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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 30, No. 4, April 1964

ACCURACY OF THE POTENTIOMETRIC TITRATION OF COBALT WITH FERRICYANIDE IN AMMONIACAL MEDIUM

With authentically pure metallic cobalt and purified potassium ferricyanide, the accuracy of the titration of +2 cobalt to the +3 state with ferricyanide in strongly ammoniacal medium was examined critically. Quantities of cobalt from about 18 to 200 mg were titrated with a mean error of only +0.02 mg and an average deviation of ± 0.03 mg. The accuracy of this titration is greater than has ever been demonstrated for any other method of determining cobalt. Because of its high accuracy, and since very few other metallic elements interfere, this titration is the best currently available method for the critical assay of cobalt materials.

J. J. LINGANE,

Anal. Chim. Acta, 30 (1964) 319–327.

MANOMETRIC PRECISION DETERMINATION OF CARBON AND HYDROGEN IN MILLIGRAM AMOUNTS OF ORGANIC MATERIAL

A method is described for the precise determination of carbon and hydrogen in milligram amounts of sample. The method is based on the manometric measurement of the amounts of carbon dioxide and water formed on combustion. A precision mercury manometer is used in which pressures are converted to mercury volumes. The latter are measured with the aid of a commercial piston-type buret using a photo-electric level indication.

H. C. E. VAN LEUVEN AND P. GOUVERNEUR,

Anal. Chim. Acta, 30 (1964) 328–334.

DETERMINATION OF TRACE QUANTITIES OF TIN BY NEUTRON ACTIVATION ANALYSIS

A neutron activation method of general applicability has been developed for determining traces of tin in a variety of samples. The samples and comparative standards, sealed into ampoules, are irradiated intermittently for 3 days at a neutron flux of *ca.* $3 \cdot 10^{11}$ n/cm²/sec, followed by carrier radiochemical separations mainly consisting of solvent extraction steps. As little as 0.1 μg Sn can be easily determined by comparing the induced β-activity of ^{121}Sn (27.5 h) with that of a standard. The method is rapid and has a reasonably high chemical yield of about 50%. Results are quoted for the tin contents of a number of materials including silicate rocks, sea waters, biological materials and steels.

H. HAMAGUCHI, K. KAWABUCHI, N. ONUMA AND R. KURODA,

Anal. Chim. Acta, 30 (1964) 335–345.

PHOTOMETRIC INVESTIGATION OF PRECIPITATION TITRATIONS

Photometric investigation of precipitation reactions, by automatically recording the changes in absorbance of a stirred suspension with titrant added, showed that end-points and reacting mole ratios are quickly and easily evaluated. Quantitative analysis in the concentration range 10^{-2} to 10^{-4} M is possible with an error of about 1%. The use of breaks in titration curves to formulate intermediate reaction products is doubtful. A rapid change in the physical form of the precipitate is a limitation of the method.

ST. J. H. BLAKELEY AND D. E. RYAN,
Anal. Chim. Acta, 30 (1964) 346–352.

SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM IN SOIL EXTRACTS WITH CALCICHROME

A simple direct method is presented for the spectrophotometric determination of calcium in hydrochloric acid soil extracts. The chromogenic agent used is Calcichrome (self-coupled diazotized H-acid), and the method covers the range 4 to 175 μg of calcium. A comprehensive study of interferences has been carried out, and a cation-exchange procedure described for the preliminary separation of large amounts of phosphate.

P. PAKALNS AND T. M. FLORENCE,
Anal. Chim. Acta, 30 (1964) 353–357.

COLORIMETRIC DETERMINATION OF TRACES OF ZINC IN BAUXITE, ALUMINA AND REFINED ALUMINIUM

(in French)

A method for the colorimetric determination of traces of zinc in bauxite, alumina and refined aluminium by means of dithizone is proposed. Ga, Fe, Si, Ti, Ni, Pb, Ca, Mg, Na, etc. do not interfere; Co interferes but can be masked with cyanide. The limit of sensitivity of the method is 2 p.p.m. for bauxite and alumina and 0.4 p.p.m. for aluminium.

D. MONNIER ET G. PROD'HOM,
Anal. Chim. Acta, 30 (1964) 358–368.

THE STABILITY OF SOME LANTHANIDE COMPLEXES WITH METHYLETHYL GLYCOLATE AND WITH METHYLPROPYL GLYCOLATE

The 4 successive stability constants have been determined for the methylethyl glycolate and methylpropyl glycolate complexes of some lanthanide elements by potentiometric titration. For all the metal ions, except lanthanum, the average ligand number exceeds a value of 3 indicating the formation of uninegative tetra-ligand complexes, ML_4^-. The stability constants are close to the values of the corresponding α-hydroxyisobutyrate complex systems.

L. EECKHAUT, F. VERBEEK, H. DEELSTRA AND J. HOSTE,
Anal. Chim. Acta, 30 (1964) 369–376.

BARIUM NITRATE CAN BE DRIED AT 375° TO CONSTANT WEIGHT

(Short Communication)

J. SMILTENS,

Anal. Chim. Acta, 30 (1964) 403–404.

A NEW SPECIFIC SPOT TEST FOR URANYL IONS BASED ON THE BEHAVIOUR OF PROTONATED SCHIFF BASES OF *p*-DIMETHYLAMINOANILINE WITH AROMATIC ALDEHYDES

(Short Communication)

E. JUNGREIS AND L. BEN-DOR,

Anal. Chim. Acta, 30 (1964) 405–407.

STUDIES ON ADSORPTION INDICATORS

PART V. APPLICATION OF METALLOCHROME INDICATORS AS ADSORPTION INDICATORS

(Short Communication)

K. N. TANDON AND R. C. MEHROTRA,

Anal. Chim. Acta, 30 (1964) 407–409.

ROBERT FLATT

1897—1963

Le professeur R. FLATT, directeur de l'Institut de chimie minérale et analytique de l'Université de Lausanne, est mort subitement le 24 novembre 1963 après une très belle carrière scientifique de plus de 24 ans.

Né à Bâle le 1er juillet 1897, c'est dans cette ville qu'il fit ses études primaires et secondaires. En 1916 il obtient sa maturité et entreprend alors des études de chimie à l'Ecole Polytechnique Fédérale où il obtient son diplôme d'ingénieur-chimiste. Il commence alors une thèse avec le professeur Treadwell et à la mort de celui-ci il poursuit ses recherches avec le professeur Treadwell fils jusqu'en 1923, date à laquelle il publie sa thèse intitulée: "Über Atomvolumen und Löslichkeit", et devient ainsi Docteur ès sciences technique de l'E.P.F. C'est au contact de ces deux maîtres illustres très en avance sur leur temps que le professeur FLATT découvrit les possibilités de l'analyse chimique moderne. Il s'y intéressa durant toute sa vie.

En 1923, il entre aux usines de Saint-Fons de la société chimique des Usines du Rhône et deux ans après, en mars 1925, sa carrière à l'université recommence; il est en effet nommé professeur de chimie minérale et analytique à l'école supérieure de chimie de Mulhouse. Dès 1934 il donne, tout en poursuivant son enseignment dans cette école, un cours de privat-docent à l'Université de Bâle. C'est en avril 1939 qu'il est appelé à l'Université de Berne en tant que professeur extraordinaire de chimie analytique et de technologie chimique et enfin il est nommé professeur de chimie minérale et analytique à l'Université de Lausanne; il y restera jusqu'à sa mort.

Le professeur FLATT était très apprécié de ses collaborateurs et de ses étudiants; il leur a consacré une grande partie de son temps et de ses forces, ce qui ne l'empêcha pas de faire de nombreuses recherches dans le domaine de la chimie analytique, mais ses travaux les plus nombreux et les plus originaux ont pour objet l'étude de systèmes hétérogènes, particulièrement des systèmes de solubilité dans le domaine des engrais phosphatés.

En ce qui concerne la partie analytique citons la mise au point de dosages particulièrement difficiles tel que celui de traces d'iode ou de brome en présence de grandes quantités de chlorures ou celui du dosage de traces de chromate dans les ciments. Il s'occupa aussi du problème des ions hydratés.

Ses travaux sont résumés dans plus de 60 publications dans un style clair et concis. Elles ont paru dans diverses revues scientifiques: Helvetica Chimica Acta, Analytica Chimica Acta, Bulletin de la Société Chimique de France, Bulletin de la Société Industrielle de Mulhouse. Beaucoup de collaborateurs, dont le professeur Brunisholz est le plus éminent, passionnés par ce maître, ont participé à des remarquables recherches au cours desquelles plusieurs composés nouveaux ont été découverts et où les problèmes de la solubilité ont été particulièrement étudiés.

C'est à lui que Pascal fit appel pour la rédaction de l'article sur l'uranium pour le traité de chimie minérale en 1932. Citons aussi son précis d'analyse qualitative,

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2 éditions (1949 et 1959), où l'on retrouve ses dons pédagogiques et la clarté de son esprit.

Robert FLATT a reçu en 1939 le prix de la Société Suisse de Chimie; il était membre de nombreuses sociétés et du comité de rédaction de ce journal. Dès 1950 atteint gravement dans sa santé il a dû réduire quelque peu son activité. C'est ainsi qu'il n'avait pu accepter de faire partie du comité de rédaction d'un nouveau périodique de chimie minérale. Proposé comme doyen de la faculté des sciences de l'Université de Lausanne et comme président de la Société Suisse de Chimie, il avait dû renoncer à ces charges honorifiques.

Robert FLATT s'est dévoué corps et âme à ses collaborateurs et à ses étudiants. C'était un excellent collègue. Il était venu faire une conférence à la Société Chimique de Genève au cours de laquelle nous avons pu apprécier ses dons de clarté et de précision, sa modestie et sa gentillesse. Nous avons été tous très touché de la mort subite de cet homme de sciences éminent et nous garderons de lui un souvenir plein de respect et d'estime.

D. MONNIER, Genève, janvier 1964

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ACCURACY OF THE POTENTIOMETRIC TITRATION OF COBALT WITH FERRICYANIDE IN AMMONIACAL MEDIUM

JAMES J. LINGANE

Department of Chemistry, Harvard University, Cambridge, Mass. (U.S.A.)

(Received November 8th, 1963)

Few methods of cobalt determination have been demonstrated to be sufficiently accurate (error smaller than ± 0.1% relative) to be really satisfactory for the critical assay of cobalt materials (see *e.g.*, the recent reviews by WILLIAMS[1], by DIEHL[2], and by DALE AND BANKS[3]). Even the electrogravimetric method, usually regarded as very accurate, is subject to greater error than is commonly appreciated. This has recently been pointed out by SALYER AND SWEET[4], who studied 10 of the most commonly recommended procedures for the electrogravimetric determination of cobalt and found that they all entailed a positive error which ranges rather erratically from a few tenths of a milligram to as much as 2 mg when 50 mg of cobalt was deposited. The present investigation was undertaken because the writer felt that the oxidimetric titration of +2 cobalt to the +3 state with ferricyanide in ammoniacal medium ought to be capable of greater accuracy than has heretofore been demonstrated, and thus should be more satisfactory than other methods for precise cobalt assays. This expectation has been realized.

If the solution contains enough excess ammonia so that the predominant cobalt species are $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ the stoichiometry of the titration reaction may be represented by

$$Co(NH_3)_6^{2+} + Fe(CN)_6^{3-} = Co(NH_3)_6^{3+} + Fe(CN)_6^{4-}$$

This titration was proposed independently by TOMIČEK AND FREIBERGER[5] and DICKENS AND MAASSEN[6] in 1935. Because the intense dark red color of the ammonia complexes of +3 cobalt precludes visual end-point indication, the equivalence point is detected potentiometrically with a platinum indicator electrode.

Although this titration has become popular in the field of metallurgical analysis its absolute accuracy has never been established with a precision better than a few tenths of a per cent. The usual recommendation is that the potassium ferricyanide titrant solution be standardized against a known amount of cobalt, in spite of the fact that potassium ferricyanide is known to be an excellent primary standard substance for other reactions (*e.g.*, iodimetry). Although TOMIČEK AND FREIBERGER performed the titration directly, most later authors[2,7-11] recommend that the cobalt solution be added to an excess of standard ferricyanide solution and that the excess ferricyanide be back-titrated with a standardized cobalt solution. In agreement with TOMIČEK AND FREIBERGER's original recommendation, the writer found that direct titration is entirely satisfactory, and there is no need to employ the more involved back-titration procedure.

In their original study TOMIČEK AND FREIBERGER standardized the potassium ferricyanide titrant solution iodimetrically (which involved using a thiosulfate solution which also had to be standardized); they used anhydrous $CoSO_4$ (whose reliability has been doubted by other investigators) as a standard cobalt source, and they also employed relatively small titration volumes (11 to 18 ml) delivered from an ordinary buret. Consequently it may have been somewhat fortuitous that they found an average error in 6 trials of only ± 0.1%. Nonetheless their study definitely suggested that the method is not subject to any very large systematic errors.

The most important systematic error is air-oxidation of the +2 cobalt in the ammoniacal medium. Although this reaction is not very rapid, a solution of +2 cobalt in the air-saturated ammonia–ammonium chloride solution does begin to acquire the characteristic red color of the +3 cobalt ammonia complex within 2 or 3 min. TOMIČEK AND FREIBERGER removed dissolved air from the ammoniacal cobalt test solution with carbon dioxide. The back-titration technique (*vide supra*) used by most other investigators seems to have been introduced in an attempt to circumvent this error, but it is less effective (and certainly less logical) than the simple, direct expedient of removing dissolved oxygen with an inert gas, and very probably is responsible for obscuring the inherently high accuracy of this titration.

The equilibrium constant of the titration reaction is only about 10^6, so that a measurable amount of the +2 cobalt remains unoxidized at the equivalence point. This led BAGSHAWE AND HOBSON[7] to draw the incorrect conclusion that "the low value for the equilibrium constant of the reaction system accounts for incomplete titration at the point of inflection", and this erroneous notion has been further propagated by YARDLEY[10], by CASSY[11], and by WILLIAMS[1]. The fact is that no titration reaction ever is prefectly complete at an equivalence point, and it is fallacious to conclude that this incompleteness constitutes an error. The equivalence point is defined by the condition that the quantity of titrant added is exactly equivalent to the quantity of substance titrated, regardless of how complete the reaction is. For a symmetrical titration reaction, like the present one, the equivalence point corresponds to the point of inflection in the potentiometric titration curve where the rate of change of potential with fraction titrated (*i.e.*, dE/df) is maximal. The magnitude of the equilibrium constant does indeed govern the actual maximal value of dE/df (and thus the *precision* with which the point of maximal slope can be detected), but it does not affect the position of this point of maximal slope on the "fraction titrated" axis.

In the present investigation the direct titration of cobalt with ferricyanide has been studied critically, using authentically pure metallic cobalt and purified potassium ferricyanide. The results demonstrate that the error is so small (+ 0.02 ± 0.03%) that the titration is admirably suited to the critical assay of cobalt compounds.

EXPERIMENTAL

The cobalt standard used in this study was pure metallic cobalt manufactured by Johnson, Matthey and Co., Ltd., London, and obtained from Jarrell-Ash Co., Newtonville, Mass. The certificate of spectrographic analysis furnished by the manufacturer reported 5 p.p.m. nickel, 3 p.p.m. silicon, and 1 p.p.m. each of copper, iron, and silver.

Forty other elements were sought but were not detected.

A standard cobalt solution by weight was prepared by dissolving 4.1593 g of the pure cobalt in hot 1 : 1 hydrochloric acid with precautions to avoid "spray loss". The solution was then evaporated to dryness. The residue of cobaltous chloride was treated with 1 ml of 12 *M* hydrochloric acid, dissolved in water, and the solution was finally diluted to a weight of 1004.81 g. Samples of this solution (containing 4.1394 mg of cobalt per gram) were dispensed by weight to ± 1 mg, so that the uncertainty in the weight of "cobalt taken" probably was not larger than ± 0.004 mg.

The starting material for the preparation of purified potassium ferricyanide was Mallinckrodt AR potassium ferricyanide guaranteed to meet American Chemical Society specifications for the following maximum limits of impurities: chloride 0.01%, sulfate 0.01%, ferro compounds as $Fe(CN)_6^{4-}$ 0.05%, and insoluble matter 0.005%. A nearly saturated solution of 450 g of this potassium ferricyanide in 600 ml of water at the boiling point was prepared and filtered through a sintered glass filter. The filtered solution was then cooled in an ice bath with constant stirring, and the fine crystals were collected on a sintered glass filter and sucked free of mother liquor. This recrystallized salt was then air-dried for 3 days at room temperature in a dark cupboard protected from dust. It was then finally dried in a vacuum desiccator over anhydrous magnesium perchlorate at room temperature, and stored in the desiccator in darkness.

The cobalt solution and solid potassium ferricyanide were weighed out on a balance sensitive to ± 0.01 mg, with a weight set which had been calibrated by the "internally consistent" RICHARDS method. Correction was applied for air-buoyancy; which for potassium ferricyanide amounts to +0.050% because of its relatively small density (1.84), but is only −0.008% for metallic cobalt (against brass weights of density = 8.4).

The potentiometric titrations were performed in the usual manner[12], with a small platinum wire indicator electrode and a saturated calomel reference electrode (S.C.E.). The platinum indicator electrode had been cleaned with aqua regia at the start of this study, and was stored in dilute hydrochloric acid when not in use. Potentials were measured with a Wolff potentiometer in the ordinary way. The titration cell was a cylindrical glass vessel (capacity *ca.* 125 ml) whose top was ground flat. It was closed with a Teflon cover, provided with appropriate holes to accommodate the electrodes, buret tips, etc. The solution was stirred with a magnetic stirrer, and air was removed by passing pure nitrogen continuously through the cell over the surface of the solution. To minimize loss of ammonia, the nitrogen was first passed through a wash bottle containing an ammonia solution of about the same concentration as the test solution. The titrations were performed at room temperature (24–28°).

RESULTS AND DISCUSSION

Some preliminary titrations were carried out in the ordinary volumetric way to gain familiarity with the characteristics of the titration curve. In these cases, a 25-ml sample of 0.0500 *M* cobalt solution was pipetted into the cell, 5.3 g (0.1 mole) of solid ammonium chloride was added, and the solution was diluted to about 50 ml. After air had been removed with nitrogen, the appropriate volume of concentrated (nominally 17 *M*) aqueous ammonia solution was added. The titration was then performed with 0.0500 M potassium ferricyanide solution from which the dissolved air had not been removed.

Figure 1 shows typical complete titration curves, which demonstrate that the titration curve is equally satisfactory with concentrations of ammonia between 1 and 3 M. As expected, because the +2 cobalt and ferricyanide react in a 1 : 1 mole ratio, the titration curves are symmetrical about the inflection point (maximal value of $\Delta E/\Delta V$), which thus corresponds very closely to the equivalence point. Furthermore, the slopes of the curves at all points in the titration correspond closely to the values expected from the Nernst relation, which means that the $Co(NH_3)_6^{3+}/Co(NH_3)_6^{2+}$ and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couples both behave very nearly reversibly.

This reversible behaviour is also reflected by the fact that at all points in the titration (including the immediate vicinity of the equivalence point) the indicator electrode quickly acquires an approximately constant potential after each increment of ferricyanide solution is added; *i.e.*, within about 2 min the potential drift has become smaller than 0.1 mV/min. This favorable behaviour makes easy the detection of the equivalence point with high precision in spite of the fact that the rate of potential change at the equivalence point is not exceptionally large (*vide infra*).

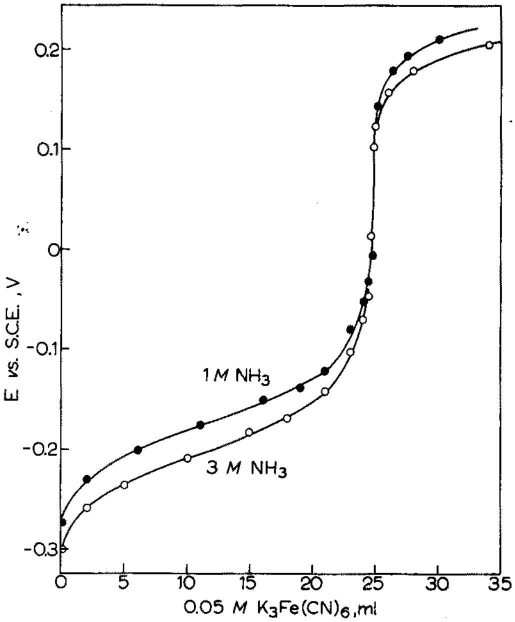

Fig. 1. Typical titration curves in air-free 1 M ammonium chloride with 1 and 3 M ammonia.

The presence of a fairly large concentration of ammonium ion is not only "harmless and seems to have a beneficial effect . . ." as remarked by TOMIČEK AND FREIBERGER, but is essential. With 3 M ammonia much of the +2 cobalt precipitates if the concentration of ammonium ion is only 0.1 M, presumably because of the relatively high pH. This is prevented by increasing the ammonium ion concentration to about 1 M (which decreases the pH from about 10.7 to 9.7). Presumably TOMIČEK AND

FREIBERGER did not notice this effect because they used carbon dioxide to remove dissolved air, and the reaction of the carbon dioxide with the ammonia automatically produced a large concentration of ammonium ion. For a given concentration of ammonia, enough ammonium ion must be present to keep the pH below about 10. In the following precise titrations, a solution containing 1 *M* ammonium chloride and 3 *M* ammonia was employed.

The technique of the precise titrations was as follows. A sample of the standard cobalt solution (weighed to ± 1 mg) was delivered into the titration cell from a weight buret. Then 5.3 g of ammonium chloride (0.1 mole) was added, the solution was diluted to about 50 ml, and air was removed with pure nitrogen. After the air was removed, 20 ml of oxygen-free, concentrated aqueous ammonia solution (17 *M*) was added.

The oxygen-free ammonia solution was prepared by bubbling pure ammonia gas through commercial concentrated aqueous ammonia for a few minutes. This was done with the ammonia solution in a cylindrical, graduated separatory funnel, from which it could conveniently be dispensed into the cell.

Meanwhile, a few milligrams less than the theoretical quantity of the purified potassium ferricyanide was weighed out to ± 0.01 mg into a small Erlenmeyer flask and dissolved in about 10 ml of water. This Erlenmeyer flask had a side-arm sealed in near the bottom, which extended up to near the top and was then bent over to the horizontal, and ended in a drawn-out tip. This kind of "goose neck" side-arm served as an inlet tube for the nitrogen used to remove dissolved air from the solution, and, after the nitrogen supply tubing was disconnected, it became a convenient delivery tube through which to pour the solution (and subsequent washings) into the cell with a minimal danger of loss.

Immediately after the ammonia solution had been added to the cell, the deaerated potassium ferricyanide solution was added, and the Erlenmeyer flask was washed out carefully with 5 to 6 small portions of air-free water. The final volume of the solution was 100 to 110 ml.

The titration was concluded with 0.01000 *M* potassium ferricyanide solution, prepared determinately from the purified salt the same day that it was used, and delivered from a microburet. Dissolved air was not removed from this solution. The solution was added in 0.20-ml increments throughout the region of the equivalence point, and the exact equivalence point was then located in the usual way as the point where the second derivative $\Delta^2E/\Delta V^2$ (*i.e.*, the slope of the $\Delta E/\Delta V$ *vs.* V curve) becomes zero (see *e.g.*, ref. 12, p. 93). The weight of potassium ferricyanide corresponding to the volume of the 0.01000 *M* solution required to reach the equivalence point was then added to the original weight to obtain the total weight required.

