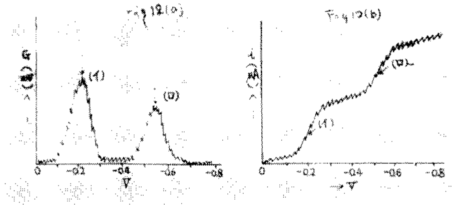


FIG. 4. Compensating bridge circuit.

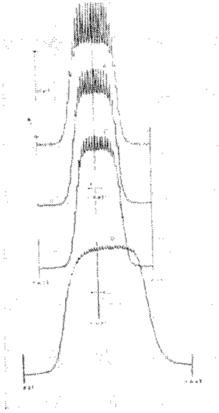


FIG. 8. Half-wave potential shift. (A) no damping, (B) $a = 2$, (C) $a = 1/1{\cdot}5$, (D) $a = 1/4$, due to damping.

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).

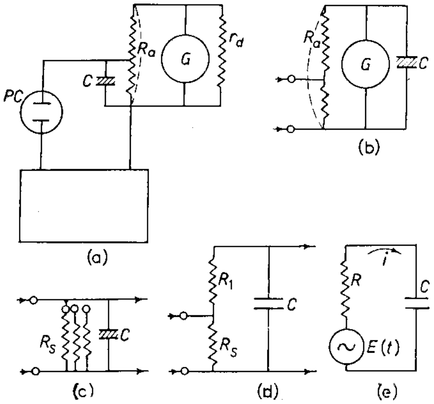


FIG. 5. Damping circuit.

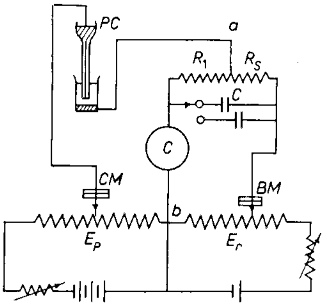


FIG. 6. Combination of the definite time-constant circuit and the compensating bridge circuit.

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:

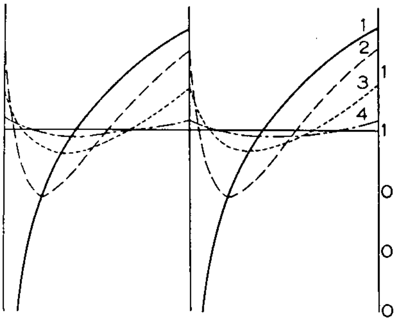


FIG. 7. Damping and wave form. (1) no damping ($R = 50$ KΩ, $C = 0$), (2) $a = 2$, ($R = 50$ KΩ, $C = 10\,\mu$F), (3) $a = 1/1{\cdot}5$, ($R = 50$ KΩ, $C = 30\,\mu$F), (4) $a = 1/6$, ($R = 50$ KΩ, $C = 120\,\mu$F).

$$Ei = ae_0 e^{-at}\left(\int_o^t e^{a\xi}\xi^{1/6}\,d\xi + \frac{e^{-at}}{1-\beta^{-at}}\int_o^t e^{a\xi}\xi^{1/6}\,d\xi\right) \tag{4}$$

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.

$+1{\cdot}2\%$ at $a = 2$, $+1{\cdot}4\%$ at $a = 1/1{\cdot}5$, and $+0{\cdot}4\%$ 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-Vergrösserung, und der potentiometrische Typus mit automatischem Gleichgewicht vor. Der rekordierende Polarograph mit kompensierender Brücke 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.

REFERENCES

[1] H. Hohn, *Metal. u. Erz.*, 1943, **40,** 197.
[2] L. Lykken, D. J. Pompeo and J. R. Weaver, *Ind. Eng. Chem. Anal.*, 1945, **17,** 724.
[3] M. Maruyana, *Japan Analyst*, 1955, **4,** 67.
[4] S. Kikuchi and K. Honda, *Bull. Chem. Soc. Japan*, 1952, **25,** 98.
[5] I. M. Kolthoff and J. J. Lingane, Polarography. Interscience, New York, 1952, Vol. I, p. 316.
[6] Sargent Model XXI Visible Polarograph.
[7] S. Suzuki, *J. Electrochem. Assoc. Japan*, 1948, **16,** 154; 1949, **17,** 12.
[8] M. Yasumori, *Polarography, Japan*, 1955, **2,** 26.
[9] M. P. Leveque and F. Roth, *J. Chim. phys.*, 1949, **46,** 480.