Table I summarizes the results of 11 trials with quantities of cobalt that varied over a 100-fold range. The 0.01000 *M* potassium ferricyanide solution used to finish the titration was delivered from a microburet graduated to 0.02 ml, and the uncertainty in the volume reading was not greater than about ± 0.005 ml. In the last 2 trials with only 2 mg of cobalt the entire titration was performed with the 0.01000 *M* ferricyanide solution, and 0.02-ml increments were added throughout the equivalence point region.

The remarkable accuracy of the titration is immediately evident. In the 6 trials with 100 to 200 mg of cobalt the mean error is +0.04 mg with an average deviation

TABLE I

ACCURACY OF THE TITRATION OF COBALT WITH POTASSIUM FERRICYANIDE

(The atomic weights used were those of the new scale based on $^{12}C = 12$, according to which Co = 58.933 and $K_3Fe(CN)_6$ = 329.261. All weights were corrected for air buoyancy)

Co taken (mg)	*$K_3Fe(CN)_6$ initially (mg)*	*0.01000 M $K_3Fe(CN)_6$ (ml)*	*$K_3Fe(CN)_6$ total (mg)*	*Co found (mg)*	*Error (mg)*	*Error (%)*
208.02	1150.58	3.53	1162.20	208.02	0.00	0.00
167.00	930.66	0.85	933.46	167.07	0.07	0.04
148.54	825.47	1.31	829.78	148.52	−0.02	−0.01
131.20	730.47	0.89	733.40	131.27	0.07	0.05
106.49	590.36	1.50	595.30	106.55	0.06	0.06
104.94	580.46	1.85	586.54	104.98	0.04	0.04
91.65	510.32	0.47	511.87	91.62	−0.03	−0.03
45.385	250.11	1.09	253.60	45.391	0.006	0.01
18.288	100.05	0.66	102.22	18.296	0.008	0.04
2.140	0	3.640	—	2.145	0.005	0.23
2.109	0	3.556	—	2.096	−0.013	0.62

of ± 0.03 mg, and in the 5 trials with 2 to 90 mg of cobalt the mean error is −0.005 mg with an average deviation of ± 0.01 mg. With 18 to 200 mg of cobalt the mean percentage error is +0.02% with an average deviation of ± 0.03%. The preponderance of positive errors indicates that this small net error of +0.02% is real. That it is not caused by oxidizable impurities in the water or reagents is evident from the correct results obtained with only 2 mg of cobalt. Very probably it is caused by a trace of water in the potassium ferricyanide (dried in a vacuum desiccator at room temperature over anhydrous magnesium perchlorate), because it is well known that removal of the last traces of water from a recrystallized salt usually can only be accomplished by heating to the melting point. This technique cannot be used with potassium ferricyanide because it decomposes before it melts.

To ascertain whether removal of dissolved air (oxygen) from the ferricyanide solution was really necessary, the trial with 106 mg of cobalt was run after the others and air was not removed from the main ferricyanide solution nor from the water used to wash out its containing flask. Since the error is just as small (and positive) as in the other cases it is evident that removal of air from the ferricyanide solution is unnecessary.

However, it is important that the dissolved oxygen be removed from the concentrated, commercial ammonia solution before it is added to the cobalt solution. In a trial with 207 mg of cobalt in which this was not done the error was −0.25 mg.

The observed precision (± 0.03 mg with 100 to 200 mg of cobalt and ± 0.01 mg with the smaller quantities) is about what one would expect from the titration curves. Figure 2 shows as one extreme case the actual titration curve obtained with one of the 2-mg samples of cobalt and as the other extreme that obtained in the final titration with the 208-mg sample. As expected the rate of change of potential at the equivalence point with 208 mg of cobalt is much smaller than with 2 mg of cobalt, because in the former case a given increment of the ferricyanide solution corresponds to a much smaller increment of the total cobalt present. In Fig. 3 the data from Fig. 2 have been re-plotted in terms of *percentage* of the cobalt titrated, rather than as a function of the volume of the ferricyanide solution. The curves in Fig. 2 explain why the *absolute* precision (mg of cobalt) is poorer with the largest than with the smallest cobalt sample, and those in Fig. 3 demonstrate why the *relative* precision is just the opposite.

From many trials the potential in the immediate vicinity of the equivalence point (as well as the potential at the equivalence point itself) was found to be reproducible to ± 3 mV when, as was done in all cases, a waiting period of about 2 min was allowed after each increment of ferricyanide solution was added. From Fig. 2 with 208 mg of cobalt the rate of potential change at the equivalence point is 100 mV/ml, and with 2 mg of cobalt it is 1500 mV/ml. Thus an uncertainty of ± 3 mV corresponds to ± 0.03 ml or ± 0.02 mg of cobalt with the 208-mg sample, but to only ± 0.002 ml or ± 0.001 mg of cobalt with the 2-mg sample. Similarly from Fig. 3, a ± 3 mV uncertainty should cause an uncertainty of ± 0.05% with the 2-mg sample, but only ± 0.01% with the 208-mg sample. With 18 to 208 mg of cobalt the observed average deviation from the mean (± 0.03 mg) agrees quite closely with the foregoing prediction (± 0.02 mg) showing that with the larger quantities of cobalt the precision of the equivalence point detection is indeed the limiting factor. With only 2 mg of cobalt the precision was limited by the uncertainty of ± 1 mg (± 0.004 mg of cobalt) in weighing out the cobalt standard solution.

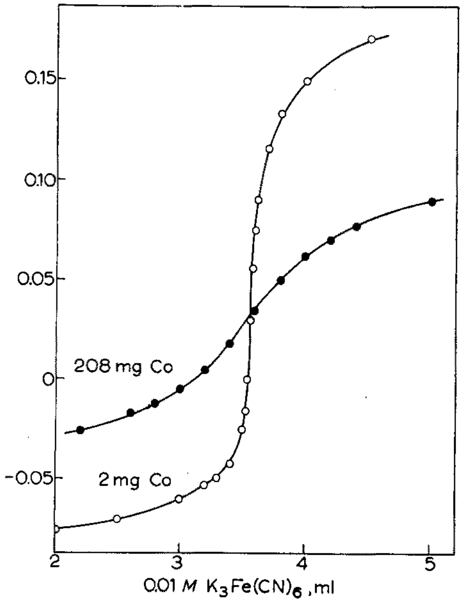

Fig. 2. Titration curves in the vicinity of the equivalence point obtained with one of the 2-mg cobalt samples and the 208-mg sample of Table I.

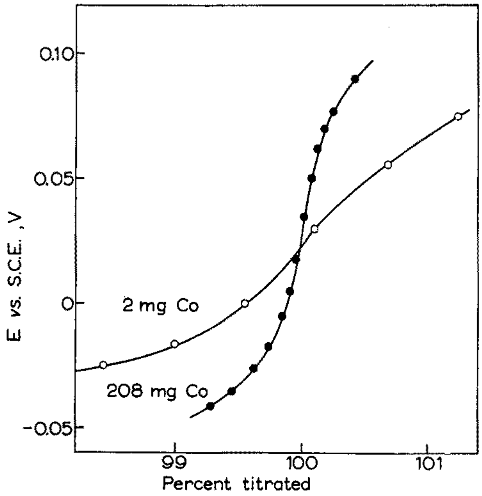

Fig. 3. The same titrations as in Fig. 2 replotted in terms of per cent titrated in the immediate vicinity of the equivalence point.

Ideally, for a symmetrical titration reaction (1 : 1 mole ratio of reactants and number of moles of products equal to number of moles of reactants), and when both half-reactions behave reversibly, titration curves based on per cent titrated (like those in Fig. 3) should be identical regardless of dilution. In practice a smaller slope of the titration curve at the equivalence point when very small concentrations are titrated (the 2-mg sample of Fig. 3 corresponds to only $3 \cdot 10^{-4}$ *M* total cobalt) is usually observed. In spite of this non-ideal behaviour at very small concentrations the equivalence point potential (defined by the point of maximal rate of potential change) is the same for the smallest as for the largest quantity of cobalt titrated. With a solution containing 3 *M* ammonia and 1 *M* ammonium chloride, the average value of the equivalence point potential from all the titrations in this study is 0.031 V *vs.* S.C.E. The extreme deviations from this mean value were +0.010 V and −0.007 V, and the average deviation was ± 0.003 V.

DIEHL AND BUTLER[13] demonstrated that a much larger potential change at the equivalence point is obtained when ethylenediamine is used instead of ammonia in this titration. Presumably because of chelation, the stability constant of the ethylenediamine complex of +3 cobalt is greater than that of the ammonia complex, and consequently the formal potential of the cobalt couple is smaller (more reducing) by several tenths of a volt. Thus, with ethylenediamine the *precision* of equivalence point detection might be somewhat better than with ammonia, provided that the potentials are as reproducible. However, it probably would be more difficult to achieve an *accuracy* as good as that with ammonia, because the ethylenediamine complex of +2 cobalt is much more sensitive to air oxidation than is the ammonia complex. The one advantage of using ethylenediamine is that it permits the determination of cobalt in the presence of manganese, which is one of the few elements that interfere in ammoniacal medium.

As ordinarily performed in ammoniacal medium, the studies of previous investigators[5-9] have shown that relatively few other metals interfere with the titration of cobalt, the chief exception being manganese. In those cases where prior separation of the cobalt is required, the most expeditious and convenient method is precipitation as potassium cobaltinitrite from an acetic acid solution containing hydrogen tartrate ion, which as KALLMANN[14] has shown, very effectively separates cobalt from practically all other metallic elements.

A recent study in this laboratory[15] has demonstrated that results correct to a few tenths of a per cent can be obtained simply by weighing this precipitate as presumed $K_3Co(NO_2)_6$. When the highest possible accuracy is needed, the potassium cobaltinitrite precipitate can be decomposed by evaporation to dryness with 1 : 1 hydrochloric acid and the cobalt can then be titrated by the present method.

SUMMARY

With authentically pure metallic cobalt and purified potassium ferricyanide, the accuracy of the titration of +2 cobalt to the +3 state with ferricyanide in strongly ammoniacal medium was examined critically. Quantities of cobalt from about 18 to 200 mg were titrated with a mean error of only +0.02 mg and an average deviation of ± 0.03 mg. The accuracy of this titration is greater than has ever been demonstrated for any other method of determining cobalt. Because of its high accuracy, and since very few other metallic elements interfere, this titration is the best currently available method for the critical assay of cobalt materials.

RÉSUMÉ

L'auteur a effectué une étude sur l'exactitude du titrage potentiométrique du cobalt, au moyen de ferricyanure, en milieu fortement ammoniacal. On a pu doser ainsi des quantités de cobalt d'environ 18 à 200 mg, avec une erreur moyenne de + 0.02 mg seulement et une déviation moyenne de ± 0.03 mg. Cette exactitude est supérieure à celle obtenue avec n'importe qu'elle autre méthode de dosage du cobalt. En raison de sa haute précision et du fait que très peu d'éléments métalliques gênent, ce titrage constitue la meilleure méthode couramment utilisable pour le dosage du cobalt.

ZUSAMMENFASSUNG

Die potentiometrische Titration des 2-wertigen Kobalts mit Hexacyanoferrat(III)-Ionen und Oxydation zum 3-wertigen Kobalt in stark ammoniakalischem Medium wurde kritisch geprüft. Etwa 18–200 mg Kobalt konnten mit einem mittleren Fehler von nur +0.02 mg, bei einer mittleren Abweichung von ± 0.03 mg, bestimmt werden. Die Genauigkeit dieser Methode ist grösser als die irgendeiner anderen. Da ferner nur wenige andere metallische Elemente stören, ist diese Titration die zur Zeit beste verfügbare Methode zur kritischen Beurteilung von Kobaltmaterialien.

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MANOMETRIC PRECISION DETERMINATION OF CARBON AND HYDROGEN IN MILLIGRAM AMOUNTS OF ORGANIC MATERIAL

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The gravimetric finish often used in micro carbon and hydrogen determinations, though basically capable of excellent precision, is tedious to carry out and is readily upset by atmospheric conditions. The latter circumstance is responsible for the situation that for high-precision hydrogen (second decimal place) and carbon determinations in hydrocarbon material, recourse is usually had to macro-scale methods which are based on samples of 200 mg or more[1].

An attractive alternative for micro samples would be to use a manometric finish. Manometric finishes in carbon and hydrogen determinations have been proposed since 1950 for use with samples of over one milligram[2-6], as well as below that amount[7-10], but the accuracy attained has not always been satisfactory.

In the present paper a method is described in which the amounts of water and carbon dioxide produced on combustion are measured by means of a precision mercury manometer system, in which height differences are converted to volume differences. The latter are measured with the aid of a commercial piston-type buret and a photoelectric level indicator. The new method combines the convenience of the manometric method with a high degree of accuracy.

EXPERIMENTAL

Brief description of the method

A sample of 3 to 4 mg is burned in oxygen using Körbl's decomposition product of silver permanganate[11] as a catalyst. The water and carbon dioxide formed are trapped in dry ice/acetone and liquid nitrogen, respectively, and the excess of oxygen is removed by pumping. After thawing and expansion into a known volume the pressures of water and carbon dioxide are measured with the aid of the precision mano-

Apparatus and procedure

Figure 1 is a schematic drawing of the apparatus. The combustion section and the freezing/measuring system are separately drawn in Figs. 2 and 3, respectively. The quartz combustion tube carries a narrow capillary exit of such dimensions that approximately 10 ml of oxygen per min are allowed to flow into the freezing system, the latter being evacuated. The freezing and measuring apparatus consists of freezing traps for water (5) and carbon dioxide (6), an expansion bulb (7) and the manometer (8, 9, 10). The system is controlled by 4 teflon membrane valves* (1,2,3,4) and the whole (except parts 5 and 6) is contained in a box, in which the temperature is kept constant at 50 ± 0.1°.

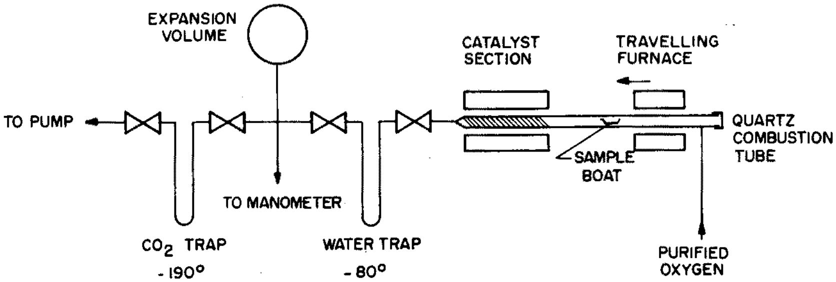

Fig. 1. Schematic drawing of apparatus.

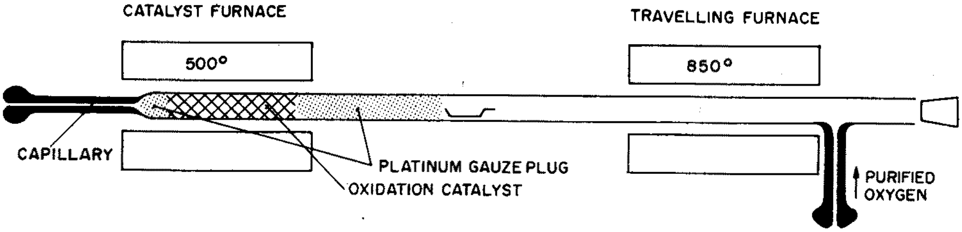

Fig. 2. Combustion section.

The manometer is basically of the U-tube mercury type and is operated in the following way. A level displacement in the right-hand leg (8) is compensated by supplying extra mercury from a piston buret (10) until the original mercury level position is restored. This is detected by means of a photo-electric system. Since the left-hand leg (9) is purely cylindrical, the volume of added mercury is proportional to the pressure originally shown by the manometer. The sensitivity of the photo-electric level indicator is such that pressure changes of 5 microns Hg are visible on the microammeter (Fig. 4).

In the apparatus described a 20-ml capacity piston buret** and a cylindrical manometer leg (9) of 22 mm internal diameter are used. This allows the measurement of pressures up to 40 mm mercury (15 ml useful buret range). Level readings can be reproduced to well within 0.01 ml of mercury. This margin of error includes the level indication, the mechanical setting of the buret and the effect of residual temperature fluctuations inside the thermostatted box. It means that pressures in a range between 20 and 40 mm of mercury can be measured with a precision (expressed as standard deviation) of better than one per thousand.

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* Obtainable from P. M. Tamson N.V., Zoetermeer, The Netherlands.

** Metrohm A.G., Herisau, Switzerland.

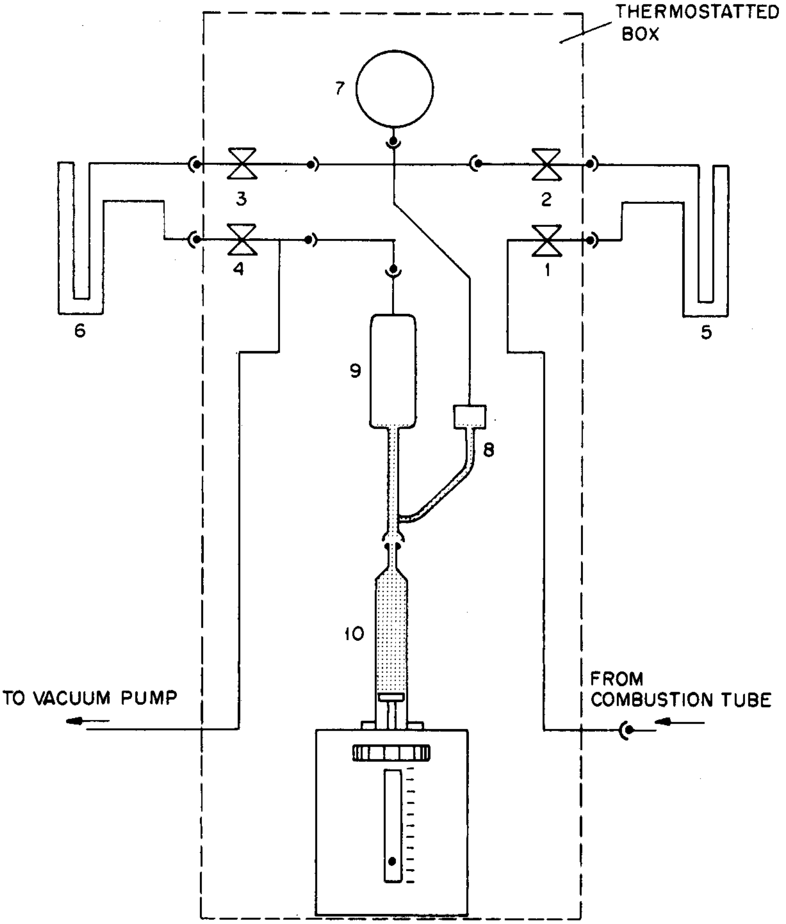

Fig. 3. Freezing/measuring system: 1–4, teflon membrane valves; 5, freezing trap for water; 6, idem for carbon dioxide; 7, expansion bulb; 8–10, manometer; 10, piston buret.

The expansion bulb has a capacity of about 150 ml. The freezing traps are mounted outside the thermostatted box so that the Dewar vessels containing the cooling media can be handled without disturbing the thermal equilibrium of the main measuring system. The water trap is provided with a short length of heating coil to promote the quantitative evaporation of the water trapped, by gentle heating (to about 80°). Since the volumes of the traps represent only small fractions (*ca.* 1%) of the total volume available for expansion, the effect of ambient-temperature changes is negligible.

The Metrohm piston buret has been modified to carry a hemispherical ground joint on top of the buret body, the piston being provided with extra O-rings to seal the mercury adequately.

Before combustion of a sample the measuring system is evacuated (valve 1 closed and 2, 3 and 4 opened). After the sample has been placed in the combustion tube, valve (1) is opened and the oxygen pressure in the system adjusted to about 3 cm

Hg with the aid of valve (4). Oxygen now flows through the system at a rate of approximately 10 ml (NTP) per min.

The traps are cooled with dry ice/acetone (trap 5) and liquid nitrogen (trap 6), and the combustion is started. In our case the travelling combustion furnace needed 8 min to reach the catalyst furnace and another 6 min was taken for continued heating of the sample boat and the platinum gauze plug. After combustion the oxygen is pumped off by closing valve (1) and fully opening valve (4). After two min, the manometer is adjusted and the zero position read.

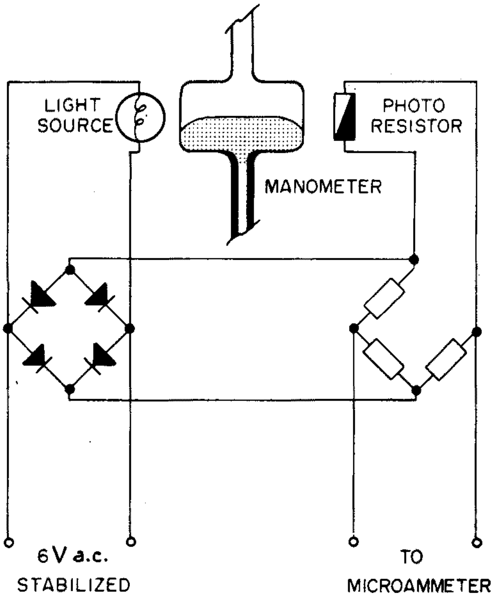

Fig. 4. Photo-electric level indicator.

Next valves (4) and (2) are closed, the Dewar vessels removed and the heating coil of the water trap is switched on. The carbon dioxide is then evaporated by allowing it to warm up to −80° with the dry ice/acetone mixture and after 2 min the manometer is adjusted and read. By opening valve (4) for 2 min the gas is pumped off. By closing valve (3) and opening valve (2) the water vapour is allowed to expand; its pressure can be read after 2 min. Finally valve (3) is opened and the water pumped off, so that the next measurement can be started.

RESULTS AND DISCUSSION

In order to convert buret volume readings (pressures) to masses of hydrogen and carbon, internal calibration factors are used based on the combustion of known amounts of a pure compound. *n*-Hexadecane ($C_{16}H_{34}$) was selected for this purpose in view of its stability and high hydrogen content. From a series of ten combustions of 2.5 to 4.5-mg portions of this compound, an average calibration value of 268.43 was calculated for carbon and 45.30 for hydrogen, both expressed as micrograms of the element for each ml buret reading (see Table I).

Table II shows the results obtained on a number of test compounds (BDH-Organic Analytical Standards); Table III shows those obtained on a number of research samples.

An average standard deviation (σ) of 0.068 for carbon and 0.032 for hydrogen was calculated from the results shown in Table II. These values are in satisfactory agreement with values suggested by the calibration experiments listed in Table I, which are 0.042 for carbon and 0.035 for hydrogen. These precision values are better than those of most Pregl-type procedures or of published methods using the manometric principle[2-5], save one[6] which is intended for use on the centigram scale. The precision offered by the present milligram method is believed to be due partly to the use of the highly active Körbl catalyst and the special manometer system, and also to the fact that adsorption effects of water vapour have been satisfactorily suppressed by using soda glass at an elevated temperature and teflon membrane valves instead of greased stopcocks in the freezing and measuring system.