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 0·5*N*.

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.

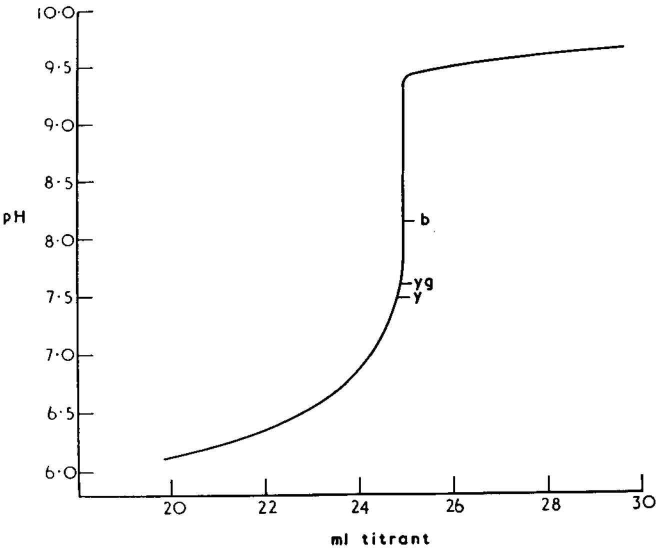


FIG. 1

EXPERIMENTAL

The variation in the pH of 0·1*N* mercuric chloride on addition of 0·1*N* 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 0·1*N* solutions of mercuric chloride with 0·1*N* 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 $+0{\cdot}35\%$, *i.e.* $+0{\cdot}09$ 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.

R. L. Moss
J. McC. Pollock
R. J. Magee

Department of Chemistry,
The Queen's University,
Belfast,
Northern Ireland.

REFERENCES

[1] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis.* Macmillan, London 1950, p. 575.
[2] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis.* Interscience, New York, 2nd Edn., 1947, Vol. II, pp. 197, 198.

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 Schöniger.[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. Jörgensen'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 $0{\cdot}2N$ 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
$CF_3C_6H_4P(C_2H_5)_2{\cdot}CuI$	4·059	7·12	7·29	13·42
$CF_3C_6H_4P(C_2H_5)_2{\cdot}HgBr_2$	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.

R. Belcher
A. M. G. Macdonald

Department of Chemistry,
The University,
Birmingham, England.

REFERENCES

[1] W. Hempel, *Z. angew. Chem.*, 1892, **13**, 393; *cf.* E. Graefe, *ibid.*, 1904, **17**, 616.
[2] J. Marcusson and H. Döscher, *Chem.-Ztg.*, 1910, **34**, 417; E. Votoček, *Chem. Listy*, 1922, **16**, 248.
[3] O. Mikl and J. Pech, *ibid.*, 1952, **46**, 382; 1953, **47**, 904.
[4] W. Schöniger, *Mikrochim. Acta*, 1955, 123.
[5] *Idem, ibid.*, 1956, 869; also private communication.
[6] L. Erdey, L. Mazor and T. Meisel, *ibid.*, 1958, 140.
[7] H. Wagner, *ibid.*, 1957, 19.
[8] I. Lysyj and J. E. Zarembo, *Analyt. Chem.*, 1958, **30**, 428.
[9] K. D. Fleischer, B. C. Southworth, J. H. Hodecker and M. M. Tuckerman, *ibid.*, 1958, **30**, 152.
[10] J. E. Fildes, M.Sc. Thesis, Birmingham University, 1953.
[11] H. N. Wilson, *Analyst*, 1951, **76**, 65; 1954, **79**, 535.
[12] R. Belcher and A. L. Godbert, *Semimicro Quantitative Organic Analysis*, 2nd Edition, Longmans, Green, London, 1954.
[13] T. R. F. W. Fennell, M. W. Roberts and J. R. Webb, *Analyst*, 1957, **82**, 639.
[14] U. Fernlund, S. Zechner and T. Andersson, *Z. analyt. Chem.*, 1953, **138**, 41.
[15] U. Fernlund and S. Zechner, *ibid.*, 1955, **146**, 111.
[16] R. Belcher and A. J. Nutten, *Quantitative Inorganic Analysis*, Butterworths, London, 1955, p. 24.
[17] S. Meyer and O. G. Koch, *Z. analyt. Chem.*, 1957, **158**, 434.

Talanta, 1958, Vol. 1, pp. 189–191, Pergamon Press Ltd., London.

BOOK REVIEWS

Complexometric Titrations. G. SCHWARZENBACH, translated by H. IRVING. Methuen, London, 1957. Pp. xviii + 132. 21s.

THE long awaited English edition of Schwarzenbach's book is now available. The excellent translation is based on the manuscript of the revised second German edition, and contains theory and practice in a well-balanced ratio.

The decimal classification is used throughout the book, and this simplifies considerably the work of finding references. Symbols are simple, carefully selected and consistently used throughout, thus increasing the clarity, especially of the theoretical part.

The first 59 pages present a very clearly written theory of titration, end-point detection, masking, etc. The more important indicators and masking reagents are treated in detail, and many diagrams are used to assist the text. Formulae are given for the calculation of titration curves and indicator curves. Calculations are included for important special cases. A proper understanding of this theoretical part may be regarded as a pre-requisite to understanding what really occurs during a titration.

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.

The final chapter contains many suggestions which may be of importance for further research in this and related fields. There are 305 references which may be consulted for detailed information, and these cover the literature up to and including papers appearing in 1955. There are some references dated 1956.

The book fills a recognised gap in the English literature of analytical chemistry, and is, in the reviewer's opinion, a "must" on the shelf of every chemical analyst.

H. FLASCHKA

The Analytical Uses of Ethylenediaminetetra–acetic Acid. FRANK J. WELCHER. D. Van Nostrand Co. Ltd., London, 1958. Pp. xiv + 366. 64s.

IT is probably true to say that ten or fifteen years ago EDTA would have been rejected by analytical chemists as a reagent, since one of its most outstanding properties is to form complexes under ordinary conditions with most cations. At that time a reagent with such non-specific characteristics would scarcely have been considered of great importance. Yet, owing to exhaustive studies that have been made with this compound it has become, without question, the most useful single reagent in the analytical laboratory. The importance of this reagent is so well known that it is not the function of this review to justify the publication of a book on it.

Those who follow the analytical literature are continually impressed, if not overcome, by the number of papers dealing with the analytical uses of EDTA. The author summarises it very neatly in his preface when he says "With time an important factor in research, it is becoming increasingly difficult to conduct a thorough search for all the information relating to a specific problem." By 1957, approximately 950 papers had appeared on the application of EDTAs and the number, continues to increase steadily.

The author has therefore seen the need to collect information from all papers describing the use of EDTA in inorganic analysis and present them in a manner to assist future study. Few will question this need in the light of the foregoing remarks. No attempt is made to discuss the merit of any particular procedure. The author makes this point quite clear. If, therefore, this volume is accepted as a reference source and not as a text-book or a manual of approved procedures, it will prove to be an excellent and valuable publication. In this connection the reviewer has, since undertaking the review, found it to have been of assistance on two occasions in tracing references.

The book contains eighteen chapters and 963 bibliographical references. The first chapter deals with the reagent, its salts and complexes in chemical analysis. This is followed by a review of the methods of end-point detection in EDTA titrations. One of these methods, metal indicators, is covered in great detail in a subsequent chapter. The fourth chapter deals with the determination of cations in mixtures followed by a chapter on the determination of water hardness. The main part of the book, however, covers the determination of different cations. This has been organised on the basis of groups, *e.g.* calcium and magnesium; barium and strontium; zinc, cadmium, mercury, etc. In all, thirty elements and the rare earths are covered. The author, however, does not ignore anions, to which a chapter is devoted.

Also included are sections dealing with polarographic and colorimetric methods of determination and the use of EDTA in qualitative analysis; and the book ends with a chapter on the elimination of interference, and separation.

This book will be welcome by all who wish to keep abreast of developments in the use of EDTA. It is well written and edited. The reviewer is able to find only minor typographical errors; page iii, line 15, a mis-spelling of *approximately*: page 30, line 7, *millileters* instead of *milliliters*.