TABLE I

CALIBRATION FACTORS

(μg/ml buret reading)

	Carbon	*Hydrogen*
	268.35	45.28
	268.37	45.23
	268.61	45.41
	268.29	45.21
	268.58	45.43
	268.59	45.13
	268.26	45.35
	268.14	45.35
	268.50	45.20
	268.62	45.44
Mean value	268.43	45.30
Standard deviation	0.16	0.11
Standard deviation, in % relat.	0.05	0.23

TABLE II

ANALYSIS OF TEST COMPOUNDS

Compound	*Theory*	*Found*			*No. of detns.*
		Average	*Lowest value*	*Highest value*	
Anthracene	94.34% C	94.33	94.28	94.46	
	5.66% H	5.64	5.61	5.69	6
Chlorobenzoic acid	53.69% C	53.73	53.67	53.83	
	3.22% H	3.22	3.18	3.26	5
Carbon tetrachloride	7.81% C	7.87	7.85	7.89	
	0.00% H	0.00	−0.01	0.01	3
Sulphonal	36.82% C	36.77	36.62	36.89	
	7.06% H	7.06	7.01	7.10	12

Samples G and H from Table III are of an extreme nature and the results suggest that the method is also applicable to trace hydrogen determinations in samples such as perchloro compounds, or to low carbon determinations in aqueous solutions. The method is not yet suited to nitrogen-containing compounds.

TABLE III

ANALYSIS OF RESEARCH SAMPLES

(containing oxygen, sulphur and/or chlorine)

Sample	*Carbon, %w*	*Hydrogen, %w*
A	42.17; 42.27	6.49; 6.53
B	79.62; 79.80	13.78; 13.80
C	52.85; 52.72	6.66; 6.64
D	34.79; 34.57	5.07; 5.09
E	34.77; 34.63	5.27; 5.20
F	34.52; 34.59	5.23; 5.20
G	8.07; 8.09	0.02; 0.02
H; aqueous solution [a]	0.63; 0.63	Not measured

[a] 40 mg sample intake.

Blank values are low and stable (0.003 mg carbon and 0.002 mg hydrogen). The average duration of one determination in a series is 30 min.

The authors are indebted to Mr. E. D. ENGELHARDT for prompting this investigation, to Mr. W. HOEDEMAN for cooperating in the early stages, to Miss A. TIMMERMAN for carrying out much of the experimental work and to Dr. E. A. M. F. DAHMEN and Dr. P. N. DEGENS Jr. for their interest and support.

SUMMARY

A method is described for the precise determination of carbon and hydrogen in milligram amounts of sample. The method is based on the manometric measurement of the amounts of carbon dioxide and water formed on combustion. A precision mercury manometer is used in which pressures are converted to mercury volumes. The latter are measured with the aid of a commercial piston-type buret using a photo-electric level indication.

RÉSUMÉ

On décrit une méthode pour le dosage exact du carbone et de l'hydrogène dans des échantillons de quelques milligrammes. Un système manométrique est utilisé pour mesurer les quantités de gaz carbonique et d'eau formées lors de la combustion. Le manomètre est du type à mercure, de haute précision, dans lequel les pressions se traduisent en des volumes de mercure. Ceux-ci sont mesurés à l'aide d'une burette à piston conventionnelle, avec repérage du niveau par une cellule photoélectrique.

ZUSAMMENFASSUNG

Ein Verfahren zur genauen Bestimmung des Gehalts an Kohlenstoff und Wasserstoff in Probemengen von nur einigen Milligrammen wird beschrieben. Die bei Verbrennung entstehenden Mengen Kohlendioxyd und Wasser werden manometrisch gemessen. Dazu wird ein Präzisions-Quecksilbermanometer benutzt, in dem sich der Druck in ein entsprechendes Quecksilbervolumen umwandelt. Letzteres wird mit Hilfe einer Bürette vom üblichen Kolbentyp gemessen, wobei die Niveau-Anzeige mittels einer photoelektrischen Zelle erfolgt.

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DETERMINATION OF TRACE QUANTITIES OF TIN BY NEUTRON ACTIVATION ANALYSIS

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Many conventional analytical methods have been proposed for the determination of traces of tin in a variety of samples. However, sufficiently sensitive methods for tin are few. In addition, there are serious reagent contamination problems for the determination of traces of tin by the conventional analytical methods. Special attention has been paid to the radioactivation method in the field of trace analysis during the past decade, because of its great advantages over other chemical or instrumental methods of analysis. As far as the radioactivation analysis of tin is concerned, several methods have been described for different materials, *e.g.* silicon[1], germanium[1], silicate[2,3], beryllium[4], and iron and alloy steels[5,6]. These methods, however, involve rather complicated radiochemical procedures for tin, so that it is of interest to study more rapid and convenient procedures having general applicability to a variety of samples. A method has also been explored for the activation analysis of tin using 14-MeV fast neutrons[7]; but it is only of limited applicability, because of various competing nuclear reactions and lack of sensitivity.

In the present work, a rapid procedure was developed for the activation analysis of tin, down to the 0.1 μg level, in silicate rocks, sea waters, biological materials, and several kinds of iron alloys.

There are no data available in the literature about the activation analysis of tin in biological materials and in sea water. We were also particularly interested in trace analysis of tin in silicate rocks, because there is still considerable doubt about the abundance of tin in silicate materials of geochemical interest[8,9]. In international collaborative tests involving various analytical techniques for two standard rocks, the agreement in values for tin has not been very satisfactory, which implies that evaluation of conventional trace methods for tin is required[10]. Matrix effects in spectrochemistry, and contamination from reagents or incomplete decomposition of tin-bearing minerals in wet methods, are likely to affect the trace determination of tin.

EXPERIMENTAL

Nuclear data

The nuclear characteristics of tin relevant to activation with thermal neutrons are

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TABLE I

NUCLEAR DATA FOR TIN

Isotope	*Abundance (%)*	*Cross-section (barns)*	*Half-life of activation product*	*Principal β radiation*	*Principal γ radiation*
^{112}Sn	0.95	1.3 ± 0.3	119 d	EC	0.392
^{114}Sn	0.65		S[a]		
^{115}Sn	0.34		S		
^{116}Sn	14.24	6 ± 2 mb	14.0 d	None	IT
^{117}Sn	7.57		S		
^{118}Sn	24.01	10 ± 6 mb	~250 d	None	IT
^{119}Sn	8.58		S		
^{120}Sn	32.97	1 ± 1 mb	>400 d	0.42	
		0.14 ± 0.03	27.5 h	0.38	None
^{122}Sn	4.71	1.0 ± 0.5 mb	136 d	1.42	None
		0.16 ± 0.04	40 m	1.26	0.153
^{124}Sn	5.98	0.2 ± 0.1	9.5 m	2.04	0.326
		4 ± 2 mb	9.4 d	2.37	M[b]

[a] S = stable

[b] M = multiple gammas

listed in Table I. Tin-120 is convenient as a target nuclide for activation analysis, because of its greater abundance, relatively high cross-section and the suitability of the half-life, radiation and energy of the activation product.

Irradiation and activity measurement

The solid sample was weighed and sealed in a polyethylene tube. Tin in sea-water samples was collected into 30 mg of iron hydroxide through coprecipitation from 10 l of sea-water samples. The air-dried iron hydroxide was then processed in the same way as solid samples. An aliquot of standard tin solution (414 μg Sn) was impregnated into a piece of filter paper placed in a polyethylene tube and sealed. Samples and standard were then positioned inside a polyethylene capsule with aluminum packing foil and irradiated for 3 days (intermittently 5 h a day) at a power level of 50 kW and a neutron flux of about $3 \cdot 10^{11}$ n/cm^2/sec, using the water-boiler type Japan Research Reactor JRR-1. After cooling for a day, the irradiated samples were processed chemically to obtain radiochemically pure tin(IV) oxide for β-counting. β-Counting was performed using a standard-type methane-flow proportional counter. Appropriate decay, geometry and self-absorption corrections were applied.

Sensitivity

If a counting efficiency of 35%, and an effective lower limit of detection of 10 counts/min are assumed for the proportional counter, and if the time required for cooling and chemical separation (totalling 48 h) are taken into account, as well as the 50% chemical yield, then the detection sensitivity attainable can be estimated to be $2 \cdot 10^{-7}$ g. This sensitivity should be good enough for most determinations of tin in a variety of samples.

Reagents

Standard tin solution. Dissolve 0.0528 g of pure tin metal in 5 ml of 1 : 1 nitric acid along with 3 g of tartaric acid and dilute to 25 ml with water. Standardize gravimetrically by taking an aliquot of the solution.

Carrier solution. Tin. 10 mg Sn/ml. Dissolve 1.91 g of tin(II) chloride in 17 ml of hydrochloric acid, and dilute to 100 ml with water. Standardize the solution gravimetrically.

Holdback carrier solution. Antimony. 0.5 mg Sb/ml. Dissolve 0.05 g of pure antimony metal in 13 ml of sulfuric acid. Boil the solution with 0.2 g of hydrazine sulfate, cool and dilute to 100 ml with water.

Arsenic. 2 mg As/ml. Dissolve 0.27 g of arsenic trioxide in 4 ml of 1 *N* sodium hydroxide, dilute with water, acidify slightly with hydrochloric acid and dilute to 100 ml with water.

Copper. 2 mg Cu/ml. Dissolve 0.78 g of copper sulfate in 100 ml of water.

Iron. 2 mg Fe/ml. Dissolve 1.0 g of iron(III) chloride in 100 ml of 1 *N* hydrochloric acid.

Diethylammonium diethyldithiocarbamate solution. Dissolve 1 g of the reagent in 100 ml of chloroform. Prepare just before use.

Isopropylacetone. $(CH_3)_2CHCH_2COCH_3$. Analytical grade.

All the chemicals used were of analytical-grade quality.

RADIOCHEMICAL PROCEDURE

Decomposition of irradiated samples and preliminary separation of tin

An outline of the radiochemical separation scheme is shown in Fig. 1.

Silicate rocks

Silicate rocks are obtained in solution either by digestion with sulfuric–hydrofluoric acid or by fusion with sodium peroxide. For the digestion, transfer an irradiated silicate rock sample quantitatively to a 50-ml platinum dish. Add 2 ml of tin carrier solution, 5 ml of 18 *N* sulfuric acid, 1 ml of nitric acid and 10 ml of hydrofluoric acid. Evaporate to strong fumes of sulfur trioxide, occasionally adding a few ml of hydrofluoric acid to complete the decomposition. Take up the residue in 100 ml of water and 20 ml of 25% tartaric acid solution. Pass hydrogen sulfide through the solution to precipitate tin(IV) sulfide. Proceed as described under *Radiochemical separation of tin* below.

For the fusion with sodium peroxide, add 2 ml of tin carrier solution to a 50-ml nickel crucible, then add dilute ammonium hydroxide to precipitate tin(IV) hydroxide and evaporate to dryness. Put the irradiated silicate rock sample into the crucible and fuse for 5 to 10 min with 6 g of sodium peroxide. Dissolve the melt in 20 ml of hydrochloric acid and dilute to 200 ml with water. Add 20 ml of 25% tartaric acid and pass hydrogen sulfide to precipitate tin(IV) sulfide. Continue as described under *Radiochemical separation of tin.*

Sea water

To recover tin in sea-water samples, add 30 mg of iron(III) to a 2-l portion of sea water containing 40 ml of hydrochloric acid, heat and precipitate iron hydroxide by

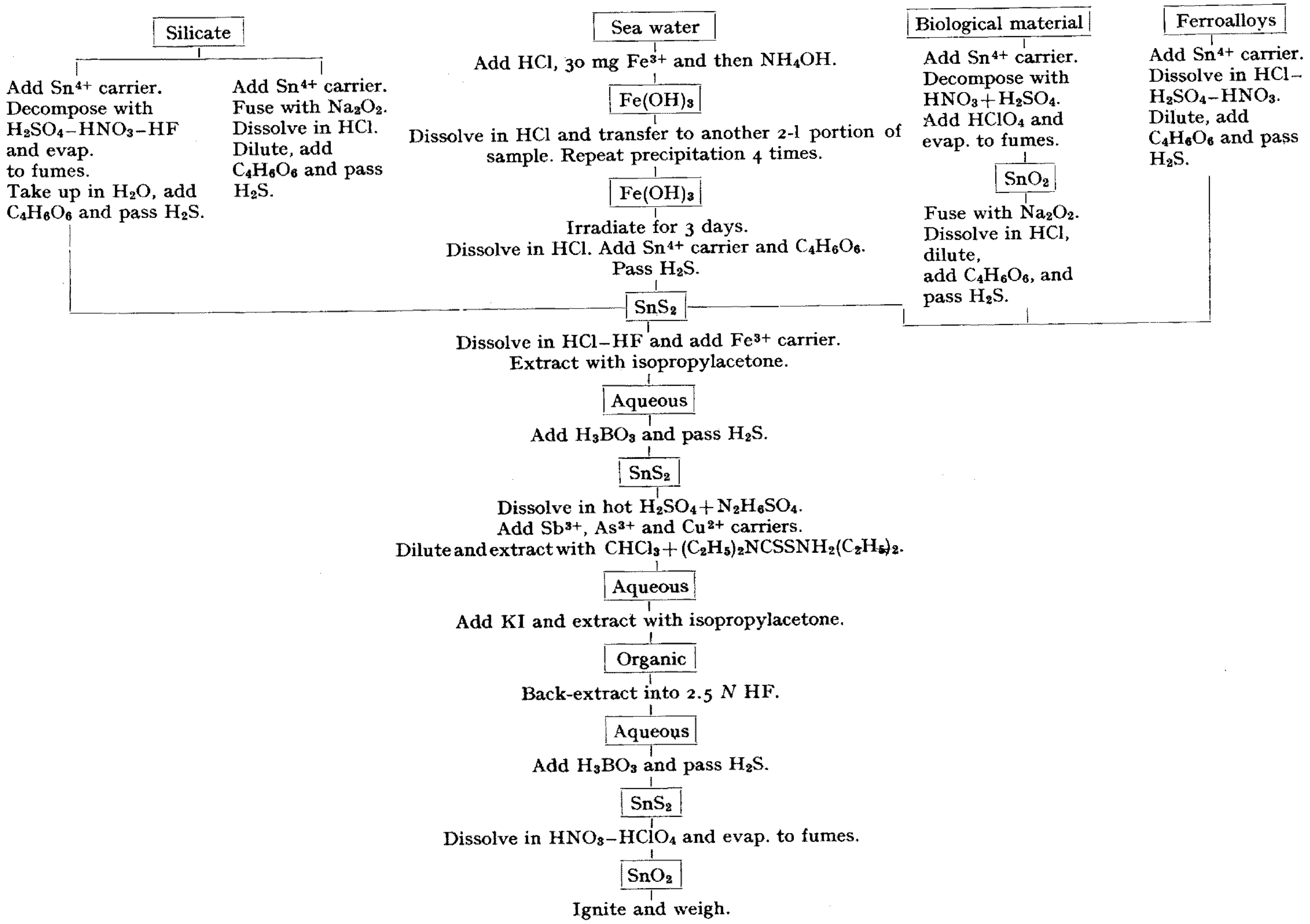

Fig. 1. Chemical separation scheme for tin.

dropwise addition of 1 : 1 ammonia solution. Dissolve the precipitate in 40 ml of hydrochloric acid and transfer to another 2-l portion of water sample. Precipitate iron hydroxide in the same way. Repeat the precipitation 5 times to recover tin from 10 l of the sample water. Wash the final precipitate thoroughly with 2% ammonium nitrate solution, dry and irradiate as mentioned above. Dissolve the irradiated iron hydroxide in 20 ml of 6 *N* hydrochloric acid containing 2 ml of tin carrier solution. Adjust the acidity to about 1 *N* in hydrochloric acid and precipitate tin(IV) sulfide as described above.

Biological materials

Decompose the irradiated biological sample with 3 ml of sulfuric acid and 4-ml portions of nitric acid in the presence of 2 ml of tin carrier solution. When the decomposition is complete, add 3 ml of perchloric acid and heat until white strong fumes begin to appear. Dilute and filter the precipitated tin(IV) oxide through a filter paper. Fuse the tin(IV) oxide with 5 g of sodium peroxide, following the procedure described for silicate rocks.

Ferroalloys

Transfer an irradiated sample of ferroalloy to a 50-ml beaker containing 2 ml of tin carrier solution, 20 ml of 6 *N* hydrochloric acid, 4 ml of 18 *N* sulfuric acid and 2 ml of nitric acid. Heat gently on a hot plate until the sample has dissolved. Filter off the residue consisting of graphite and dilute the filtrate to 150 ml with water. Add 1 to 2 g of tartaric acid and precipitate tin(IV) sulfide as before.

Radiochemical separation of tin

Dissolve the tin(IV) sulfide in 5 ml of hydrochloric acid. Add 2 mg of iron(III) carrier, 5 ml of 2.5 *N* hydrofluoric acid and 5 ml of water and shake for 30 sec with 15 ml of isopropylacetone. Drain the aqueous phase (lower) into a 50-ml centrifuge tube containing 10 ml of saturated boric acid solution. Pass hydrogen sulfide to precipitate tin(IV) sulfide. Centrifuge and discard the supernate. Dissolve the precipitate in 4 ml of sulfuric acid in the presence of 0.2 g of hydrazine sulfate, and 2 mg each of Sb^{3+}, As^{3+} and Cu^{2+} carriers. Add 22 ml of water and extract foreign activities by shaking with 20-ml portions of diethylammonium diethyldithiocarbamate solution in chloroform until the color of the extract disappears. Add 5 g of potassium iodide to the aqueous phase and extract tin(IV) iodide by shaking for 30 sec with 20 ml of isopropylacetone. Wash the organic phase twice with 10-ml portions of 1.5 *N* potassium iodide in 3 *N* sulfuric acid. Strip tin(IV) iodide by shaking with 10 ml of 2.5 *N* hydrofluoric acid; 20 sec is enough for stripping. Add 15 ml of saturated boric acid solution to the aqueous phase and pass hydrogen sulfide to precipitate tin(IV) sulfide. Dissolve the precipitate in a mixture of 1 ml of nitric acid and 2 ml of perchloric acid and evaporate to strong fumes. Dilute with water, filter the precipitate through a filter paper, dry and ash. Slurry the tin(IV) oxide with a few ml of water, transfer to a weighed small filter paper, and wash with water and then with acetone. Dry at 110° for 10 min, cool and weigh to determine the chemical yield. Mount for the activity measurement.

Treat the comparative standard in a similar way.

RESULTS AND DISCUSSION

Separation of tin from arsenic, antimony, molybdenum and tellurium presents the most difficulties in the radiochemistry of tin[11]. The isopropylacetone–hydrochloric acid extraction system has been found effective for tin(IV) but it is not specific[12]. However, most of the interfering elements in this system can be removed by extraction with a solution of diethylammonium diethyldithiocarbamate in chloroform from sulfuric acid medium; this leaves only tin(IV), antimony(V) and arsenic(V) in the aqueous phase[13,14].

Extraction of antimony and arsenic can be achieved by reducing to the lower oxidation (trivalent) state with, for example, hydrazine sulfate in sulfuric acid solution[15], which leaves tin(IV) unchanged.

In order to shorten the chemical separation, an attempt was made to extract foreign activities by isopropylacetone from a solution which was 6 *N* in hydrochloric acid and 0.8 *N* in hydrofluoric acid, the tin remaining in the aqueous phase. This extraction can be omitted in the radiochemical separation involving silicate rocks, sea-water samples and biological materials, because the carbamate extraction followed by the iodide extraction–stripping system provides a satisfactory separation from molybdenum as well as from most other contaminants, including antimony and arsenic. However, the first isopropylacetone extraction is an essential step for ferroalloys, particularly if they contain appreciable amounts of molybdenum as an alloy constituent. For high-molybdenum alloys like SCS 14 steel in Table II, additional puri-

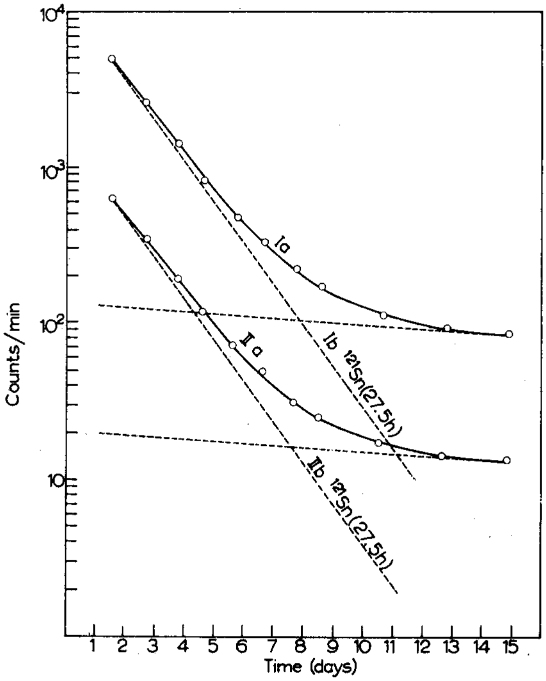

Fig. 2. Decay curve of induced ^{121}Sn activity isolated from an irradiated steel. (Ia) Gross decay of comparative standard; (Ib) ^{121}Sn decay obtained by subtraction of long-lived fraction in comparative standard; (IIa) gross decay of tin activities isolated from the sample; (IIb) ^{121}Sn decay obtained by subtraction of long-lived activities in the sample.

fication is necessary in order to obtain radiochemically pure tin(IV) oxide. For this purpose a single scavenge with molybdenum sulfide or α-benzoinoxime is effective.

In Fig. 2 a typical decay curve is illustrated for induced tin activities obtained from an irradiated ferroalloy sample. Analytical results for several kinds of ferroalloys are given in Table II along with the main constituents other than iron. In the same Table are listed results which have been obtained by the present authors using an activation method of analysis accompanied by chemical separation as reported by Leader[16] (abbreviated to "precipitation procedure").

TABLE II

DETERMINATION OF TIN IN FERROALLOYS

Sample	*Major constituents (%)*		*Weight of sample (g)*	*Sn (p.p.m.)*
Ni · Cr · Mo steel	Mn	0.45	0.4786	291[a]
	Ni	3.23		
	Cr	0.56	0.3506	288[b]
	Mo	0.32		
	Cu	0.14		
Carbon steel	Mn	0.66	0.5278	168[a]
	Cr	0.03		
	Cu	0.10	0.2239	165[b]
24Cr · 20Ni steel	Mn	0.45	0.2523	101[a]
	Ni	22.17		
	Cr	24.04	0.3686	119[b]
SCS 14 steel	Mn	0.86	0.3030	53.5[a]
	Ni	12.17		
	Cr	17.78	0.2007	57.5[b]
	Mo	2.31		

[a] "Precipitation procedure" (see text)
[b] The present extraction procedure

There remain problems in the conventional analytical procedures for traces of tin in silicate rocks. Values for tin in the two international rock standards G-1 and W-1 provide the evidence for this point (Table III). It can be seen that the agreement in values for tin is not very satisfactory between analysts. Further evidence may be found by literature surveys on the abundance of tin in materials of geochemical interest, in which markedly controversial results have been reported. For example, Goldschmidt and Peters[25] gave a spectrographic value of 40 p.p.m. Sn for a composite of 36 European Paleozoic shales, whilst Onishi and Sandell[19] found colorimetrically the much lower value of 5 p.p.m. Sn on the same sample. A matrix effect in spectrochemistry or incomplete decomposition of silicate materials (or a reagent blank) in wet methods could be responsible for such controversial results. Activation analysis with a radiochemical procedure involves the assumption that the radioisotopes induced are in an identical chemical form with the carrier which is to be added. In the development of the radiochemical procedure, we first tried to find a proper method of attack for silicate materials, because certain tin-bearing minerals

TABLE III

VALUES FOR TIN IN G-1 AND W-1

G-1 (p.p.m.)	*W-1 (p.p.m.)*	*Method*	*Reference*
< 2	< 2	Spectrochemical	TUREKIAN (1957)[17]
5	—	Spectrochemical	CHODOS (1957)[18]
2.3 (av.)	2.8 (av.)	Chemical	ONISHI AND SANDELL (1957)[19]
5.1 (av.)	—	Spectrochemical	HERZ AND DUTRA (1960)[20]
8.8 (av.)	8.7 (av.)	Spectrochemical	BROOKS *et al.* (1960)[21]
< 5	< 5	Spectrochemical	HÜGI (1961)[22]
<20	<20	Spectrochemical	CLARK AND SWAINE (1961)[23]
3.3 (av.)	2.5 (av.)	Chemical	CARMICHAEL AND MCDONALD (1961)[24]
3.4 (av.)	3.4 (av.)	Activation	HAMAGUCHI *et al.* (1962)[3]

TABLE IV

COMPARISON OF DETERMINATIONS OF TIN (p.p.m.) IN SILICATE ROCKS BY TWO TYPES OF OPENING-UP

Type of decomposition	*G-1*	*Biotite granite*
H_2SO_4–HF digestion	3.5, 3.4, 3.2, 3.3 (av. 3.4)	6.1
Na_2O_2 fusion	3.8, 4.0, 3.5 (av. 3.7)	6.2, 6.0, 6.1, 6.4 (av. 6.2)

like cassiterite in silicate rocks are strongly resistant to hydrofluoric acid. In Table IV the results obtained by digestion with hydrofluoric acid and by sodium peroxide fusion are given for G-1 granite; there is no significant difference in results between the two procedures. The same is true for determinations of tin in a biotite granite (Table IV). So far as the usual types of igneous rocks are concerned both opening-up procedures seem to be satisfactory. In order to determine tin in sea water it is not adequate to irradiate sea water itself, because of the high activities induced by irradiation and of the small sample size which is limited by the irradiation space. Accordingly, tin was concentrated from 10 l of sea water by coprecipitation with iron(III) hydroxide. In order to check the recovery of tin, a tin-121 tracer was added to 2 l of sea water along with a μg amount of inactive tin carrier (tin(IV) chloride form). Iron(III) hydroxide was then precipitated by dropwise addition of ammonium hydroxide. Recovery of tin was satisfactory (Table V), provided that sufficient iron(III) was added as the collector. The overall yield for the collection of tin from 10 l of sea water, in which the precipitation of iron(III) hydroxide from 2-l portions of sea water was repeated 5 times, averaged 98%; this figure was applied as a correction factor for the practical determination of tin in sea waters. Values for tin in several sea-water samples are given in Table VI. The total reagent blank from the iron collector (30 mg Fe^{3+}, ammonium hydroxide and hydrochloric acid which are used to collect tin from 10 l of water sample) was checked each time; the figures are also given in Table VI. The use of double amounts of hydrochloric acid (runs 1 and 2) increased blank values by a factor of two. The blanks are probably contributed mainly from hydrochloric acid or ammonium hydroxide.

The results of determinations of tin in marine organisms are summarized in Table VII.

The proposed radiochemical procedure is reasonably rapid and gives a high degree of radiochemical purity with rather uniform chemical yields running to about 50%. In most cases it takes less than 3 h to complete the whole procedure, because tedious precipitation steps have been replaced as far as possible by rapid and effective solvent extraction methods.

TABLE V

COLLECTION OF TIN BY IRON(III) HYDROXIDE

Fe^{3+} added (mg)	*Activity taken (counts/min)*	*Activity found (counts/min)*	*Recovery (%)*
20	5309 ± 37	5232 ± 36	98.4 ± 1.0
20	5309 ± 37	5193 ± 36	97.1 ± 1.0
30	5309 ± 37	5295 ± 36	99.7 ± 1.0
30	5309 ± 37	5306 ± 37	99.7 ± 1.0
40	5146 ± 36	5135 ± 36	99.8 ± 1.0
40	5146 ± 36	5207 ± 36	101.2 ± 1.0

TABLE VI

DETERMINATION OF TIN IN SEA WATER

Run no.	*Station no.*	*Location*	*Depth (m)*	*Sn found (μg/10 l)*	*Blank (μg)*	*Sn (μg/10 l)*	*Sn corrected*[a] *(μg/10 l)*	*Sn (μg/l)*
1	D_1	30°00′N 147° 30′E	500	11.0	2.7	8.3	8.5	0.85
2	D_4	30°00′N 144° 30′E	500	14.7	2.7	12.0	12.2	1.22
3	D_6	30°00′N 142° 30′E	500	9.8	1.3	8.5	8.7	0.87
4	D_8	30°00′N 139° 30′E	500	4.2	1.3	2.9	3.0	0.30

[a] Corrected for the average recovery of tin (98%) from 10 l of sample.

TABLE VII

DETERMINATION OF TIN IN MARINE BIOMATERIALS

Samples	*Sn (p.p.m.)*
Metapenaeus joineri (Tokyo Bay)	2.9
Watasenia scintillans (Tokyo Bay)	1.6
Meretrix meretrix lusoria (Tokyo Bay)	0.7
Hypomesus olidus (Lake Kasumigaura)	0.3

Correction for self-absorption and back-scattering in sources for measuring β-activity is necessary because of the rather weak maximum β^- energy, 0.38 MeV, of ^{121}Sn. The correction curve indicates that the combined effect of self-absorption and scattering increases with increasing thickness of the tin(IV) oxide sources. In actual practice, however, the correction was not always carried out because of the uniform chemical yields obtained throughout the work. Attention must also be paid to the self-shielding effect of the sample against neutrons during irradiation, leading to a reduction of the effective neutron flux through a sample and causing unequal activation of the sample. For practical purposes, weights up to 1.3 g of the usual types of silicate rocks and 1.6 g of iron meteorites can be tolerated for irradiation[26,27]. To investigate this effect in comparative standards, varying amounts of tin (as nitrate) were irradiated and the induced specific activities were determined. No significant change in the specific activity was detectable over the tested range of 104 to 620 μg Sn. The possible competing nuclear reactions, ^{121}Sb (n, p) ^{121}Sn and ^{124}Te (n, α) ^{121}Sn, seem unlikely to contribute to the final result unless these reactions have exceptionally high cross-sections. In addition, the elemental abundances of antimony and tellurium are so low that interference at any significant level is unlikely to be serious. For samples containing an appreciable amount of uranium, the production of ^{121}Sn through a fission reaction ^{235}U (n, f) ^{121}Sn must be taken into consideration. Although the fission yield for this reaction is only 0.014%, 1 μg of natural uranium gives a ^{121}Sn activity corresponding to approximately 0.01 μg Sn under the irradiation conditions stated above. In almost all cases the contribution of ^{121}Sn from uranium fission is unlikely to become serious so far as samples containing little uranium are concerned.

SUMMARY

A neutron activation method of general applicability has been developed for determining traces of tin in a variety of samples. The samples and comparative standards, sealed into ampoules, are irradiated intermittently for 3 days at a neutron flux of *ca.* $3 \cdot 10^{11}$ n/cm²/sec, followed by carrier radiochemical separations mainly consisting of solvent extraction steps. As little as 0.1 μg Sn can be easily determined by comparing the induced β-activity of ^{121}Sn (27.5 h) with that of a standard. The method is rapid and has a reasonably high chemical yield of about 50%. Results are quoted for the tin contents of a number of materials including silicate rocks, sea waters, biological materials and steels.

RÉSUMÉ

Une méthode par activation au moyen de neutrons est appliquée au dosage de traces d'étain dans divers échantillons (silicates, eaux de mer, substances biologiques et aciers). Cette méthode est rapide et permet de doser jusqu'à 0.1 μg d'étain, en comparant l'activité β induite de ^{121}Sn (27.5 h) avec celle d'un étalon.

ZUSAMMENFASSUNG

Es wurde eine allgemein anwendbare Methode zur Bestimmung von Spuren Zinn mit Hilfe der Neutronenaktivierungsanalyse entwickelt. Die Proben und Vergleichsstandards wurden insgesamt 3 Tage lang bei einem Neutronenfluss von *ca.* $3 \cdot 10^{11}$ n/cm²/sec bestrahlt. Es folgte eine radiochemische Trennung mit Träger vorwiegend durch Flüssigextraktion. Noch 0.1 μg Zinn kann leicht durch Vergleich der β-Aktivität des ^{121}Sn (27.5 h) mit der eines Standards bestimmt werden. Die Methode ist schnell und hat eine chemische Ausbeute von etwa 50%. Es werden die Zinngehalte von einer Reihe Materialien wie Silikatgestein, Seewasser, biologisches Material und Stahl angegeben.

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PHOTOMETRIC INVESTIGATION OF PRECIPITATION TITRATIONS*

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Classical turbidimetric and nephelometric procedures involve the comparison of light absorbed by a sample with that absorbed by a known standard suspension; both the sample and the standard must be prepared under identical conditions. Photometric titrations to a maximum turbidity have the advantage in that the reproducibility of the particles in the suspension is relatively unimportant. In this paper the term turbidimetric is reserved for the measurement of light transmitted horizontally through the suspension; the term 'heterometric' as introduced by BOBTELSKY[1,2], is used for titrations in which the light is passed vertically through the solution.

Some of the heterometric titration curves obtained by BOBTELSKY showed a number of critical points, or breaks, which were formulated as corresponding to partial reactions which proceeded consecutively until the final stable state was reached. The intermediate breaks appeared when insoluble intermediate compounds were formed which, on the addition of titrant, were transformed into more stable compounds. The solid state change of a compound AB into a second more stable compound AB_2, by the addition of titrant B, must take place either by the ions of B diffusing through the solid AB, or by the solid AB dissolving and reacting with B in solution to give AB_2 which is then precipitated. The formation of all possible intermediates, whilst theoretically feasible, is unlikely as the stability varies, and only the most energetically stable compounds would be formed. However, the formation of intermediate compounds 'consecutively from one another like a building being gradually built up, brick upon brick'[3] and the detection of the transformation, at a definite point, of solid intermediates into one another by the gradual addition of titrant, seemed to us to be questionable.

The present work, therefore, was undertaken to investigate the potential of the turbidimetric and heterometric methods, and to test the validity of drawing breaks in a heterometric curve.

EXPERIMENTAL

Apparatus

(*a*) *The turbidimeter.* An Eel titrator unit (Evans Electroselenium Ltd., England) was adapted by remounting on a magnetic stirrer, the speed of which was varied

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* Presented at the 46th Annual Conference of the Chemical Institute of Canada, Toronto, June 1963.

by changing the belt drive from a synchronous motor. The unit contained a cell holder, filter mount, barrier-layer photo-cell and a light source supplied by a 6 V lead acid battery. The light beam passed horizontally through the sample solution and fell on to the photo-cell via an optical system, which was arranged so that the instrument was unaffected by external illumination. The output of the photo-cell was fed, via a potential divider, to a multi-range millivolt recorder having a response time of 1 sec for full scale deflection (Phillips Electronics Ltd.); the sensitivity could be increased by up to twenty-fold by changing the recorder range as the end-point of the titration was approached. The titrant was added from a 0.5-ml micrometer syringe to a reaction cell 1.5 cm in diameter and of 5 ml capacity.

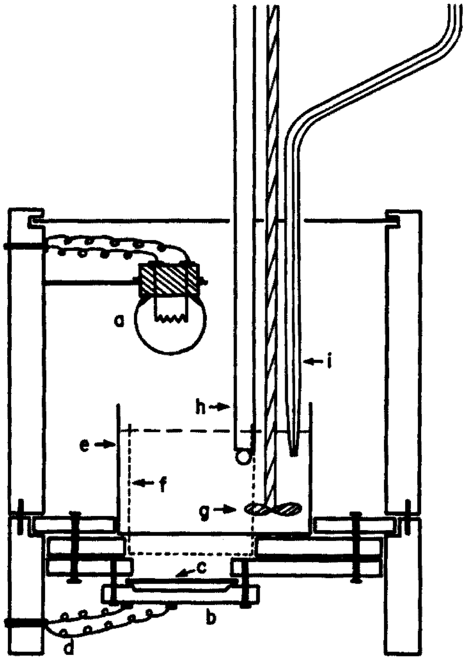

Fig. 1. The heterometer. (a) lamp, (b) photo-cell, (c) filter, (d) leads to recorder, (e) titration vessel, (f) position of small titration vessel, (g) glass-paddle stirrer, (h) pH-electrode, (i) micro-buret.

(*b*) *The heterometer.* The heterometer was designed and built, with some modifications, in a similar way to that described by Bobtelsky[1], and is shown in Fig. 1. The light from a 6 V, 6 watt lamp was passed vertically through the sample and filter on to a photo-cell, the output of which was fed to the recorder. The sample was contained in a cylindrical glass cell having an optically plane base; cells of diameter 3.6 and 5.6 cm and capacities of 25 and 50 ml respectively were used (Precision Glass Co., U.S.A.). The sample was stirred by a glass paddle driven by a G. K. Heller 2T60 electronically controlled motor. Provision was made for a simultaneous potentiometric titration, a Beckman combination electrode and a Radiometer 4 pH meter being used. The apparatus was enclosed to prevent interference from external illumination and the titrant was added from a calibrated micro-buret.

Procedure

The recorder was set to an appropriate range (*e.g.* 0–200 mV with no filter or 0–50 mV with filter) and adjusted to read 100% transmission. An aliquot of titrant was added to the stirred sample solution, and the percentage absorbance was automatically recorded for each addition. Further aliquots of titrant were added when steady state readings of absorbance were obtained. The speed of stirring was the maximum permissible for steady state readings and was constant throughout a titration.

In the initial experimental stages a highly sensitive and stable galvanometer (Eel Unigalvo Type 20, full-scale sensitivity 0.55 μA) was used to measure optical densities. It soon became apparent, however, that the use of a fast response recorder was preferable in determining the steady state values of absorbance, especially in slow precipitation reactions. The time interval between additions of titrant depends, of course, on the nature of the precipitate and therefore varies from one reaction to another. A fixed time interval between additions in any one titration cannot be used because, in general, the reaction proceeds more slowly as the end-point is approached. Thus, to ensure that a steady state was obtained in the reaction, further additions of titrant were made only when the recorded absorbances reached constant values. Typical recorder charts are shown in Fig. 2. In the normal titration the optical density was calculated from the steady state values of the absorbance, and was plotted as a function of volume of reagent added. Contributions to the optical density from color changes in the solution were eliminated by the use of suitable filters.

Changes in the physical form of the precipitate associated with an aging phenomenon were sometimes encountered. In such titrations steady state readings were not

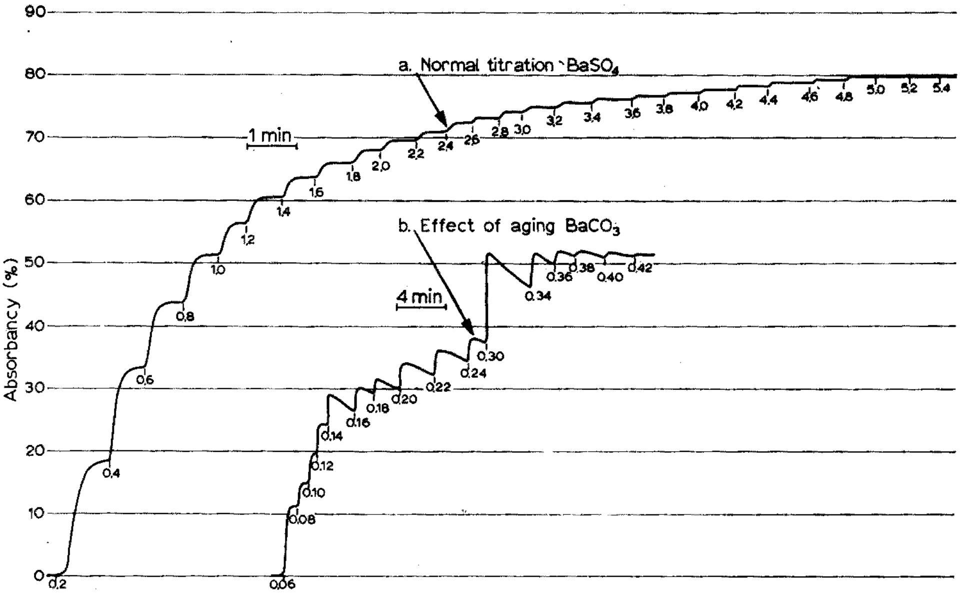

Fig. 2. Typical recorder charts showing (*a*) normal titration and (*b*) effect of aging.

obtained quickly on the addition of titrant, but the absorbance rose to a maximum and decreased with time (Fig. 2b); end-points, therefore, could not be determined by the normal method, but were estimated from the chart when no further increase in absorbance was recorded.

Shapes of titration curves

The shapes of titration curves obtained by the turbidimetric and heterometric procedures were essentially the same. A curve characteristic of many such titrations is shown in Fig. 3a. The end-point and hence reacting mole ratios were readily evaluated from the intersection of the curve with the maximum density line. In some titrations the point of initial precipitation was delayed, and in others the precipitate dissolved in an excess of reagent. An example showing both these features is the titration of 8-hydroxyquinoline by aluminium ions (Fig. 3b). Initial precipitation did not occur at any definite mole ratio, and the delay was probably due to a combination of an induction period and a solubility or complex formation. The optical density decreased after the theoretical end-point as the precipitate dissolved in an excess of aluminium ions due to a complex formation. The change in slope of the dissolution curve may be indicative of the presence of more than one compound, but the position of the break did not appear at any definite mole ratio, as has been reported[4], and is very sensitive to pH.

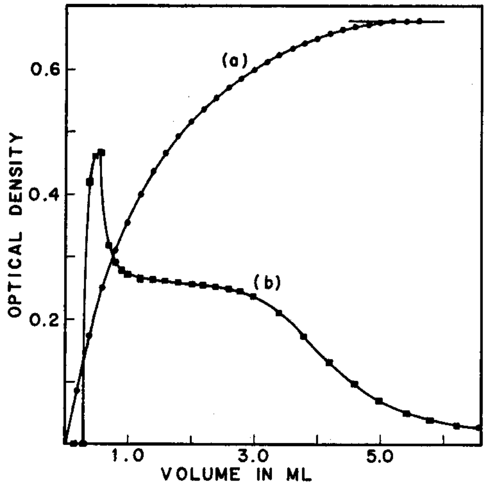

Fig. 3. Typical titration curves. (a) 9.98 ml of 0.0518 *M* H_2SO_4 + 2 ml of 4 *N* HCl + 8 ml of 95% ethanol titrated by 0.1015 *M* Ba^{2+}. End-point 5.07 ml (theoretical 5.09 ml). (b) 4.98 ml of 0.0202 *M* oxine + 3 ml of 2 *M* NaOAc + 32 ml of water titrated by 0.0516 *M* $AlCl_3$.

Breaks in titration curves

In the investigation of over 50 precipitants, both of the simple type such as sulphates, halides and carbonates, and more complex examples such as oxalates, phosphates and organic reagents (*e.g.* oxine, aluminon, phytic acid, benzoylphenylhydroxylamine), no breaks indicative of partial reactions or intermediate compounds have been found. For example, a smooth curve was obtained for the titration of palladium with *o*-phenanthroline, with the end-point at a mole ratio of 1:1. This complex has been used for the gravimetric determination of palladium[5]. BOBTELSKY[6], however, reported a final end-point at a mole ratio of 2:3, palladium to reagent, with intermediates of composition Pd_3P_2 and PdP.

Because of the failure to obtain intermediate breaks in the curves for titrations involving possible stepwise reactions between metal ion and reagent, titrations were performed in which it was known that two compounds were precipitated consecutively. The curve for a mixture of iodide and chloride titrated by mercurous ion is shown in Fig. 4. Although iodide is theoretically completely precipitated before the chloride, assuming that coprecipitation and adsorption are negligible, no intermediate break is detectable in the curve; the overall end-point is in good agreement with the theoretical value for the mixture. A plot of the slope of the curve against volume of reagent added confirmed that there was no break in the vicinity of the iodide end-point. Similarly, for a mixture of barium and strontium ions titrated by sulphate, a smooth curve was obtained; the final end-point was again in good agreement with the theoretical value for the mixture.

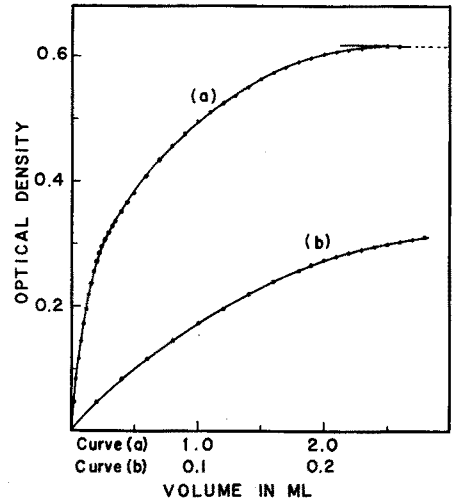

Fig. 4. (a) 4.98 ml of $4.22 \cdot 10^{-4}$ *M* KI + 0.99 ml of $2.33 \cdot 10^{-2}$ *M* NaCl + 10 ml of water titrated by $5.25 \cdot 10^{-3}$ *M* Hg_2^{2+}. Final end-point found, 2.36 ml. Theoretical end-points, I^- 0.20 ml, Cl^- 2.20 ml, final 2.40. (b) As (a) from 0 to 0.3 ml on an extended scale.

The curve for a titration of a mixture of fluoride and oxalate by calcium, however, did show a point of inflection (Fig. 5a). Although the change in the slope of the curve is indicative of a mixture, the break occurs before the fluoride end-point (*cf.* Fig. 5b) at a mole ratio of approximately 2.5:1, fluoride to calcium, and thus its use to evaluate the composition of the precipitated product is not valid. The final end-point agrees with the theoretical value for the mixture.

These results show that even in known mixtures, the use of breaks in precipitation titration curves for the identification of intermediate products does not seem possible.

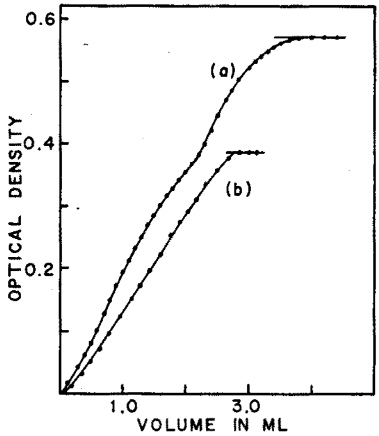

Fig. 5. (a) 2.98 ml of 0.189 M F^- + 5 ml of 0.0209 M oxalate + 5 ml of buffer ($HOAc/OAc^-$, pH 5) + 2 ml of water titrated by 0.1 M Ca^{2+}. End-points from standardization: F^-, 2.76 ml, oxalate, 1.03 ml. End-point found, F^- + Ox^{2-}, 3.72 ml. (b) 2.98 ml of 0.189 M F^- + 5 ml of buffer + 7 ml of water titrated by 0.1 M Ca^{2+}. End-point found, 2.76 ml.