It is strongly recommended.

R. J. MAGEE

Organo-Metallic Compounds. G. E. COATES. Methuen, London, 1956. Pp. viii + 197. 12s. 6d.

FOR the purpose of this book, an organo-metallic compound is considered to be one in which the metal atom is linked directly to a carbon atom by covalent or ionic bonds. This, of course, eliminates consideration of practically all organic reagents of analytical importance, *viz.* chelate formers, but nevertheless, whilst this may disappoint the analytical chemist it should be borne in mind that organic analytical reagents are well covered in a variety of text books. This volume covers many of the important developments in the chemistry of compounds containing carbon–metal bonds and draws attention to the importance of these developments in relation to diverse other branches of chemistry such as valency theory and organic synthesis.

There are six chapters in all. These concern: the Alkali metals; Group II metals (Ca, Ba, Sr, Mg, Be, Zn, Cd, Hg); Group III metals (B, Al, Ga, In, Tl); Group IV metals (Ge, Sn, Pb); Group V metals (Sb, Bi) and the Transition elements (Ti, Cr, Mn, also Group VIII, Cu, Ag, Au and the *cyclo*pentadienyls). All the chapters are provided with a fairly extensive bibliography which very largely makes up for the lack of preparative methods and experimental detail in the text. The book is intended primarily as a reference work and in the reviewer's opinion it fulfills its purpose admirably, for it avoids the pitfall of supplying much unnecessary detail and equally well it is not so condensed that the novice has difficulty in appreciating its content. In this respect the final section which deals collectively with the *cyclo*pentadienyls is particularly praiseworthy—it is the best account I have so far met. It is certain that the analytical chemist will find much interesting material in this book as well as his organic, inorganic and physico-chemical co-workers. It is of interest to note that one of the most elegant procedures recently devised for the determination of chlorine in organic compounds makes use of an organo-metallic compound, sodium diphenyl.[1] No doubt many other similar applications will be forthcoming and this moderately priced booklet is strongly recommended for its clear and concise account of these little known compounds.

T. S. West

---

[1] L. M. Liggett, *Analyt. Chem.*, 1954, **26**, 748.

The Development of Titrimetric Analysis till 1806. E. Rancke Madsen. G. E. C. Gads forlag, Copenhagen, 1958. Pp. 239. 20.-d.kr., 20s. 8d., $3.00

"History," Mr. Henry Ford is reputed to have claimed, "is bunk." More seriously, perhaps, Trevelyan tells us that "it is the detailed study of history that makes us feel that the past was as real as the present," and is, as Carlyle has written, "growing ever clearer the farther we recede in time."

It is particularly appropriate in the first issue of a Journal dealing primarily with the growing flood of today's work that we should be able to review a work dealing deliberately—and delightfully—with the past. Those of us who are concerned with the growth of knowledge must recognise that the seeds of the present are in the past; and the reader of this book will realise even more clearly than before that it is not always easy to recognise from the seed what the ultimate growth may be.

Dr. Rancke Madsen gives us ample basis for this line of thought. He shows us how titrimetric analysis, as we know it today, sprang from a variety of sources—experiments with colour changes which were in no way intended to provide quantitative knowledge, "titrations" with teaspoons and beer glasses, giving no hint of the extreme precision that can now be achieved or the minute quantities that can be confidently handled.

The period concerned begins with Boyle, and ends with the year 1806; for from that date other authors have already surveyed the field. The careful examination by the author of all the available scientific literature leads one to believe that many hitherto unrecognised contributions to titrimetry are now added to our historical background, and that little that is really important is now missing. Now we can assess more clearly the relative claims that have been variously made for Descroizilles, for Mohr, and for Home, as "the father of volumetric analysis."

In an appendix Dr. Rancke Madsen gives a useful discussion of the nomenclature of titrimetry. This is particularly of importance since it has a bearing on his choice of processes which historically went to produce titrimetry; but it is of interest in itself for any who are concerned to use the right word in the right place.

On the whole the author's English is clear, only minor errors (*e.g.*, fluorescens) having been noted; and although original quotations in French and German (and a few in Latin) have been allowed to stand, quotations from other languages have been rendered into English.