CONCLUSIONS

Turbidimetric and heterometric methods are very useful in the investigation of precipitation reactions. End-points and reacting mole ratios are readily determined, and the presence of soluble complexes can be detected. Dilution effects in the turbidimetric method were very small, and appeared to be absent in the heterometric method; no advantage of one method over the other was found. No evidence of the formation of solid metastable compounds was obtained; no intermediate breaks in the titration curves were found where stepwise formation was possible, nor were significant breaks obtained in titrations involving the consecutive precipitation of known compounds.

The overall end-point in either titration procedure can be used for quantitative analysis with an error usually within 1%. Changes in the physical form of the precipitate are sometimes encountered, and for such reactions the error in end-point determination may be as high as 5%. The concentration range depends on the form and solubility of the precipitate, but generally varies between 10^{-2} and 10^{-4} M; 3 to 15 ml of solution are required for an analysis.

Simultaneous photometric and potentiometric titrations are finding particular use in this laboratory for the determination of optimum conditions for performing a precipitation reaction, and for the determination of the composition of reaction products. The combined information from this and other methods leads to a much clearer understanding of the reactions involved.

St. J. H. B. gratefully acknowledges the award of a Canadian Industries Ltd. Fellowship. This work was supported by a grant from the National Research Council of Canada.

SUMMARY

Photometric investigation of precipitation reactions, by automatically recording the changes in absorbance of a stirred suspension with titrant added, showed that end-points and reacting mole ratios are quickly and easily evaluated. Quantitative analysis in the concentration range 10^{-2} to 10^{-4} *M* is possible with an error of about 1%. The use of breaks in titration curves to formulate intermediate reaction products is doubtful. A rapid change in the physical form of the precipitate is a limitation of the method.

RÉSUMÉ

Une étude photométrique de réactions par précipitation, avec enregistrement automatique de l'absorption, a montré que les points finals et les rapports moléculaires peuvent être rapidement et facilement évalués. Une analyse quantitative pour des concentrations de 10^{-2} à 10^{-4} *M* est possible, avec une erreur d'environ 1%. D'après les courbes obtenues, il est douteux de pouvoir déceler des produits de réactions intermédiaires. Un changement rapide de la forme physique du précipité constituerait une l'imitation de la méthode.

ZUSAMMENFASSUNG

Photometrische Untersuchungen von Niederschlagsreaktionen durch automatische Aufzeichnung des Wechsels der Absorption einer gerührten Suspension bei Zugabe von Masslösung zeigen, dass die Endpunkte und die reagierenden Molverhältnisse schnell und leicht bestimmt werden können. Quantitative Analysen im Konzentrationsbereich von 10^{-2} bis 10^{-4} *M* sind mit einem Fehler von etwa 1% möglich. Aus einem unstetigen Verlauf der Titrationskurven Schlüsse über Zwischenprodukte zu ziehen ist zweifelhaft. Ein schneller Wechsel der physikalischen Beschaffenheit des Niederschlags ist eine Beschränkung der Methode.

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SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM IN SOIL EXTRACTS WITH CALCICHROME

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Methods generally used for the determination of calcium in soil extracts involve the removal of heavy metals by a double ammonia precipitation, followed by precipitation of calcium as the oxalate[1,2]. The separated calcium may be determined either gravimetrically, titrimetrically[1], or by flame photometry[3,4]. These methods are quite time-consuming, and errors can be caused by losses incurred in the handling and washing of the small calcium oxalate precipitate[5].

CLOSE AND WEST[6] developed the azo-dye Calcichrome (self-coupled diazotized H-acid) as a selective metallochromic indicator for the compleximetric titration of calcium. The present paper describes the use of Calcichrome as chromogenic agent in a direct spectrophotometric method for the determination of calcium in hydrochloric acid soil extracts. The procedure is simple and rapid, and as little as 4 µg of calcium can be readily determined in the extract sample.

EXPERIMENTAL

Apparatus

A Unicam SP600 spectrophotometer with 1-cm covered glass cells was used throughout.

A small cation-exchange column (0.8 cm diameter) was prepared from 4 ml of Permutit Zeo-Karb 225 (−30 to + 80#) resin. It was found that both Zeo-Karb 225 and Amberlite IR-120 A.R. (−20 to +50#) resins contained considerable calcium impurity, about 1.1 mg Ca/ml, and 0.5 mg Ca/ml, respectively. The ion-exchange column was purified by washing with 200 ml of 3.2 *M* hydrochloric acid, 25 ml of water, another 100 ml of 3.2 *M* hydrochloric acid, and finally conditioned with 25 ml of 0.2 *M* hydrochloric acid.

Reagents

Calcichrome solution, 0.1%. Dissolve 0.25 g of Calcichrome (prepared as described by CLOSE AND WEST[6]) in a small amount of water, add 0.75 ml of 10% sodium hydroxide, and stir to dissolve. Dilute to 250 ml with water.

Standard calcium solution, 80.0 µg/ml. Dissolve 0.1998 g of pure calcium carbonate in a slight excess of hydrochloric acid and dilute to 1 l.

Recommended procedure

Direct spectrophotometric method. Pipet an aliquot of the sample, 5 ml or less, containing 4–175 µg of calcium, into a 50-ml volumetric flask. Dilute to about 5 ml with water. Add an amount of 2.5 *M* hydrochloric acid so that the total acid present is equivalent to 1.0 ml of 2.5 *M* acid. Add 2.0 ml of 10% triethanolamine and 3.4 ml of 10% sodium hydroxide, and allow to stand for 5 min. Dilute with water to about 35 ml, add 5.0 ml of acetone, mix, and let stand for another 5 min. Now add 5.00 ml of 0.1% Calcichrome, dilute to volume with water, and mix. Measure the absorbance after 10 ± 2 min at 510 mµ against a reagent blank, using 1-cm cells. Prepare a calibration curve from the standard calcium solution, using the same procedure.

Ion-exchange separation. Dilute an aliquot of the extract (2 ml) to 25 ml with water, and run through a conditioned column at the rate of 2 ml/min. Wash the column with 25 ml of 0.2 *M* hydrochloric acid, and elute the calcium using 200 ml of 3.2 *M* hydrochloric acid. Boil the eluate down to a volume of about 3 ml, then dilute to 25 ml in a volumetric flask. Determine the free acid[7] for final acidity adjustment, prior to the spectrophotometric calcium determination.

DISCUSSION

Sensitivity and adherence to Beer's law. The calcium–Calcichrome complex does not obey Beer's law, the calibration curve being slightly curved from 0 to 3.5 µg Ca/ml. The curvature becomes more pronounced at higher calcium concentrations. The molar absorptivity at the 3.2 µg Ca/ml level is 4250, or 0.0094 µg of Ca/cm^2 on the Sandell scale. The sensitivity is almost doubled if the final pH is 12.0 instead of 13.0 as used in the recommended procedure. However, as described later, the higher pH is necessary to avoid interferences. Addition of acetone increases the sensitivity by about 50%.

The absorbance of the calcium complex increases with increasing dye concentration, but it is impracticable to raise the dye concentration above 0.01%, because of the high blank absorbance (0.690 at 0.01% dye).

Stability and effect of pH. The absorbance of both the reagent blank and the calcium complex change slowly on standing. At 22° the blank absorbance increases by 4% per hour, and the calcium complex (measured against a blank) decreases by 6% per hour. The colour becomes somewhat less stable at higher temperatures. Readings on a series of standards showed the relative standard deviation at the 3.2 µg Ca/ml level to be ± 0.5%.

Increase in pH above 12.0 causes a decrease in absorbance readings. At pH 13.0 an error of 0.05 ml of 10% sodium hydroxide leads to an error of about 1% in the determination.

Study of interferences. Triethanolamine was found to be the only complexing agent which would complex iron, manganese, copper, and other metals at the high alkalinity used, and yet would not interfere with the formation of the calcium–Calcichrome complex. The initial formation of iron and manganese hydroxides was avoided by the addition of a large excess of sodium hydroxide. A minimum amount of 2.75 ml of 10% sodium hydroxide was needed to convert 10 mg of iron(III) in a 5-ml volume to a soluble form. A waiting time of 5 min was necessary to ensure complete dissolution, otherwise the presence of undissolved hydroxides led to low results. After dilution with water, another 5 min was required to allow complete conversion to the triethanolamine complexes. Several elements commonly found in soil extracts were tested for their effect on the calcium determination, but only chromium and large amounts of aluminium and phosphate caused serious errors (Table I).

At alkalinities lower than pH 13.0, phosphate caused large negative errors. At pH 13.0, however, 160 μg of calcium could be determined in the presence of 200 μg of phosphate ion. With 500 μg of phosphate the error increased with increasing calcium concentration (Table I). If phosphate was present, manganese was found to cause low results. Magnesium is not complexed by triethanolamine, and precipitates as magnesium hydroxide. The flocculent hydroxide precipitate adsorbed calcium and other metal ions and produced negative errors. The presence of magnesium and phosphate together caused serious interference, and only a very low level of each of these ions could be tolerated (Table II).

The recoveries of calcium from solutions containing large amounts of neutral salts were low (Table III).

TABLE I

STUDY OF INTERFERENCES IN THE DIRECT DETERMINATION OF CALCIUM WITH CALCICHROME

Foreign ion added	*Amount taken (mg)*	*Calcium taken (μg)*	*Calcium found (μg)*	*Relative error (%)*
Al^{3+}	4.0	160	165	+3
Al^{3+}	10.0	160	178	+11
Ba^{2+}	0.5	160	160	0
Co^{2+}	0.1	160	160	0
Cr^{3+}	0.01	160	150	−6
Cr^{3+}	0.1	160	45	−72
Cr(VI)	0.1	160	156	−2
Cu^{2+}	0.5	160	160	0
Fe^{3+}	4.0	160	162	+1
Fe^{3+}	10.0	160	166	+4
Mg^{2+}	0.1	160	157	−2
Mg^{2+}	0.5	160	150	−6
Mn^{2+}	0.2	160	162	+1
Mn^{2+}	0.5	160	165	+3
Mo(VI)	0.1	160	160	0
Ni^{2+}	0.1	160	144	−10
Pb^{2+}	1.0	160	160	0
Si(IV)	1.0	160	156	−2
Sn^{2+}	0.1	160	160	0
Sr^{2+}	0.15	160	163	+2
Sr^{2+}	0.5	160	170	+6
Ti^{4+}	0.1	160	150	−6
V(V)	0.1	160	160	0
Zn^{2+}	1.0	160	154	−4
F^-	0.2	160	160	0
PO_4^{3-}	0.2	160	160	0
PO_4^{3-}	0.5	80	80	0
PO_4^{3-}	0.5	112	106	−5
PO_4^{3-}	0.5	160	116	−28

TABLE II

INTERFERENCE BY SOME COMBINATIONS OF IONS IN THE DETERMINATION OF CALCIUM WITH CALCICHROME

Ion added (mg)					*Calcium taken (µg)*	*Calcium found (µg)*	*Relative error (%)*
Fe^{3+}	Al^{3+}	Mn^{2+}	Mg^{2+}	PO_4^{3-}			
4.0	4.0	0.0	0.0	0.0	160	167	+4
4.0	4.0	0.0	0.0	0.2	160	167	+4
4.0	4.0	0.2	0.0	0.0	160	169	+6
4.0	4.0	0.2	0.0	0.2	160	160	0
4.0	4.0	0.2	0.1	0.0	160	159	−1
0.0	0.0	0.0	0.1	0.2	160	142	−11
2.0	2.0	0.15	0.08	0.15	160	146	−9[a]
1.0	1.0	0.08	0.04	0.08	80	76	−5[a]
2.0	2.0	0.15	0.08	0.00	160	152	−5[a]
1.0	1.0	0.08	0.04	0.00	80	76	−5[a]

[a] These mixtures represent aliquots of a soil extract from source B.

TABLE III

EFFECT OF NEUTRAL SALTS ON THE DETERMINATION OF CALCIUM WITH CALCICHROME

Salt	*Amount added (mg)*	*Calcium recovery (µg)*[a]	*Relative error (%)*
NaCl	200	120	−25
$NaNO_3$	200	126	−21
Na_2SO_4	200	122	−24
$NaCH_3COO$	200	122	−24

[a] 160 µg of Ca taken in each case.

TABLE IV

DETERMINATION OF CALCIUM IN SOIL EXTRACTS USING CALCICHROME

Source of soil	*Analysis of soil extract (mg/ml)*							*Calcium by flame spectrophotometry*[b] *(µg/ml)*	*Calcium by Calcichrome*[c] *(µg/ml)*	*Relative error (%)*
	Al	*Fe*	*Mg*	*Mn*	*PO_4*	*Si*	*Sr*[a]			
A										
1	1.0	6.2	0.08	0.12	—	0.02	0.20	285	279	−2
2	1.3	6.3	0.08	0.09	0.12	0.02	0.20	265	271	+2
B										
1	5.0	9.0	0.25	0.47	—	0.02	0.20	565	538	−5
2	4.1	7.2	0.25	0.44	0.50	0.02	0.20	540	518	−4
C										
1	6.4	9.6	—	0.08	—	0.03	0.20	230	228	−1
2	4.9	5.3	—	0.04	0.05	0.02	0.20	135	140	+3

[a] Inactive strontium added to soil extract for subsequent ^{90}Sr determination.
[b] Flame spectrophotometric analysis carried out on filtrate after double ammonia precipitation.
[c] Direct spectrophotometric method.

Applications. Six soil extracts from three localities A, B, and C were analysed for calcium and other major elements present (Table IV). Soil A was a sandy loam, soil B a heavy caly, and soil C a fine sandy loam.

The extracts were prepared by mixing 500 g of soil with 1 l of 5 *M* hydrochloric acid, allowing to stand for 16 h, adding 400 mg of strontium as nitrate, filtering, and diluting to 2 l with water. The inactive strontium carrier was added to facilitate subsequent ^{90}Sr determinations.

The spectrophotometric calcium determinations on samples from A and C were made at the 130 µg Ca level, but on samples from source B about 80 µg of calcium was used to minimize the combined interference of magnesium and phosphate. The free acid[7] in the extracts was found to be between 1.1 and 1.6 *N*. The calcium results were checked by a flame spectrophotometric method[4], carried out on the filtrate after a double ammonia precipitation.

To overcome the effect of phosphate in samples from source B, a cation-exchange procedure was developed for the separation of microgram amounts of calcium (*Recommended procedure*). After phosphate had been removed by this ion-exchange procedure, consistent calcium results were obtained from aliquots containing both 80 µg and 160 µg of calcium. Magnesium was the main interference after phosphate removal, and caused slightly low results.

Several mixtures of the major interfering elements were prepared to study their combined effect on calcium determinations (Table II). The last 4 mixtures represent aliquots of synthetic soil extracts from source B. The calcium recoveries from these synthetic mixtures explain the slightly lower results obtained by the direct spectrophotometric method compared with those found using flame spectrophotometry.

It is a pleasure to acknowledge the assistance of Mr. K. P. CHAMPION in carrying out the flame spectrophotometric analyses.

SUMMARY

A simple direct method is presented for the spectrophotometric determination of calcium in hydrochloric acid soil extracts. The chromogenic agent used is Calcichrome (self-coupled diazotized H-acid), and the method covers the range 4 to 175 µg of calcium. A comprehensive study of interferences has been carried out, and a cation-exchange procedure described for the preliminary separation of large amounts of phosphate.

RÉSUMÉ

Une méthode directe et simple est proposée pour le dosage spectrophotométrique du calcium dans des extraits chlorhydriques de sols, utilisant le Calcichrome comme réactif. Cette méthode permet de doser des teneurs en calcium de 4 à 175 µg. Les auteurs ont examiné l'influence d'autres ions et décrivent un procédé, avec échangeur de cations, permettant une séparation préliminaire de fortes quantités de phosphate.

ZUSAMMENFASSUNG

Es wird eine einfache direkte Methode für die spektralphotometrische Bestimmung von Calcium in salzsauren Erdextrakten angegeben. Als farbbildendes Reagenz wurde Calcichrom benutzt. Die Methode eignet sich für einen Bereich von 4–175 µg Calcium. Der Einfluss einer grossen Zahl von Ionen auf die Bestimmung wurde untersucht. Es wird ein Kationenaustauscherverfahren zur vorherigen Abtrennung grösserer Mengen Phosphat beschrieben.

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DOSAGE COLORIMETRIQUE DE TRACES DE ZINC DANS LA BAUXITE, L'ALUMINE ET L'ALUMINIUM RAFFINE

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La dithizone est le seul réactif colorimétrique couramment utilisé pour le dosage de traces de zinc à cause de sa sensibilité. Le coefficient d'extinction moléculaire du dithizonate de zinc est 90700. Ce réactif est peu spécifique et il possède une coloration propre, l'excès doit donc être éliminé.

D'autres réactifs ont été proposés: le 2-carboxy-2'-hydroxy-5-sulfoformazyl-benzène[1], la rhodamine B et le thiocyanate[2], la 8-hydroxyquinoléine[3], etc. Mais ils sont moins sensibles et aussi peu sélectifs que la dithizone. Des analogues de celle-ci ont été également employés, en particulier la di-β-naphtyl-thiocarbazone[4], mais elle possède aussi une coloration propre et l'excès est difficile à éliminer.

Pour pouvoir doser des traces de zinc par la dithizone dans la bauxite, l'alumine et l'aluminium raffiné, il faut éliminer les éléments gênants: l'aluminium, le gallium et le fer, car ils précipitent comme hydroxydes en milieu neutre ou légèrement alcalin; quant au cuivre, il réagit avec la dithizone. Les autres impuretés (Si, Ti, Ca, Mg, Na) ne gênent pas le dosage du zinc, elles sont d'ailleurs éliminées avec l'aluminium, le gallium et le fer.

Une telle séparation ne peut se faire en une seule opération, comme c'est le cas dans la méthode de FISCHER ET LEOPOLDI[5], plusieurs étapes sont nécessaires: *cf.* SANDELL[6] et BRICKER *et al.*[7]. Le zinc est d'abord séparé de l'aluminium, du gallium et du fer, puis dans une seconde opération, du cuivre. La mesure de la densité optique s'effectue après élimination de l'excès de dithizone.

ÉTUDE ANALYTIQUE

Une étude théorique de la séparation par extraction, des éléments gênants cités, a été faite[8] dont nous donnons ici l'essentiel:

Considérations générales

L'extraction d'un métal Me^{n+} par la dithizone (DzH_2) selon la réaction:

$$[Me^{n+}]_a + n\,[DzH_2]_o \rightleftarrows [(DzH)_nMe]_o + n\,[H^+]_a$$

(a = solution aqueuse, o = solution organique) obéit à la loi suivante[8,9]

$$x = 50\,[1 - \mathrm{tgh}\ 1.15 \cdot n \cdot (\mathrm{pH}_{\frac{1}{2}} - \mathrm{pH})] \qquad (1)$$

où x est le % du métal extrait dans la phase organique, n, sa valence, et $\mathrm{pH}_{\frac{1}{2}}$, le pH de demi-extraction. La fonction est de la forme tangente hyperbolique, son point d'inflexion se trouve à 50% d'extraction et à $\mathrm{pH}_{\frac{1}{2}}$.

Le $\mathrm{pH}_{\frac{1}{2}}$ peut être calculé à partir de la constante d'équilibre K de la réaction ci-dessus au moyen de la formule suivante[8]

$$\mathrm{pH}_{\frac{1}{2}} = -\frac{1}{n}\log K - \log\,[\mathrm{DzH_2}]_o \qquad (2)$$

Séparation du zinc; de l'aluminium, du gallium et du fer par la dithizone

Le zinc est extrait d'une solution citrique de pH 8.5 par la dithizone en milieu chloroformique. L'ion citrate prévient la précipitation des hydroxydes d'aluminium, de gallium et de fer (à raison d'un ion citrate pour deux ions d'aluminium, de gallium ou de fer). Ce réactif permet de maintenir en solution 0.5 g d'aluminium dans un volume de 50 ml, à n'importe quel pH, ce que ne peuvent faire ni le tartrate, ni l'oxalate, ni l'acétate.

La réaction réversible du zinc, de la dithizone et du dithizonate de zinc en présence de chloroforme et de citrate:

$$[\mathrm{Zn}^{2+}]_a + 2\,[\mathrm{DzH_2}]_o \rightleftarrows [(\mathrm{DzH})_2\mathrm{Zn}]_o + 2\,[\mathrm{H}^+]_a$$

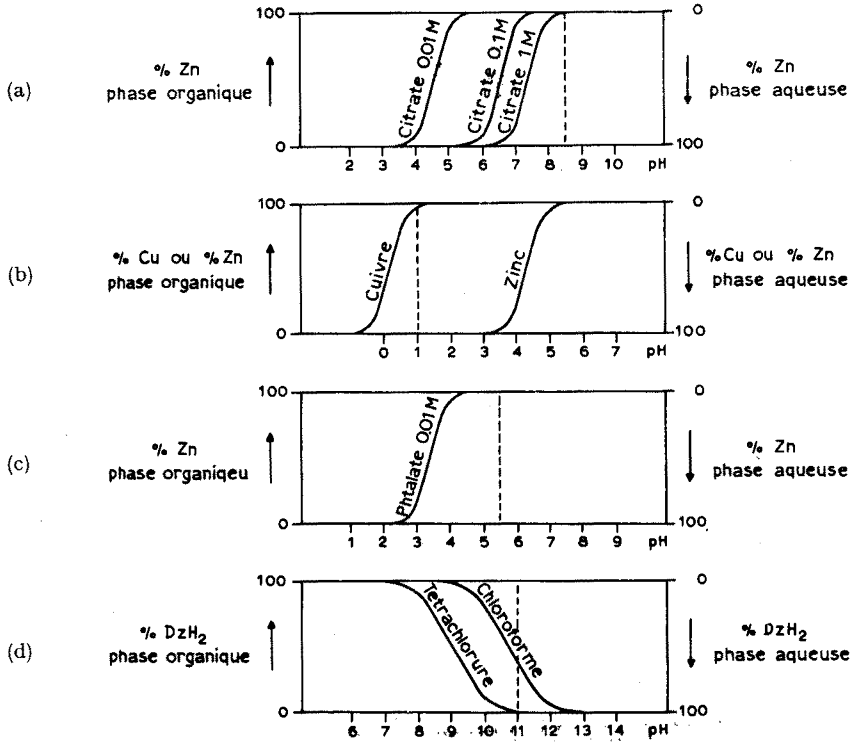


Fig. 1. Courbes d'extraction. (a) Extraction du Zn par la dithizone dans le chloroforme à partir d'une solution aqueuse de citrate. (b) Extraction du Cu et du Zn par l'acide chlorhydrique 0.1 N à partir d'une solution de dithizonates dans le chloroforme. (c) Extraction du Zn par la dithizone dans le tétrachlorure de carbone à partir d'une solution aqueuse de phtalate. (d) Extraction de la dithizone en solution organique par une solution aqueuse de sulfure de sodium.

est commandée par les constantes d'équilibre suivantes[10]: en milieu citrate 0.01 $M : K = 5 \cdot 10^{-3}$; en milieu citrate 0.1 $M : K = 5 \cdot 10^{-7}$; en milieu citrate 1 $M : K = 1 \cdot 10^{-8}$. Nous avons calculé les valeurs de $\mathrm{pH}_{\frac{1}{2}}$ au moyen de la formule (2) pour une concentration de dithizone de $4 \cdot 10^{-4}$ M (0.01%). En milieu citrate 0.01 M: $\mathrm{pH}_{\frac{1}{2}} = 4.6$; en milieu citrate 0.1 M: $\mathrm{pH}_{\frac{1}{2}} = 6.6$; en milieu citrate 1 M: $\mathrm{pH}_{\frac{1}{2}} = 7.4$. Les courbes d'extraction qui en résultent, calculées au moyen de l'équation (1) sont représentées sur la Fig. 1a.

Le pH d'extraction optimum est compris entre 8 et 9. La concentration en citrate doit toutefois être inférieure à 1 M, sans quoi l'extraction ne serait plus quantitative. A pH < 8, l'extraction est lente et parfois incomplète, à pH > 9 la dithizone repasse dans la phase aqueuse sous forme ionique.

L'équilibre entre les phases s'établit plus rapidement en milieu tétrachlorure de carbone qu'en milieu chloroformique. Ce dernier est pourtant plus avantageux, car il permet une meilleure séparation du cuivre et du zinc. D'autre part la dithizone en solution dans le tétrachlorure de carbone est dissociée au contact d'une phase aqueuse légèrement alcaline et repasse dans cette dernière à pH > 7.

Dans les conditions sus-indiquées, le zinc est séparé quantitativement de l'aluminium, du gallium et du fer, mais pas du cuivre.

Séparation cuivre–zinc

On y parvient par réextraction quantitative du zinc dans une phase aqueuse chlorhydrique 0.1 M on a:

$$[(\mathrm{DzH})_2\mathrm{Me}]_o + 2\,[\mathrm{H}^+]_a \rightleftarrows [\mathrm{Me}^{2+}]_a + 2\,[\mathrm{DzH}_2]_o$$

où Me^{2+} représente soit Zn^{2+}, soit Cu^{2+}. Les constantes d'équilibre et les $\mathrm{pH}_{\frac{1}{2}}$ sont en milieu chlorure 1 M: pour le zinc[10]: $K = 2 \cdot 10^{-2}$, $\mathrm{pH}_{\frac{1}{2}} = 4.3$; pour le cuivre[11]: $K = 3 \cdot 10^{6}$, $\mathrm{pH}_{\frac{1}{2}} = 0.2$. Les valeurs de $\mathrm{pH}_{\frac{1}{2}}$ ont été calculées au moyen de la formule (2) pour une concentration de dithizone de $4 \cdot 10^{-4}$ M. Les courbes d'extraction qui en résultent ont été calculées au moyen de l'équation (1) et sont représentées sur la Fig. 1b. A pH 1, le zinc repasse rapidement et quantitativement dans la phase aqueuse, alors que le dithizonate de cuivre, très peu dissocié à ce pH, reste presque entièrement dans le chloroforme.

Les dernières traces de cuivre sont éliminées lorsqu'on extrait une nouvelle fois le zinc comme dithizonate dans le tétrachlorure en présence d'un tampon phtalique de pH 5.5. Le cuivre, complexé par le thiosulfate, reste dans la phase aqueuse. Pour cette dernière extraction on doit utiliser le tétrachlorure à la place du chloroforme, car l'excès de dithizone est plus facile à éliminer. Le milieu phtalique a été choisi, car le $\mathrm{pH}_{\frac{1}{2}}$ du dithizonate de zinc est plus faible qu'en milieu chlorure, acétate, tartrate ou citrate, ce qui permet l'extraction de ce métal en milieu légèrement acide.

La constante d'équilibre de la réaction ci-dessus est $K = 1$ pour le zinc en milieu phtalique 0.01 M[10]. Pour une concentration dithizone de $4 \cdot 10^{-4}$ M, $\mathrm{pH}_{\frac{1}{2}} = 3.4$. La courbe d'extraction correspondante, calculée au moyen de la formule (1) est représentée sur la Fig. 1c. Elle montre que le pH d'extraction optimum du zinc est compris entre 5 et 6. En dessous, l'extraction n'est plus quantitative, en dessus le cuivre n'est plus complexé par le thiosulfate, il est extrait avec le zinc.

On obtient finalement une solution de dithizonate de zinc dans le tétrachlorure de carbone, tous les éléments gênants ayant été séparés.

Elimination de l'excès de dithizone

Soit l'équilibre

$$[DzH_2]_o \rightleftarrows [DzH^-]_a + [H^+]_a$$

dont les constantes sont: $K = 10^{-9}$ dans le tétrachlorure de carbone et $2 \cdot 10^{-11}$ dans le chloroforme[11]. Par une étude analogue à celle donnée pour les dithizonates on trouve que le $pH_{\frac{1}{2}}$ est de 9.0 dans le tétrachlorure et 10.7 dans le chloroforme[8]. Les courbes d'extraction qui en résultent sont représentées sur la Fig. 1d. On remarque qu'à pH 11 on peut éliminer quantitativement et rapidement l'excès de dithizone de la phase tétrachlorure. Dans ces conditions le dithizonate de zinc n'est pas dissocié et reste quantitativement dans le tétrachlorure. Le pH 11 est obtenu par addition de sulfure de sodium, réactif qui a en outre l'avantage de ne pas nécessiter de purification: une filtration suffit, les sulfures de métaux lourds étant ainsi éliminés.

Dosage colorimétrique

Le dosage colorimétrique s'effectue directement sur la solution de dithizonate de zinc dans le tétrachlorure de carbone à 538 mμ.

DESCRIPTION DE LA MÉTHODE

Le dosage de traces exige l'emploi de récipients aussi peu adsorbants que possible, leurs surfaces doivent donc être parfaitement lisses. Pour la même raison on doit éviter les rodages. De plus le matériel doit être parfaitement lavé. Quant aux réactifs pro anal, il est nécessaire le plus souvent de les purifier.

Appareillage

Deux ampoules à décanter de 100 ml (selon Squibb) en pyrex, munies d'un bouchon de polyéthylène et d'un robinet téflon. Nettoyage: on laisse reposer les ampoules une nuit dans HCl 6 N, on lave à l'eau distillée, puis avec une solution de NH_3 0.01 M; on ajoute 10 ml d'une solution chloroformique de dithizone à 0.1 % et agite énergiquement. L'opération est répétée jusqu'à ce qu'on n'observe plus de changement de coloration de la dithizone. Les ampoules sont alors rincées à l'eau bidistillée, puis à l'acétone (purifiée par distillation) et enfin séchées. Les statifs doivent être en acier inox avec anneaux recouverts de polyéthylène pour éviter les contaminations.

Pour la préparation et la purification des réactifs, on utilise des bechers de 250 et 500 ml, 1 et 2 l (avant l'emploi, ils sont lavés avec HCl 6 N à chaud, et rincés à l'eau bidistillée jusqu'à neutralité), des ampoules à robinet de 250, 500 et 1000 ml en pyrex (on les traitera comme indiqué pour les ampoules coniques). Un vibreur: brevet Ing. Muller (Zürich).

Pipettes de 1, 2, 5, 10 et 20 ml, jaugées et graduées. Ces pipettes sont abandonnées une nuit dans HCl 6 N, rincées à l'eau bidistillée, puis à l'acétone purifiée, et enfin séchées.

Spectrophotomètre Beckman DU avec cuves de 1 cm d'épaisseur.

Réactifs (pro anal.)

Solution standard de zinc (100 µg/ml). On dissout 50 mg de zinc en copeaux dans 10 ml HCl 6 N, diluer à 500 ml avec de l'eau bidistillée.

Na_2S 10%, Na_2S 0.5%. Cette dernière solution est préparée au moment de l'emploi.

Chloroforme (contenant 1% d'alcool absolu).

Tétrachlorure de carbone. Purifié comme suit: agiter 1 l CCl_4 avec 100 ml NH_3 6.5 *N* pendant 10 min au moyen d'un vibreur. On jette la phase aqueuse, CCl_4 est lavé à l'eau bidistillée jusqu'à neutralité et séché avec Na_2CO_3 anhydre. On filtre et on distille CCl_4 en présence de 100 mg de dithizone. Le distillat est traité par 100 ml de Na_2S 10% et homogénéisé. On agite ensuite pendant 10 min avec 100 ml d'eau bidistillée et sèche avec K_2CO_3 pro anal. On distille et on conserve le CCl_4 dans un flacon brun.

Dithizone 0.01% dans $CHCl_3$. On dissout 35 mg de dithizone dans 50 ml de CCl_4, filtre, et ajoute 100 ml NH_3 0.5 *N*. Après 10 min d'agitation on sépare la phase aqueuse rouge et la traite avec 250 ml de $CHCl_3$. On ajoute, à raison de une goutte par sec, 120 ml de HCl 6 *N*. On sépare la phase organique verte et la conserve dans un flacon brun sous une couche de 1 cm de H_2SO_4 *N*.

Dithizone 0.01% dans CCl_4. On dissout 35 mg de dithizone dans 50 ml de CCl_4, on filtre et ajoute 100 ml de NH_3 6 *N*. Après 10 min d'agitation, on sépare la phase aqueuse rouge et la traite par 250 ml de CCl_4. On ajoute, à raison de une goutte par sec, 120 ml de HCl 6 *N*. On récupère la phase organique verte et la conserve dans un flacon brun sous une souche de 1 cm de H_2SO_4 *N*.

Citrate d'ammonium 1 M. On dissout 50 g d'acide citrique dans 100 ml d'eau bidistillée, neutralise et alcalinise à pH 9.5 au moyen d'ammoniaque 13 *N*. On dilue à 250 ml. Pour purifier ce réactif on le mélange par agitation à une solution chloroformique de dithizone 0.01%. Après élimination de celle-ci, on lave la phase aqueuse avec du chloroforme.

Phtalate sodico-potassique 0.1 M. On dissout 5 g de phtalate acide de potassium dans 200 ml de NaOH 0.1 *N*. Après dilution à 250 ml avec de l'eau bidistillée, le pH de cette solution doit être de 5–6. Ce réactif est purifié par agitation avec une solution de dithizone 0.01 % dans le CCl_4, puis on lave avec du CCl_4.

Thiosulfate de sodium 15%. On dissout 37.5 g de $Na_2S_2O_3 \cdot 5H_2O$ dans de l'eau bidistillée et dilue à 250 ml.

Rouge de crésol 0.1%. On dissout 100 mg de rouge de crésol dans 2.5 ml de NaOH 0.1 *N*, dilue à 100 ml et filtre.

Mode opératoire

20 ml de solution à analyser sont introduits dans une ampoule à robinet avec 1 ml de citrate 1 *M* et une goutte de rouge de crésol 0.1%. Après alcalinisation par l'ammoniaque 6.5 *N* (pH de la solution 8.5), ajouter 10 ml de la solution chloroformique de dithizone 0.01% et agiter vigoureusement pendant 1 min. La phase chloroformique est introduite dans une seconde ampoule à robinet et la phase aqueuse lavée par agitation avec 5 ml de solution chloroformique de dithizone. Les phases chloroformiques renfermant la totalité du zinc sont réunies. La phase aqueuse contient Al, Ga, Fe, etc. Elle est jetée.

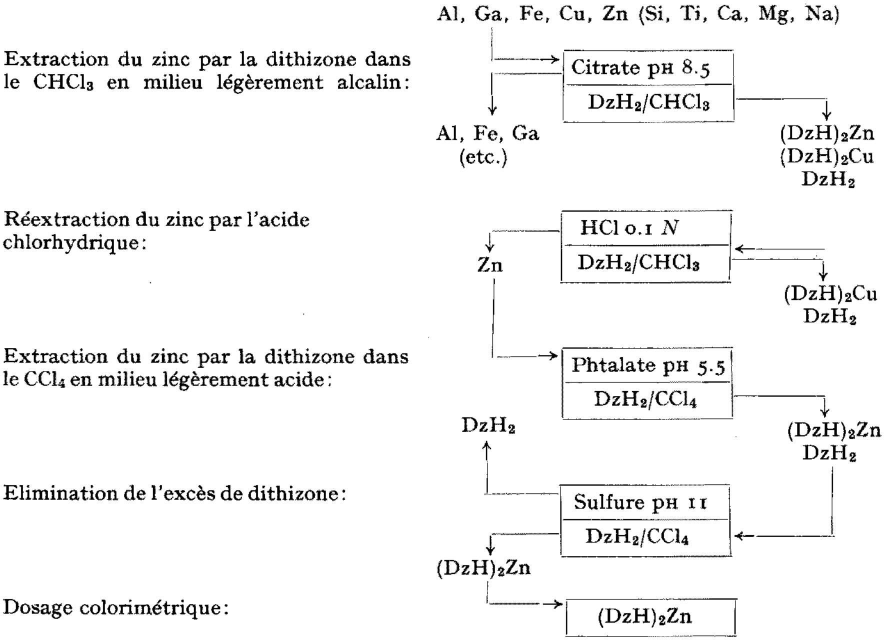
Pour réextraire le zinc, on traite la phase organique par une solution de HCl 0.1 *N* et on agite pendant 1 min. La solution chloroformique qui contient la plus grande partie du cuivre est jetée. La solution aqueuse est lavée deux fois avec 1 ml de $CHCl_3$ pour éliminer la dithizone. La deuxième solution de lavage doit être incolore.

On extrait le zinc par la dithizone dans CCl_4. On ajoute à la solution aqueuse acide une goutte de méthylorange 0.1% et on titre au jaune par NH_3 0.1 *N**. On ajoute 1 ml de thiosulfate 15%, 5 ml de phtalate 0.1 *M* et exactement 25 ml de dithizone 0.01% dans CCl_4 et on agite vigoureusement pendant 1 min. Après séparation on prélève la phase aqueuse quantitativement au moyen d'un siphon.

Pour éliminer l'excès de dithizone, on ajoute, à la solution organique, 22.5 ml d'eau bidistillée et 2.5 ml de Na_2S 0.5%, on agite 15 sec et on prélève la phase aqueuse au moyen d'un siphon. La phase organique est traitée une seconde fois par 22.5 ml d'eau bidistillée et 2.5 ml de solution Na_2S 0.5%; on agite pendant 15 sec et on sépare la phase aqueuse au moyen d'un siphon.

La mesure colorimétrique s'effectue sur une partie aliquote de la solution organique à 538 mμ, par rapport au CCl_4 pur, dans une cuve de 1 cm. La quantité de zinc est déterminée au moyen d'une courbe d'étalonnage obtenue dans les mêmes conditions ou par étalon interne. Un essai à blanc doit être effectué parallèlement à l'analyse pour déterminer la teneur en zinc des réactifs.

Schéma de l'analyse



Courbe d'étalonnage

Elle a été effectuée pour des valeurs de zinc comprises entre 0.25 et 20.00 μg. Les densités optiques correspondantes sont données dans le Tableau I. La correction de l'essai à blanc a été effectuée. On y trouve en outre le rapport densité optique/quantité de zinc, qui a été calculé pour chaque essai. La moyenne de celui-ci est de 0.052 μg^{-1} pour un volume final de 25 ml.

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* Si Co est présent, *cf.* p. 365.

TABLEAU I

DOSAGE COLORIMÉTRIQUE DE ZINC PAR LA DITHIZONE

(Volume final 25 ml)

Prise zinc (μg)	*Densité optique (D)*	*D/μg Zn*
0.25	0.010	0.040
0.50	0.030	0.060
0.75	0.045	0.060
1.00	0.050	0.050
2.00	0.105	0.053
2.00	0.110	0.055
2.00	0.100	0.050
2.50	0.140	0.056
2.50	0.140	0.056
4.00	0.215	0.054
4.00	0.215	0.054
5.00	0.205	0.041
6.00	0.310	0.053
7.50	0.390	0.052
8.00	0.420	0.053
8.00	0.370	0.046
10.00	0.485	0.049
10.00	0.610	0.061
15.00	0.805	0.054
16.00	0.780	0.049
20.00	0.960	0.048

Une étude statistique a été faite sur 21 déterminations pour une probabilité de 95%. La déviation standard $S = 0.0056$ et les limites de confiances pour la moyenne des 21 déterminations sont: $0.052\ \mu g^{-1} \pm 0.0025$, c'est-à-dire 5% environ.

Essai à blanc

L'essai à blanc correspond à 0.77 μg de Zn ($D = 0.040$). Cette extinction est due aux contaminations en zinc et à des colorations étrangères provenant, entre autre, des produits d'oxydation de la dithizone (Fig. 2). En effet, l'oxydation énergique de la dithizone (par Br_2, Cl_2, H_2O_2, etc.) donne la diphénylthiocarbodiazone et des produits intermédiaires dont la composition n'est pas connue et que l'on nomme "produits d'oxydation jaunes" (gelbe Oxydationsprodukte[11]). Ceux-ci se forment déjà en présence d'air. Au cours de l'analyse on vérifie que la dithizone est quantitativement éliminée par une mesure de la densité optique à 620 mμ. Cette longueur d'onde correspond au maximum d'absorption de ce réactif et une absorption pratiquement nulle du dithizonate de zinc (Fig. 2).

Effets gênants sur le dosage du zinc de Al, Fe, Ga, Cu, Si, Ti, Ca, Mg, Na et d'autres métaux réagissant avec la dithizone

L'aluminium, le fer, ainsi que la plupart des impuretés de la bauxite, de l'alumine, et de l'aluminium raffiné: Si, Ti, Ca, Mg et Na, ne réagissent pas avec la dithizone, ils ne gênent donc pas. Pourtant l'aluminium et le fer ne doivent pas précipiter comme hydroxydes ce qui provoquerait une coprécipitation du zinc. On les masque donc avec une quantité suffisante de citrate.

Le gallium, contrairement à ce que pensent certains auteurs[11], réagit avec la dithizone[12]. Dans la méthode proposée, il est éliminé au cours des séparations. Il en est de même pour le cuivre. Toutefois lorsque la quantité de cet élément est supérieure à 50 μg, il faut augmenter la quantité de dithizone lors de la première extraction.

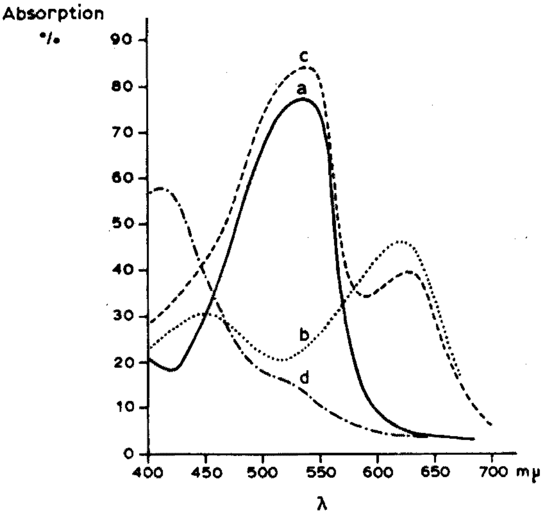

Fig. 2. Spectres d'absorption. (a) Dithizonate de zinc ($8 \cdot 10^{-6}$ M). (b) Dithizone ($3 \cdot 10^{-6}$ M) (c) Dithizonate en présence d'un excès de dithizone. (d) Produits d'oxydation de la dithizone

Nous avons aussi étudié l'influence des autres éléments réagissant avec la dithizone qui ne font pas partie des impuretés habituelles de la bauxite, de l'alumine ou de l'aluminium raffiné, mais peuvent s'y trouver occasionnellement. C'est le cas du manganèse(II) et du thallium(I): ceux-ci ne réagissent avec la dithizone qu'en milieu très alcalin (pH 10) et ne gênent par conséquent pas dans les conditions de l'analyse. Le fer(II) et l'étain(II) sont oxydés par l'air en fer(III) et étain(IV), formes sous lesquelles ils ne réagissent pas avec la dithizone. Par contre le cobalt gêne. Il doit être complexé par la cyanure lors de l'extraction du zinc par la dithizone dans le CCl_4 en milieu légèrement acide. Le mode opératoire donné à la p. 363 doit être modifié de la façon suivante: Lors de l'extraction du zinc par la dithizone dans le CCl_4, ajouter une goutte de méthylorange à la solution et 1 ml de cyanure de potassium 5%. Titrer par l'ammoniaque 0.1 N jusqu'à virage au jaune de l'indicateur, etc.

Pour éviter la formation de complexes entre le zinc et le cyanure, le pH doit être inférieur à 6 lors de la seconde extraction par la dithizone.

Le nickel est séparé lors de l'extraction du zinc par HCl 0.1 N, car le dithizonate de nickel est stable à ce pH.

Les complexes du palladium(II), de l'argent, du cadmium, de l'indium, du platine(II), de l'or(III), du mercure(II) et du bismuth avec la dithizone sont instables en présence de sulfure de sodium[11]. Ils sont éliminés en même temps que l'excès de dithizone si toutefois ils n'ont pas été séparés auparavant. Le plomb est complexé par le thiosulfate lors de l'extraction du zinc par la dithizone dans le CCl_4 en milieu légèrement acide et est ainsi séparé. Tous ces éléments ne gênent donc pas.

APPLICATION DU DOSAGE DU ZINC DANS LA BAUXITE, L'ALUMINE ET L'ALUMINIUM RAFFINÉ (RAFFINAL)

Bauxite et alumine

Appareillage. Creusets de platine de 20 ml, avec couvercle. Evaporateur I.R. en quartz. Four électrique (1000). Le reste de l'appareillage est décrit à la p. 361.

Réactifs. Soda–borax 3 : 1. On dissout 37.5 g de carbonate de sodium et 12.5 g de borax pro anal dans 400 ml d'eau bidistillée avec 1 ml de Na_2S 10%. On laisse reposer la solution pendant quelques jours, filtre et dilue à 500 ml avec de l'eau bidistillée. Les autres réactifs sont décrits à la p. 362.

TABLEAU II

ANALYSES D'ÉCHANTILLONS DE BAUXITE, D'ALUMINE ET DE RAFFINAL

Echantillons	*Zinc donné (p.p.m.)*	*Zinc trouvé (p.p.m.)*	
		Première analyse	*Deuxième analyse*
Bauxite			
S 1	20*	16.0	13.0
S 2	20*	17.0	15.0
SL 1		18.0	20.0
SL 2		12.0	11.0
Alumine			
AS 1		33.0	37.0
AS 2		5.0	6.0
AS 3		29.0	29.0
AS 4		83.0	80.0
Raffinal			
EI 1**	5**	5.2	
EI 2**	10**	9.8	10.0
EI 3**	15**	15.2	
P 1	20***	19.2	18.5
P 2		1.7	1.5
ZM (Queue)****		0.3	0.5

* Résultat obtenu par fluorescence-X.
** EI sont des étalons internes ajoutés sous forme de solution standard à un aluminium purifié par fusion de zone, dans lequel il n'a pas été décelé de zinc par la méthode décrite.
*** Résultat obtenu par spectrographie d'émission.
**** ZM (Queue) est la queue d'un échantillon de raffinal purifié par fusion de zone.