As Dr. Rancke Madsen rightly says, the history of analytical chemistry is still waiting for its author; but this book is the history of a substantial part of the early days of one of the truly classical methods of analysis. Anyone with a real interest in analytical chemistry will find this account well worth reading, and will come back to the present stimulated by this sympathetic excursion into the past.

Cecil L. Wilson

Talanta, 1958, Vol. 1, pp. 192–194. Pergamon Press Ltd., London.

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.

Quantitative Inorganic Analysis. G. Charlot and D. Bézier, translated by R. C. Murray. Methuen, London, 1957. pp. xi + 691. 84s.

Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse. G. Iwantscheff. Verlag Chemie, Weinheim, 1958. pp. 272. DM 29.80.

Radioisotope Laboratory Techniques. R. A. Faires and B. H. Parks. George Newnes, Ltd., London, 1958. pp. xii + 244. 25s.

pH Measurements. Victor Gold. Methuen and Co., Ltd., London, 1956. pp. 125. 9s. 6d.

Papierchromatographie, 4th Edition. F. Cramer. Verlag Chemie GmbH., Winheim, 1958. pp. 215. DM 21.

Gas Chromatography. A. I. M. Keulemans. Reinhold Publishing Corporation, New York: Chapman and Hall, Ltd., London. 1957. pp. xix + 217. 60s.

An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry, 2nd Edition. A. E. Gillam and E. S. Stern. Edward Arnold (Publishers) Ltd., London, 1958. pp. xi + 326. 50s.

Instrumental Methods of Analysis, 3rd Edition. H. H. Willard, L. L. Merritt Jr. and J. A. Dean. D. Van Nostrand Co., Ltd., New York, and London, 1958. pp. vi + 626. 56s. 6d.

The Book of pH. R. B. Webber. George Newnes, Ltd., London, 1957. pp. 111. 30s.

Differential Thermal Analysis. W. J. Smothers and Y. Chiang. Chemical Publishing Co., Inc., New York, 1958. pp. 444. $16.00.

Proceedings of the Congress on Modern Analytical Chemistry in Industry, St. Andrews, 1957. W. Heffer and Sons, Ltd., Cambridge, England, 1958. pp. vii + 244. 42s.

A Manual of Paper Chromatography and Paper Electrophoresis, 2nd Edition. R. J. Block, E. L. Durrum and G. Zweig. Academic Press, Inc., New York; Academic Books, Ltd., London, 1958. pp. xi + 710. $12.50.

Quantitative Analysis, 4th Edition. W. Conway Pierce, Edward L. Haenish and Donald T. Sawyer. John Wiley and Sons, Inc., New York; Chapman and Hall, Ltd., London, 1958. pp. xiii + 497. 46s.

Microdiffusion Analysis and Volumetric Error, 4th Edition. Edward J. Conway. Crosby Lockwood and Sons, Ltd., London. pp xviii + 465. 42s.

PAPERS RECEIVED

An Improved Alternating Current Polarograph. T. Takahashi and E. Niki. (2 *December* 1957.)

Titrimetric Analysis with Chloramine-T—I: The Status of Chloramine-T as a Titrimetric Reagent. E. Bishop and V. J. Jennings. (3 *February* 1958.)

Cerimetric Determination of Uranium—IV: Use of Triphenylmethane Dyes as Internal Indicators. V. Panduranga Rao and G. Gopala Rao. (5 *February* 1958.)

Use of Brucine as an Oxidation-Reduction Indicator in Cerimetry. G. Gopala Rao and T. P. Sastry. (5 *February* 1958.)

Preparation and Investigation of a Standard Solution of Bromine Chloride. E. Schulek and E. Burger. (14 *February* 1958.)

Determination of Aromatic Compounds by Bromination with Bromine Chloride. E. Schulek and K. Burger. (14 *February* 1958.)

Determination of Hydrazine and Hydrazine Derivatives Using Bromine Chloride as Standard Solution. E. Schulek and K. Burger. (14 *February* 1958.)

Uronic Acid Determination. S. A. Barker, A. B. Foster, I. R. Siddiqui and M. Stacey. (18 *March* 1958.)