Mode opératoire. 100 mg de bauxite ou d'alumine en poudre sont introduits dans un creuset de platine avec 3 ml de la solution de soda–borax. On évapore à sec aux rayons I.R., le creuset est couvert, puis introduit 10 min dans un four à 1000°. Après refroidissement on ajoute 5 ml de HCl 6 *N* et chauffe sur une plaque électrique jusqu'à dissolution totale. Après refroidissement la solution est introduite dans une ampoule à robinet, le creuset rincé 4 à 5 fois avec un peu d'eau bidistillée. L'analyse du zinc s'effectue selon le mode opératoire décrit à la p. 362. On fait un essai à blanc dans les mêmes conditions, mais en évitant la calcination au four à 1000° pour éviter l'attaque du platine par le soda-borax pur. Des analyses ont été effectuées sur des échantillons de bauxite et d'alumine. Chacun d'eux est analysé deux fois. Les résultats sont réunis dans le Tableau II.

Aluminium raffiné

Appareillage. Voir p. 361. Flacons à peser en matière plastique. Bechers en quartz de 50 ml avec verres de montre en quartz. Nettoyage: laver à HCl concentré chaud, puis rincer à l'eau bidistillée et sécher dans une étuve.

Réactifs. Voir p. 362. Citrate d'ammonium 2 *M*: on dissout 210 g d'acide citrique pro anal dans 240 ml de NH_3 13 *N* pro anal par petites portions en agitant et refroidissant. Le pH est porté à 9.5 au moyen de NH_3 3 *N* et on dilue à 500 ml. Ce réactif doit être purifié par agitation avec la dithizone dans $CHCl_3$ et lavage au $CHCl_3$.

Mode opératoire. 0.5 g d'aluminium en copeaux fins est pesé dans un flacon en matière plastique et introduit dans un becher en quartz avec 10 ml de HCl, le double de la quantité stoechiométriquement nécessaire. On couvre d'un verre de montre et chauffe légèrement. La mise en solution dure environ 4 h. La solution est refroidie, puis introduite dans une ampoule à robinet et le becher rincé 3 à 4 fois avec un peu d'eau bidistillée. Le volume final de la solution ne doit pas dépasser 25 à 30 ml. On ajoute ensuite une goutte de rouge de crésol, 5 ml de citrate 2 *M* et on alcalinise avec NH_3 13 *N* (5–6 ml) jusqu'à pH 8.5 (virage au violet de l'indicateur). Parallèlement on fait un essai à blanc. Après le virage au violet de l'indicateur, l'analyse se poursuit selon le mode opératoire de la p. 362.

Les résultats de quelques analyses sont donnés dans le Tableau II.

Précision et sensibilité de la méthode

Une étude statistique a été effectuée* sur deux échantillons d'alumine pour déterminer la précision et la sensibilité de la méthode. Un premier échantillon d'alumine (AS 1, *cf.* Tableau II) à teneur en zinc moyenne a servi à déterminer la précision. Le résultat moyen de six déterminations est 34.7 p.p.m. La déviation standard $S = 3.37$ p.p.m. et les limites de confiances pour une probabilité de 95% et pour la moyenne de deux analyses sont: 34.7 p.p.m. ± 6.15.

Un second échantillon d'alumine (AS 2, *cf.* Tableau II) à teneur en zinc faible a servi à déterminer la sensibilité de la méthode. Le résultat moyen de six déterminations est 6.25 p.p.m. La déviation standard $S = 1.06$ p.p.m. et les limites de confiances pour une probabilité de 95% et pour la moyenne de deux analyses sont: 6.25 p.p.m. ± 2.0. On peut considérer 2 p.p.m. comme la limite de détection de la méthode pour l'alumine et la bauxite. Dans le cas de l'aluminium on a une prise d'essai cinq fois plus élevée (0.5 g au lieu de 0.1 g). Comme la méthode est identique on peut admettre en première approx une limite de détection environ cinq fois plus faible. Celle-ci sera alors 0.4 p.p.m.

RÉSUMÉ

Une méthode de dosage colorimétrique de traces de zinc par la dithizone dans la bauxite, l'alumine et l'aluminium raffiné est proposée. Ga, Fe, Si, Ti, Ni, Pb, Ca, Mg, Na, etc. ne gênent pas;

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* Pour plus de détails, voir ref. 8, p. 368.

Co gêne, mais peut être masqué par le cyanure. La limite de sensibilité de la méthode est 2 p.p.m. pour l'alumine et la bauxite, 0.4 p.p.m. pour l'aluminium.

SUMMARY

A method for the colorimetric determination of traces of zinc in bauxite, alumina and refined aluminium by means of dithizone is proposed. Ga, Fe, Si, Ti, Ni, Pb, Ca, Mg, Na, etc. do not interfere; Co interferes but can be masked with cyanide. The limit of sensitivity of the method is 2 p.p.m. for bauxite and alumina and 0.4 p.p.m. for aluminium.

ZUSAMMENFASSUNG

Es wird eine Methode zur kolorimetrischen Bestimmung von Zink in Bauxit, Tonerde und raffiniertem Aluminium mittels Dithizon vorgeschlagen. Ga, Fe, Si, Ti, Ni, Pb, Ca, Mg, Na, usw. stören nicht. Co stört, kann aber mit Cyanid maskiert werden. Die Nachweisgrenze liegt für Bauxit und Tonerde bei 2 p.p.m., für Aluminium bei 0.4 p.p.m.

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THE STABILITY OF SOME LANTHANIDE COMPLEXES WITH METHYLETHYL GLYCOLATE AND WITH METHYLPROPYL GLYCOLATE

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As shown by STEWART[1] and CHOPPIN *et al.*[2,3], the efficiency of the separation by cation exchange of the lanthanides and of the actinides with α-hydroxycarboxylate ligands increases in the order: glycolate < lactate < α-hydroxyisobutyrate. This phenomenon is explained by the increase of the stability constants of the complexes involved[4-6].

It seemed possible that the substitution of one or both methyl groups in α-hydroxyisobutyrate by the larger ethyl and propyl groups would give a further improvement of the separation. In this investigation the stepwise stability constants of a number of lanthanide ions have been determined with methylethyl glycolate and with methylpropyl glycolate by a potentiometric titration technique.

Like glycolate, lactate and α-hydroxyisobutyrate, the investigated ligands form uninegative tetra-ligand complexes with the lanthanide elements; consequently the complexes ML^{2+}, ML_2^+, ML_3 and ML_4^- can exist in solution.

CALCULATION PROCEDURE

The relationship between the concentration of the free ligand, [L], in solution and $\bar{n}$ the average number of ligands bound per metal ion present, is given by the formation function[7]

$$\bar{n} = \frac{\sum_{n=1}^{n=N} n\beta_n[\mathrm{L}]^n}{1 + \sum_{n=1}^{n=N} \beta_n[\mathrm{L}]^n} \qquad (1)$$

The over-all stability constant β_n of the complex ML_n is defined by

$$\beta_n = K_1 \cdot K_2 \ldots K_n = \prod_{n=1}^{n=N} K_n \qquad (2)$$

where $K_1, K_2, \ldots, K_n$ are the stepwise formation constants of the complexes ML, $ML_2, \ldots, ML_n$ (the ionic charges are neglected).

Numerical values of $\bar{n}$ and [L] over a sufficiently large range of [L] are obtained by potentiometric or other measurements. From this data eqn. (1) can be solved by graphical methods[7-9] and also by a least squares treatment of $\bar{n}$ and [L] using a digital computer. Such calculation methods are described by RYDBERG *et al.*[10], CHOPOORIAN *et al.*[11], and by SILLÉN AND INGRI[12]. In this paper a somewhat similar procedure is used.

The formation function (1) can, for $N = 4$, be written in the form

$$\bar{n}_i = \mathrm{f}_i\,(K_1, K_2, K_3, K_4, [\mathrm{L}_i]) \tag{3}$$

The transformation of the non-linear eqn. (3) into a linear one is possible by substituting the K_n-values by an estimated value $K_n{}^0$ with a deviation $\Delta K_n{}^0$ from the "true" value K_n, thus $K_n = K_n{}^0 + \Delta K_n{}^0$, where $n = 1, 2, 3, 4$ respectively. It can be proved that

$$\bar{n}_i - \mathrm{f}_i = \sum_{n=1}^{4} \Delta K_n{}^0 \frac{\delta \mathrm{f}_i}{\delta K_n{}^0} \tag{4}$$

and

$$\sum_{n=1}^{4} \Delta K_n{}^0 \sum_{i=1}^{i} \frac{\delta \mathrm{f}_i}{\delta K_n{}^0} \cdot \frac{\delta \mathrm{f}_i}{\delta K_l{}^0} = \sum_{i=1}^{i} (\bar{n}_i - \mathrm{f}_i) \frac{\delta \mathrm{f}_i}{\delta K_l{}^0} \tag{5}$$

where f_i is written for $\mathrm{f}_i(K_1{}^0, K_2{}^0, K_3{}^0, K_4{}^0, [\mathrm{L}_i])$, $l = 1, 2, 3, 4$ successively and $i =$ the number of corresponding $\bar{n}$ and [L] pairs.

The $\Delta K_n{}^0$ values are obtained by solving of the system (5). Addition of these $\Delta K_n{}^0$ values to the first estimates of $K_n{}^0$ gives new estimates. This procedure is repeated until the $\Delta K_n{}^0$ values are sufficiently small.

Equation (5) is programmed in FORTRAN and computed with an IBM 1620 digital computer. The cycle is repeated until $\Delta K_n{}^0/K_n{}^0 \leqslant 1/1000$. It is usually only necessary to perform 3 or 4 successive iterations when the first estimates of $K_n{}^0$ are carefully selected. The approximate constants obtained by BJERRUM's half $\bar{n}$-method are taken as first estimates. The time necessary for computing the 4 constants is 10 to 15 min.

The standard deviation on β_n,

$$S_n = \prod_{n=1}^{n=N} K_n \sqrt{\sum_{n=1}^{n=N} \left(\frac{s_n}{K_n}\right)^2} \tag{6}$$

where $s_1, s_2, \ldots, s_n$ are the standard deviations on the individual stability constants $K_1, K_2, \ldots, K_n$, and are calculated by the computer. A more detailed description of this method and a comparison with three graphical methods[7-9] for some lanthanide–α-hydroxyisobutyrate complex systems is given elsewhere[6].

EXPERIMENTAL

Apparatus

A Radiometer pH M-4C potentiometer and type P 101 platinum electrodes were used. Regular cleaning of the electrodes was effected by immersion in cold chromic acid and concentrated sulphuric acid mixture, raising to 125° and slowly cooling[13]. Quinhydrone (100 mg of Merck analytical grade) was added for every 20 ml of solution being measured.

Salt bridges, of U-tube construction with porous sintered plates at the ends and filled with 1 M sodium perchlorate, made electrical contact between the compartments.

Reagents

Organic acid buffer solutions. Methylethyl and methylpropyl glycolic acid were prepared from methylethyl and methylpropyl ketone respectively, as described by ALBERT[14]. α-Hydroxyisobutyric acid was obtained from Fluka.

The buffer solutions were made by partially neutralizing the acid solutions with carbonate-free sodium hydroxide. Afterwards the concentrations of the acid and the sodium salt were checked by titration.

The buffer ratio $\delta = C_{HL}^0/C_L^0$ was respectively:

methylethyl glycolate : $C_{HL}^0 = 1.170\ M$; $C_L^0 = 1.006\ M$; $\delta = 1.163$,
methylpropyl glycolate: $C_{HL}^0 = 0.9726\ M$; $C_L^0 = 0.9737\ M$; $\delta = 0.999$,
α-hydroxyisobutyrate : $C_{HL}^0 = 1.000\ M$; $C_L^0 = 1.000\ M$; $\delta = 1.000$.

The ionic strength I of these solutions was close to unity.

Lanthanide perchlorate solutions. The solutions were prepared by dissolving the lanthanide oxides (Fluka 99.9%) in nitric acid and evaporating with perchloric acid until a negative test for nitrate resulted. The remaining small amount of perchloric acid (of the order of 2–6 mM) was determined by titration. The concentrations of the lanthanides (of the order of 50 mM) were determined by gravimetric analysis using the oxalic acid method and the oxide weighing form[15].

Sodium perchlorate. Sodium perchlorate (Fluka, crystallised analytical grade) was used for adjusting the ionic strength of the various solutions to 1.0. It was checked for purity.

Procedure

The experimental arrangement of FRONAEUS[8], modified by CHOPPIN AND CHOPOORIAN[5], was used. The initial composition of each half-cell compartment is tabulated below (top part), where $M(ClO_4)_3$ is the lanthanide perchlorate, L the complexing ligand, and I the ionic strength.

A		B		C
Pt, Quinhydrone		Pt, Quinhydrone		Pt, Quinhydrone
$C_M = 0$	1 M	C_M^0 mM $M(ClO_4)_3$	1 M	$C_M = 0$
$[H]_A$ mM $HClO_4$	$NaClO_4$	C_H^0 mM $HClO_4$	$NaClO_4$	$C_H = 0$
$NaClO_4$ to $I = 1$		$NaClO_4$ to $I = 1$		$NaClO_4$ to $I = 1$
		$C_{L'}$ mM NaL		$C_{L'}$ mM NaL
		$C_{HL'} = \delta C_{L'}$ mM HL		$C_{HL'} = \delta C_{L'}$ mM HL

Compartment A contained 20 ml of a reference solution of known perchloric acid concentration, $[H]_A = 3.876$ mM in all the titrations. Compartment B was prepared by adding 10 ml of the metal perchlorate stock solutions and 10 ml of a sodium perchlorate solution of appropriate concentration to make the ionic strength $I = 1$. The initial metal concentration C_M^0 was of the order of 25 mM. Compartment C contained only 20 ml of a 1 M sodium perchlorate solution.

The solutions in compartments B and C were titrated in the same way with the acid buffer solutions (ionic strength $I = 1$). Simultaneously an equal volume of the reference perchloric solution was added to compartment A, so that the volumes in the compartments remained the same (bottom part of the above table).

All titrations were made in thermostatted cells of approximately 30 ml. The temperature was controlled at 25.0 ± 0.1°. Rapid mixing was achieved by magnetic stirring which was stopped during the potential measurements.

Every titration series was at least duplicated. The potentials were highly stable and could usually be reproduced within 0.2 mV.

Calculation of $\bar{n}$ and [L]

The hydrogen-ion concentration in the compartments B and C, $[\mathrm{H}]_B$ and $[\mathrm{H}]_C$ respectively, are calculated as a function of the acid buffer solution added

$$E_{AB}(\mathrm{mV}) = 59.15 \log \frac{[\mathrm{H}]_A}{[\mathrm{H}]_B} \quad \text{at } 25° \tag{7}$$

$$E_{BC}(\mathrm{mV}) = 59.15 \log \frac{[\mathrm{H}]_B}{[\mathrm{H}]_C} \quad \text{at } 25° \tag{8}$$

The concentration of the free ligand [L] in compartment B is, according to AHRLAND[16], calculated from the equation

$$[\mathrm{L}] = \frac{[\mathrm{H}]_C}{[\mathrm{H}]_B}\left(C_{L'} + \frac{C_H - [\mathrm{H}]_B + (1+\delta)\,[\mathrm{H}]_C}{\delta}\right) \tag{9}$$

and the average number of ligands bound per metal ion present from

$$\bar{n} = \frac{C_{L'} + [\mathrm{H}]_B - C_H - [\mathrm{L}]}{C_M} \tag{10}$$

where C_M is the total metal concentration in compartment B.

RESULTS

A typical example of the observed potentials and the calculated values of $\bar{n}$ and [L] as a function of added buffer solution of the ligand is given in Table I.

TABLE I

DETERMINATION OF [L] AND $\bar{n}$ FOR THE NEODYMIUM–METHYLPROPYL GLYCOLATE SYSTEM

$C_M^0 = 26.25$ m*M*, $C_L^0 = 973.7$ m*M*, $[\mathrm{H}]_A = 3.876$ m*M*,
$C_H^0 = 3.150$ m*M*, $\delta = 0.999$,
initial volume = 20 ml

Volume of titrant (ml)	E_{AB} *(mV)*	E_{BC} *(mV)*	*[L] (mM)*	$\bar{n}$
0.10	16.1	63.9	0.519	0.125
0.20	21.8	57.3	1.231	0.267
0.30	25.1	53.7	2.026	0.414
0.40	28.2	50.3	2.998	0.556
0.50	30.8	47.8	4.045	0.695
0.60	33.1	45.4	5.244	0.829
0.80	37.1	41.2	8.028	1.082
0.90	39.0	39.4	9.587	1.201
1.00	40.8	37.7	11.276	1.315
1.20	44.0	34.7	14.954	1.530
1.40	47.0	31.9	19.171	1.720
1.60	49.4	29.5	23.730	1.894

TABLE I (continued)

1.80	51.8	27.2	28.824	2.046
2.00	53.8	25.2	34.214	2.176
2.20	55.5	23.8	39.279	2.318
2.50	58.0	21.5	48.024	2.476
2.80	60.0	19.8	56.576	2.632
3.10	61.9	18.1	65.920	2.744
3.50	63.8	16.4	78.004	2.894
4.00	65.9	14.5	93.781	3.025
4.50	67.8	13.1	108.96	3.154
5.00	69.2	11.9	124.16	3.253
6.00	71.6	10.0	153.93	3.396
7.00	73.7	8.7	181.64	3.502

The formation curves, representing $\bar{n}$ as a function of pL = —log [L], of the investigated lanthanide complexes with methylethyl glycolate and with methylpropyl glycolate are reproduced in Figs. 1 and 2. It is obvious that 4 ligands per metal ion present are bound, except for lanthanum(III), showing the formation of ML_4^- complexes.

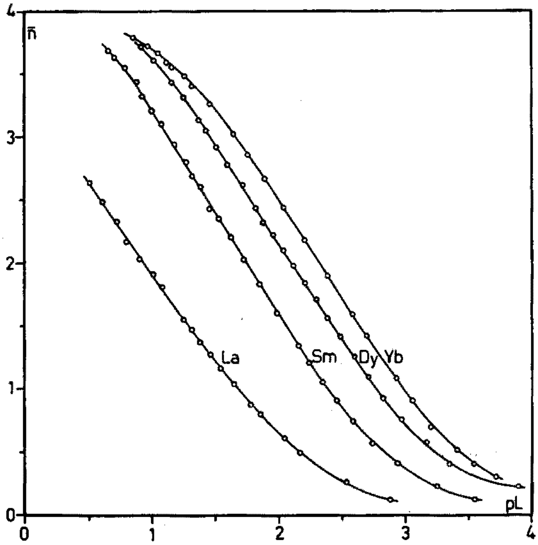

Fig. 1. Formation curves of some lanthanide–methylethyl glycolate complex systems at 25.0°.

Titrations performed at different metal-ion concentrations with both methylethyl glycolate and methylpropyl glycolate showed that no polynuclear complexes were formed with the lanthanide elements. This agrees with similar observations for the glycolate[4], lactate and α-hydroxyisobutyrate complexes[5].

Approximate values of the stability constants are read directly from the formation curves, using BJERRUM's half $\bar{n}$-method: the logarithms of K_1, K_2, K_3 and K_4 are approximately given by the values of pL at $\bar{n}$ = 1/2, 3/2, 5/2 and 7/2 respectively (Tables IIa and IIIa).

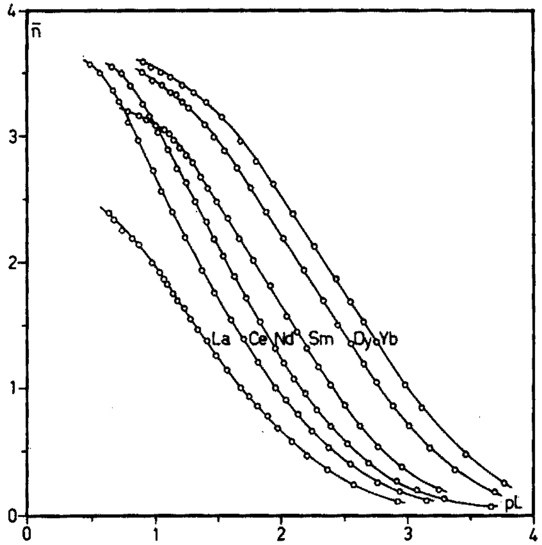

Fig. 2. Formation curves of some lanthanide–methylpropyl glycolate complex systems at 25.0°.

TABLE II

STABILITY CONSTANTS OF SOME LANTHANIDE–METHYLETHYL GLYCOLATE COMPLEX SYSTEMS AT 25.0°

Element	*log K_1*	*log K_2*	*log K_3*	*log K_4*	*log β_4*
Half $\bar{n}$-values					
La	2.16	1.29	0.57	—	4.02[a]
Sm	2.80	2.05	1.44	0.81	7.10
Dy	3.22	2.43	1.78	1.12	8.55
Yb	3.40	2.65	1.98	1.22	9.25
Calculated by computer					
La	2.01 ± 0.025	1.26 ± 0.03	0.62 ± 0.05	—	3.89 ± 0.065[a]
Sm	2.60 ± 0.04	2.14 ± 0.04	1.26 ± 0.05	1.14 ± 0.04	7.14 ± 0.085
Dy	3.03 ± 0.03	2.48 ± 0.03	1.66 ± 0.04	1.37 ± 0.03	8.54 ± 0.07
Yb	3.20 ± 0.015	2.67 ± 0.015	1.98 ± 0.015	1.42 ± 0.01	9.27 ± 0.03

[a] log β_3.

Corresponding values of $\bar{n}$ and [L] together with these approximate constants were introduced into eqn. (5) to calculate the constants and their standard deviations, using an IBM 1620 digital computer. The results are given in Tables II and III. In this investigation, 24 $\bar{n}$ and [L] pairs were always used in the calculation, as shown in Table I.

The abnormal course of the formation curve of the samarium(III)–methylpropyl glycolate complex system for $\bar{n}$-values exceeding 3 is due to the precipitation of the complex. No $\bar{n}$-values larger than 3 were taken into account for the computed stability constants of this system (Table III).

TABLE III

STABILITY CONSTANTS OF SOME LANTHANIDE–METHYLETHYL GLYCOLATE COMPLEX SYSTEMS AT 25.0°

Element	*log K_1*	*log K_2*	*log K_3*	*log K_4*	*log β_4*
Half $\bar{n}$-values					
La	2.16	1.31	0.50	—	3.97[a]
Ce	2.40	1.63	1.08	0.58	5.70
Nd	2.58	1.85	1.31	0.73	6.47
Sm	2.79	2.09	1.47	0.77[b]	7.12
Dy	3.19	2.45	1.79	0.92	8.35
Yb	3.42	2.66	2.01	1.06	9.15
Calculated by computer					
La	2.20 ± 0.01	1.25 ± 0.01	0.77 ± 0.015	—	4.22 ± 0.02[a]
Ce	2.21 ± 0.01	1.66 ± 0.02	1.03 ± 0.02	0.81 ± 0.03	5.71 ± 0.04
Nd	2.38 ± 0.015	1.85 ± 0.015	1.17 ± 0.02	1.06 ± 0.02	6.46 ± 0.03
Sm	2.59 ± 0.01	2.12 ± 0.01	1.50 ± 0.01	(0.86 ± 0.015)	7.07 ± 0.02
Dy	3.00 ± 0.015	2.47 ± 0.015	1.86 ± 0.02	1.12 ± 0.015	8.45 ± 0.03
Yb	3.29 ± 0.08	2.55 ± 0.09	2.21 ± 0.08	1.12 ± 0.05	9.17 ± 0.15

[a] log β_3.
[b] Extrapolated value.