Argentometrische Titrationen mit Redoxindicatoren: L. Erdey, K. Busas and K. Vigh. (18 *March* 1958.)

The Complexometric Titration of Calcium in the Presence of Magnesium: A Critical Study. R. Belcher, R. A. Close and T. S. West. (27 *March* 1958.)

A New Method for the Titrimetric Determination of the Ferricyanide Ion. F. Lucena-Conde and I. Sanches Bellido. (28 *March* 1958.)

Titrimetric Determination of Aluminium with Ethylenediaminetetra-acetic Acid in the Presence of Iron, Copper, Titanium, Calcium, Magnesium and Phosphate. Ch. Cimerman, A. Alon and J. Mashall. (2 *April* 1958.)

Titrimetrische, auf Reduktion durch Eisen-II-Hydroxyd Beruhende Verfahren zur Bestimmung des Nitrat-Ions. Z. G. Szabó and L. G. Bartha. (14 *April* 1958.)

Titrimetric Determination of Small Amounts of Cobalt with an Equivalent Ratio of 1 : 37. L. G. Bartha and S. Gorog. (14 *April* 1958.)

The Separation of Cobalt and Nickel by Solvent Extraction. J. H. W. Forsythe, R. J. Magee and C. L. Wilson. (23 *April* 1958.)

Differentiation of Organic Acids in Spot Test Analysis. F. Feigl and C. Stark-Meyer. (30 *April* 1958.)

The Extraction of Zirconium with Tri-*n*-Octylphosphine Oxide and Its Direct Determination in the Organic Phase with Pyrocatechol Violet. J. P. Young and J. C. White. (15 *April* 1958.)

The Separation and Determination of Niobium and Tantalum by Partition Chromatography. I. A. P. Scott and R. J. Magee. (5 *May* 1958.)

Use of Brucine as an Oxidation–Reduction Indicator in Cerimetry—II: Cerimetric Titration of Molybdenum^{V} and Hydroquinone. T. P. Sastri and G. Gopala Rao. (12 *May* 1958.)

Analytical Applications of Cacotheline—II: Cacotheline as a Specific Reagent for the Detection of Iron^{III}. G. Gopala Rao, V. Narayana Rao and G. Somidevamma. (12 *May* 1958.)

Spot Detection of Phenylhydrazine and Arsonic Acids. F. Feigl and E. Jungreis. (13 *May* 1958.)

The Use of Fluorescein Complexone. J. Körbl, F. Vydra and R. Přibil. (3 *June* 1958.)

Photometric Titrations. J. B. Headridge. (6 *June* 1958.)

The Induced Reduction of Chlorate Ions. L. J. Csányi and (Miss) M. Szabó. (13 *June* 1958.)

Amperometric Determination of Microgram Amounts of Sulphide Sulphur. L. Levin and W. B. Swann. (7 June 1958.)

Nucleation in Analytical Chemistry. D. H. Klein and Louis Gordon (16 June 1958.)

EDITORIAL NOTE

Because of the large number of papers submitted for this first issue of *Talanta*, the present double issue of 196 pages has been considered desirable. In spite of this, some of the papers submitted have of necessity been held over. It is hoped that authors who so helpfully made special efforts to complete their manuscripts and submit them at short notice will pardon any delay caused by the natural difficulties attendant on the production of a first issue.

The editors and publishers hope to offer the following publishing schedule normally to contributors: short communications, preliminary notices, and letters to the editor will 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 four issues. The next issue, which will be Number 3 of this Volume, will be published, as planned, in two months' time.

Important PERGAMON publications

TETRAHEDRON *The International Journal of Organic Chemistry*

Founded by SIR ROBERT ROBINSON, O.M., F.R.S.

Some of the papers currently being published:

TAKASHI KUBOTA: Volatile constituents of black rotted sweet potatoes.

B. HELFERICH und M. BURGDORF: Ueber Derivative der D-Xylose.

E. CLAR, W. KEMP and D. G. STEWART: The significance of Kekulé structures for the stability of aromatic systems.

P. CRABBE, G. OURISSON et T. TAKAHASHI: Le Dipterocarpol—I. Preparation de la 8,14-dimethyl 18-nortesterone.

I. CHMIELEWSKA, J. CIÉSLAK, K. GORCZYNSCA, B. KONTNIK et K. PIATKOWSKA: Structure de la yangonine. Étude spectrographique dans l'ultraviolet et l'infrarouge.

S. G. SMITH and S. WINSTEIN: Sulfoxides as nucleophiles.

Subscription rates per volume (including postage): (A) £6 ($17.00) for research institutes, libraries and industrial organisations. (B) £3. 10. 0. ($10.00) for private individuals buying the journal for their personal use only.

PROGRESS IN NUCLEAR ENERGY *The International Review Series on Atomic Energy.*

Editorial Advisory Group:

D. I. BLOKHINTSEV, J. V. DUNWORTH, D. J. HUGHES, I. I. NOVIKOV, F. PERRIN, ALVIN M. WEINBERG.

REACTORS: *Series II. Vol. I.* Price £5 net ($14). *Vol. II. In preparation.*

PROCESS CHEMISTRY: *Series III. Vol. I.* Price 84/- net ($12). *Vol II. In preparation.*

METALLURGY AND FUELS: *Series V. Vol. I.* Price 147/- net ($21). *Vol. II. in preparation.*

INTERNATIONAL SERIES OF MONOGRAPHS IN ANALYTICAL CHEMISTRY

General Editors: DR. R. BELCHER, *University of Birmingham and* DR. LOUIS GORDON, *Case Institute of Technology.*

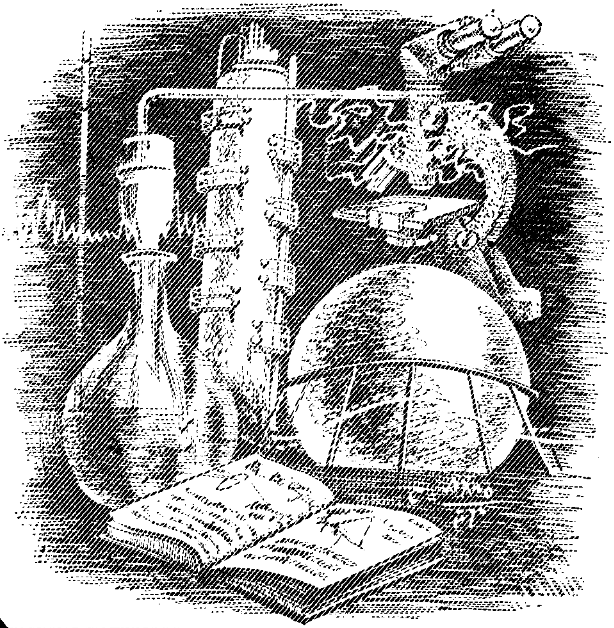
Many titles in preparation. Details supplied on application.

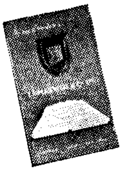
Write for fully descriptive leaflets

PERGAMON PRESS

4 & 5 Fitzroy Square, London W.1.
122 East 55th Street, New York 22, N.Y., U.S.A.
24 Rue des Écoles, Paris V^{e}.

LONDON NEW YORK PARIS LOS ANGELES





NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications (notes and preliminary announcements) and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Research papers will be expected to be of a high standard, and to make some definite contribution to the subject. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. All papers and notes which are submitted will be refereed in the normal way, and referees will be encouraged to submit signed reports. Papers may be submitted in English, French or German. It is hoped that research and review papers will be published within approximately three months of acceptance, and short communications within two months.

Fifty free reprints of each papers will be provided and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

II. Script Requirements

1. Original contributions should be submitted for publication to the Editor-in-Chief, or to the appropriate regional editor.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: Introduction, Experimental, Discussion, Conclusions (or such of these headings as apply.)

3. The essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for French or German papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages.

4. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ ⊡ □ ● ○ ◬ ⊙ ◌ ○ ○ ⊘

5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.

[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

JULY 1958 VOLUME I NUMBERS 1/2

CONTENTS

PERGAMON PRESS LTD.
4 & 5 FITZROY SQUARE, LONDON W.1. 122 EAST 55TH STREET, NEW YORK 22, N.Y.
Printed in Northern Ireland at The Universities Press, Belfast