The stability constants listed in Tables II and III, are close to the values of the corresponding α-hydroxyisobutyrate complex systems.

In the literature, the constants of the lanthanide–α-hydroxyisobutyrate systems are given at a temperature of 25.0° and ionic strengths of 2.0[5] and 0.2[6]. For comparison, some stability constants were also determined at an ionic strength of 1.0. The results calculated by computer and reproduced in Table IV agree with the constants at ionic strengths of 2.0 and 0.2.

TABLE IV

STABILITY CONSTANTS OF SOME LANTHANIDE–α-HYDROXYISOBUTYRATE COMPLEX SYSTEMS AT 25.0°

Element	*log K_1*	*log K_2*	*log K_3*	*log K_4*	*log β_4*
La	2.16	1.47	0.75	0.46	4.84
Sm	2.63	2.13	1.33	1.15	7.24
Dy	2.83	2.50	1.72	1.28	8.33
Yb	3.00	2.79	2.09	1.65	9.53

The ratios of the stability constants for the methylethyl glycolate and the methylpropyl glycolate complex systems do not appear to be more favourable than for the α-hydroxyisobutyrate systems. Consequently no improvement of the separation of the lanthanides by cation-exchange chromatography is to be expected.

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SUMMARY

The 4 successive stability constants have been determined for the methylethyl glycolate and methylpropyl glycolate complexes of some lanthanide elements by potentiometric titration. For all the metal ions, except lanthanum, the average ligand number exceeds a value of 3 indicating the formation of uninegative tetra-ligand complexes, ML_4^-. The stability constants are close to the values of the corresponding α-hydroxyisobutyrate complex systems.

RÉSUMÉ

Les auteurs ont effectué des déterminations de constantes de stabilité des complexes méthyléthylglycolates et méthylpropylglycolates de certains éléments lanthanides, par titrage potentiométrique. Pour tous ces métaux, à l'exception du lanthane, le nombre de particules complexantes dépasse trois indiquant la formation de complexes du type ML_4^-.

ZUSAMMENFASSUNG

Die Stabilitätskonstanten der Komplexe des Methyläthyl- und des Methylpropyl-Glykolats einiger Elemente der Lanthanreihe wurden mit Hilfe der potentiometrischen Titration untersucht. Für alle Metallionen, ausser denen des Lanthans, überschritt die mittlere Ligandenzahl den Wert drei. Das weist auf die Bildung von ML_4^- hin. Die Stabilitätskonstanten sind ähnlich den Werten der korrespondierenden α-Hydroxyisobutyrat-Komplexe.

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THE DETERMINATION OF SILVER IN ALUMINIUM ALLOYS BY ATOMIC ABSORPTION SPECTROSCOPY

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Experiments carried out in these laboratories[1] have shown that the addition of small quantities of silver (less than 0.5%) may have a pronounced effect on the structure and properties of certain aluminium alloys. These results have both theoretical and practical implications and a comprehensive investigation of these effects is in progress. Silver additions have been made to several alloy systems including aluminium–magnesium, aluminium–zinc–magnesium–copper, and also to some commercial alloys.

Originally the method used for the determination of silver in these alloys was a slightly modified version of the well-known VOLHARD thiocyanate titration[2]. It consisted of a preliminary separation of the silver, magnesium, manganese, copper, etc. from the bulk of the sample by precipitation from a sodium hydroxide–sodium carbonate solution. The precipitate obtained was dissolved in dilute nitric acid and the silver determined by titration with thiocyanate solution using ferric alum as indicator. Although this method has proved to be generally satisfactory, difficulties have been encountered in detecting the end-point of the titration, particularly when the ratio of copper to silver in the alloy has been high.

This paper describes experiments carried out to determine whether atomic absorption spectroscopy could be usefully applied to the determination of the quantities of silver added to these alloys.

EXPERIMENTAL

Apparatus

The atomic absorption spectrophotometer used was essentially the same as that described by BOX AND WALSH[3] except that the dispersing unit used in the A.R.L. spectrophotometer was a Zeiss monochromator (Model M4Q III).

The silver hollow-cathode tube was supplied by Ramsley Glass Instruments, Melbourne, Australia.

Reagents

Standard silver solution (1). 0.5 g of 99.99% silver dissolved in 10 ml of 50% nitric acid, boiled, cooled, and diluted to 500 ml with distilled water.

Standard silver solution (2). 100.0 ml of standard silver solution 1 diluted to 1 l with distilled water. 1 ml of this solution contained 0.0001 g of silver, and when diluted to 100.0 ml corresponded to a silver concentration of 1 part per million.

Optimum instrument settings

Investigation of the strong emission lines listed by BRODE[4] for silver revealed that only those lines at 328.1 mμ and 338.2 mμ show any appreciable absorption when tested with a solution containing 50 p.p.m. of silver.

Plots of absorbance *vs.* concentration of silver over the range 0 to 70 p.p.m. of silver were obtained for both these lines (Fig. 1). These graphs show that the silver line at 328.1 mμ is more sensitive in absorption (as, incidentally, it is in emission) than the line at 338.2 mμ. It can also be seen that the relationship between absorbance and concentration is linear up to about 30 p.p.m. of silver. The tailing-off of the curve above this value is presumably due to resonance broadening of the absorption line.

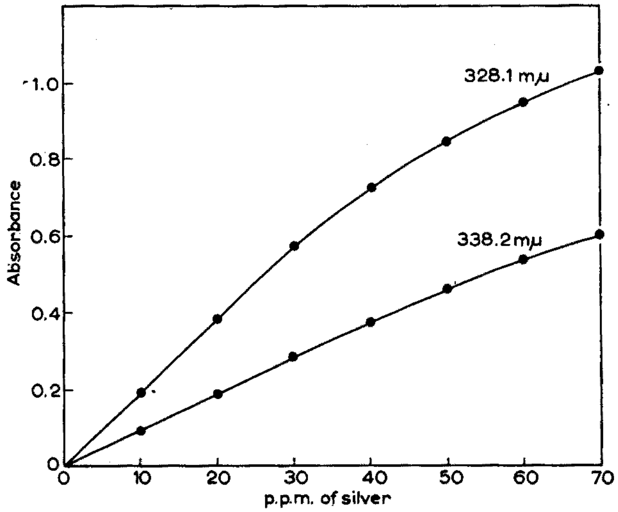

Fig. 1. Typical calibration curves for silver using the absorption lines at 328 mμ and 338 mμ.

In view of these results it was decided to use the 328.1 mμ line for the determination of silver in aluminium alloys. Also, since the concentration of silver used in the study of these alloys varied between 0.1 and 1.0 per cent, 0.5 g was chosen as the optimum sample weight. This corresponds to a range of 5 to 50 p.p.m. of silver.

The optimum hollow-cathode tube operating current and the optimum slit width were found to be 5 mA and 0.05 mm respectively.

An air–coal gas mixture was used with the air pressure kept constant at 15 lbs/square inch and the gas pressure adjusted to give a non-luminous flame. As predicted by WALSH[5], fairly wide variations in air and gas pressures had little effect on the absorption.

Other types of flame such as air–acetylene, oxygen–hydrogen, etc. were not tested.

Tests for interference

At this stage, the proposed method for determining silver in aluminium alloys was to dissolve 0.5 g of the sample in sodium hydroxide, acidify with nitric acid, dilute to 100.0 ml with water, measure the absorption of the solution, and convert this to per cent silver from a calibration graph prepared using solutions made by appropriate dilutions of standard silver solution 2. It was therefore necessary to consider the effects (if any) of nitric acid and sodium as well as the elements likely to be encountered in the alloys.

(a) Effects of nitric acid and sodium. It was found by experiment that at least 8–10 ml of concentrated nitric acid had to be added to 0.5 g of aluminium dissolved in 20 ml of 20% sodium hydroxide to produce a clear acid solution.

Absorbance measurements (Table I and Fig. 2) were obtained from 3 sets of solu-

TABLE I

EFFECT OF NITRIC ACID AND SODIUM ON THE ABSORBANCE OF SILVER

p.p.m. Ag	*Aqueous solution*		*10% Nitric acid solution*		*10 ml Conc. nitric acid plus 20 ml 10% sodium hydroxide per 100 ml*	
	Meter reading	*Absorbance*	*Meter reading*	*Absorbance*	*Meter reading*	*Absorbance*
10	64.5	0.190	66.5	0.178	66.5	0.178
20	42.0	0.377	44.0	0.357	44.0	0.357
30	27.0	0.569	29.0	0.538	29.0	0.538
40	19.0	0.721	21.0	0.678	21.0	0.678
50	14.5	0.839	16.0	0.796	16.5	0.782
60	11.5	0.939	13.0	0.886	12.5	0.903
70	9.5	1.022	10.5	0.978	10.5	0.978

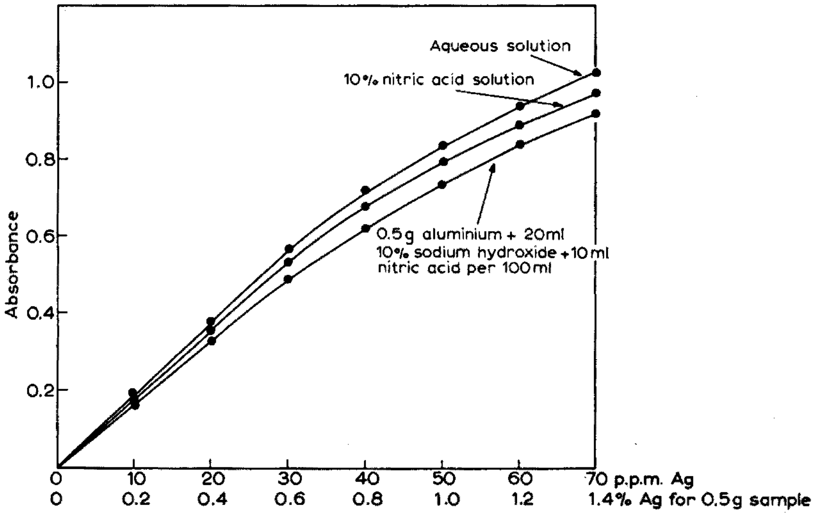

Fig. 2. Effect of nitric acid, sodium, and aluminium on the absorbance of silver.

tions containing 10, 20, 30, 40, 50, 60 and 70 p.p.m. of silver in (*1*) aqueous solution, (*2*) 10% nitric acid solution, (*3*) solutions containing 20 ml of 10% sodium hydroxide and 10 ml of nitric acid per 100 ml.

These figures show that the presence of 10% nitric acid causes a reduction in absorbance over the entire concentration range studied. Also, since the results obtained with the solutions containing both nitric acid and sodium hydroxide are practically identical to those obtained with the nitric acid solutions, it can be seen that the presence of sodium has no appreciable effect on the absorbance due to silver.

The effect of varying concentrations of nitric acid was then investigated by measuring the absorbance of solutions containing 20 p.p.m. of silver in 0, 2.5, 5, 7.5, 10, 12.5, 15, 17.5, and 20 per cent nitric acid. The average values of 3 sets of results (Table II) show a small but definite decrease in absorbance with increasing concentration of nitric acid. However, the difference in absorption caused by 2.5 ml of nitric acid is never larger than could reasonably be expected from normal experimental errors. For these reasons it was decided to make the standard silver solutions used for calibration 10% with respect to nitric acid and to specify that the amount of nitric acid to be used in preparation of samples for analysis should be such that the final concentration is 10 ± 1%.

TABLE II

EFFECT OF VARYING CONCENTRATIONS OF NITRIC ACID ON THE ABSORBANCE OF A SOLUTION CONTAINING 20 p.p.m. OF SILVER

% Nitric acid	*20 p.p.m. silver solution*	
	Meter reading	*Absorbance*
0	42.0	0.377
2.5	43.0	0.367
5.0	43.5	0.362
7.5	44.0	0.357
10.0	44.0	0.357
12.5	44.0	0.352
15.0	44.5	0.347
17.5	45.5	0.342
20.0	46.0	0.337

(b) Effects of elements present in the alloys. (1) Matrix element. The effect of aluminium was studied by comparing the absorbance of silver solutions containing 10% nitric acid over the range 0 to 70 p.p.m. of silver with the absorbance obtained from similar silver solutions to each of which had been added 0.5 g of super pure aluminium (the proposed sample weight) dissolved in 20 ml of 10% sodium hydroxide. The final volume of the solutions was 100.0 ml. The resultant calibration curves (Fig. 2) showed that the presence of aluminium caused an appreciable reduction in absorbance over the entire range.

Three techniques were considered for the elimination of this interference. (*a*) Complete removal of the aluminium. (*b*) Suppression of the interference by the addition of another element or compound which would prevent formation of compounds between the interfering element and the element being determined. (*c*) Inclusion of the same quantity of aluminium in the standard solutions used for the preparation of the working curves as in the sample solutions.

In this case, the first alternative was considered unsatisfactory for two reasons. Firstly, it meant the introduction of another step in the method with a consequent increase in the time required to complete a determination and, secondly, tests showed that it was almost impossible to remove all the aluminium by a single precipitation with sodium hydroxide. The addition of a suppressor was not attempted since the solutions under consideration already had a high salt concentration and it was thought that the addition of still more salts would greatly increase the tendency of the atomiser capillary to clog.

For these reasons it was decided to use the technique of adding 0.5 g of aluminium per 100 ml to the standard silver solutions since although this involves some initial inconvenience in their preparation the same set can be used for many different batches of samples.

(2) Alloying elements. The maximum concentrations of minor elements in the alloys studied in these experiments were zinc 10%, magnesium 7%, copper 5%, manganese 0.5%, chromium 0.3%, titanium 0.5%, iron 1.5% and nickel 1.5%. However, the following tests were carried out to ascertain the effect of the presence of 10% of each of these elements on the absorbance of solutions containing 10 and 50 p.p.m. of silver. For zinc, magnesium, copper, manganese, iron and nickel two 0.05-g portions of the spectrographically pure element were each dissolved in 10 ml of concentrated nitric acid and added to 100-ml standard flasks containing 10 and 50 ml of standard silver solution 2. These solutions were then diluted to 100 ml with distilled water. In the case of chromium and titanium, the initial solution was made in 3 ml of 25% sulphuric acid solution, as these elements would not dissolve directly in the nitric acid. The absorbance of all these solutions, as well as two solutions containing 10 and 50 p.p.m. of silver in 10% nitric acid, was then measured. The results (Table III) show that none of these elements, at least in these concentrations, have any significant effect on the absorbance of silver.

TABLE III

EFFECT OF ALLOY ELEMENTS ON THE ABSORBANCE OF SILVER

Alloy element (0.05 g/100 ml) added to 10% nitric acid silver solutions	*10 p.p.m. Silver*		*50 p.p.m. Silver*	
	Meter reading	*Absorbance*	*Meter reading*	*Absorbance*
Nil	67	0.174	16.5	0.782
Zinc	67	0.174	16.5	0.782
Magnesium	67	0.174	16.5	0.782
Copper	67	0.174	16.5	0.782
Manganese	67	0.174	16.5	0.782
Iron	67	0.174	16.5	0.782
Nickel	67	0.174	16.5	0.782
Chromium	67	0.174	16.5	0.782
Titanium	67.5	0.171	17.0	0.770

RECOMMENDED PROCEDURE

Preparation of working curve

To seven beakers, each of which contains 0.5 g of super-pure aluminium, add 10, 20, 30, 40, 50, 60 and 70 ml of standard silver solution 2. Add 20 ml of 10% sodium hydroxide solution and warm till dissolution is complete. Cool, wash down the sides of the beaker, and add 10 ± 1 ml of concentrated nitric acid. Boil until the solution is clear. Cool to room temperature and dilute to 100 ml in a standard flask. Measure the absorbance of each solution and plot absorbance *vs.* concentration of silver.

Analysis of aluminium alloys

Weigh out 0.5 g of sample, add 20 ml of 10% sodium hydroxide and proceed as in preparation of working curve.

Measure the absorbance and read off the percentage silver from the working curve. (Note that 10 p.p.m. of silver corresponds to 0.2% silver for a 0.5-g sample.)

Application of recommended procedure

A number of alloys which had previously been analysed for silver by the VOLHARD

TABLE IV

COMPARISON OF RESULTS OBTAINED BY ATOMIC ABSORPTION WITH THOSE OBTAINED BY THE VOLUMETRIC PROCEDURE

Alloy designation	*Nominal composition*	*% Silver found*					
		Volhard method Analyst			*Atomic absorption*		
		A	*B*	*C*			
DSA	5 Zn 3 Mg 0.5 Ag	0.51			0.53	0.52	0.53
USA	10 Zn 1 Mg 0.5 Ag	0.48			0.53	0.52	0.52
VSA	6 Zn 2 Mg 0.5 Ag	0.51			0.54	0.53	0.53
YSA	6 Zn 4 Mg 0.5 Ag	0.53			0.53	0.53	0.54
WSA	3 Zn 5 Mg 0.5 Ag	0.53			0.53	0.53	0.53
GSB	4 Zn 3 Mg 1.0 Ag	0.93			0.93	0.92	0.91
R.R.S.	2.5 Cu 1.5 Mg 1.0 Fe 1.2 Ni 0.1 Ti 0.5 Ag	0.49			0.48	0.49	0.48
CA	4 Cu 0.3 Ag		0.31		0.30	0.30	0.30
PA	5 Mg 0.2 Mn 0.5 Ag		0.50		0.50	0.51	0.50
MSI	5 Mg 0.1 Ag		0.10		0.10	0.10	0.10
XD	5.8 Zn 2.4 Mg 0.3 Mn 1.4 Cu 0.05 Ti 0.2 Si 0.25 Fe 0.1 Cr 0.1 Ag		0.10		0.10	0.10	0.10
391	5.8 Zn 2.9 Mg 1.2 Cu 0.06 Ti 0.23 Fe 0.08 Si 0.25 Ag			0.25	0.28	0.27	0.27
397	5.7 Zn 2.7 Mg 1.1 Cu 0.4 Mn 0.06 Ti 0.23 Fe 0.1 Si 0.25 Ag			0.26	0.26	0.26	0.26
398	5.7 Zn 2.8 Mg 1.2 Cu 0.25 Cr 0.06 Ti 0.23 Fe 0.1 Si 0.25 Ag			0.25	0.26	0.27	0.27
399	5.7 Zn 2.7 Mg 1.1 Cu 0.2 Mn 0.2 Cr 0.06 Ti 0.24 Fe 0.25 Ag			0.24	0.26	0.27	0.26
400	5.7 Zn 2.8 Mg 1.2 Cu 0.25 Mn 0.20 Cr 0.06 Ti 0.25 Fe 0.1 Si 0.75 Ag			0.72	0.70	0.70	0.71

ANALYTIK DER POLYACRYLNITRILFASERN*

V. ÜBER EINE ABGEWANDELTE REDUKTIONSMETHODE ZUR BESTIMMUNG GERINGER SCHWEFELMENGEN IN ACRYLNITRILPOLYMERISATEN

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Über verschiedene Möglichkeiten der Schwefelbestimmung in Acrylnitrilpolymeren war kürzlich von uns berichtet worden[1]. Die dort beschriebene Kombination von SCHÖNIGER-Verbrennung und indirekter komplexometrischer Sulfatbestimmung[1,2] mittels Zinkkomplexonat bewährte sich gut bei grösseren Schwefelgehalten, wie sie beispielsweise in Copolymeren mit einer schwefelhaltigen Cokomponente (Allylsulfonat) vorliegen. Bei Reinpolymeren mit Schwefelgehalten unter 0.1% dagegen ist diese Methode nicht empfindlich genug, und auch die von uns ebenfalls erfolgreich angewandte Kombination von nassem Aufschluss mit HNO_3-HClO_4 und nephelometrischer Endbestimmung[1,3] scheidet aus, wenn nur kleine Probemengen zur Verfügung stehen. Die unter diesen Konzentrationsbedingungen an sich geeignete Methylenblaumethode nach vorheriger SCHÖNIGER-Verbrennung hatte zwar in der Ausführungsform nach GUSTAFSSON[4] seinerzeit bei einigen vergleichsweise vorgenommenen Bestimmungen[3] zu brauchbaren Ergebnissen geführt; sie versagte jedoch bei einer serienmässigen Anwendung, da unreproduzierbare und zumeist recht hohe Blindwerte beobachtet wurden. Nach unseren Erfahrungen waren diese kaum auf eine ungenügende Reinheit der eingesetzten Chemikalien (einschliesslich des zur Verbrennung benutzten Filterpapiers) zurückzuführen, sondern vielmehr in erster Linie auf schwefelhaltige Verunreinigungen (SO_2, H_2S) aus der Atmosphäre, die bei den verhältnismässig vielen Manipulationen (Einengen, Umfüllen, Ausspülen) von der SCHÖNIGER-Verbrennung bis zur Methylenblaubildung aus der Laborluft aufgenommen wurden. Da gerade in Kunstfaserkombinaten mit dieser Komplikation bei einer Bestimmung von Schwefelspuren stets gerechnet werden muss, entwickelten wir eine Arbeitsmethodik, bei der die Probe vom Aufschluss bis zur Endbestimmung kaum mit der Atmosphäre in Berührung kommt und nur eine einzige Umfülloperation erforderlich ist. Hierbei konnte die unserer Auffassung nach vorteilhafte Reduktion des Schwefels zu H_2S mit Hypophosphit beibehalten werden, während der SCHÖNIGER-Aufschluss durch eine thermische Zersetzung mit KOH ersetzt wurde, und die End-

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* IV. U. BARTELS UND H. HOYME, Zur Reinheitskontrolle von Natrium-Allylsulfonat und seiner Bestimmung neben anderen monomeren Acrylverbindungen, *Faserforsch. Textiltech.*, im Druck.

bestimmung des H_2S nicht über Methylenblau, sondern durch Polarographieren der anodischen Sulfidstufe bzw. durch potentiometrische Titration vorgenommen wurde. Über die Entwicklung dieser Methode und die bisher gewonnenen Erfahrungen soll im folgenden berichtet werden.

ZUR POLAROGRAPHISCHEN BZW. POTENTIOMETRISCHEN SCHWEFELBESTIMMUNG ALS SULFID NACH REDUKTION MIT HYPOPHOSPHIT

Zur Reduktion wandten wir im Prinzip die Hypophosphitmethode von GUSTAFSSON[4] an, wobei in apparativer Hinsicht einige Veränderungen vorgenommen wurden: die erste wassergefüllte Vorlage wurde weggelassen und die eigentliche Absorptionsvorlage wie auch der Kühleransatz etwas umgestaltet. Fig. 1 zeigt die von uns benutzte, sehr leicht zu handhabende Apparatur, bei deren Verwendung nach unseren Erfahrungen H_2S-Verluste durch unvollständiges Übertreiben ausgeschlossen sind und auch keine Möglichkeit zur Sulfidoxydation durch Luftsauerstoff besteht, da die gesamte Reduktion unter N_2-Atmosphäre erfolgt und anschliessend der in einer mit 1 *N* NaOH gefüllten Absorptionsvorlage als Na_2S vorliegende Schwefel sofort polarographiert oder potentiometrisch titriert wird. Zur Abdichtung der Schliffe bewährte sich konzentrierte (*ca.* 85%ige) Phosphorsäure. Wie Kontrollversuche ergaben, reicht unter den in der "Arbeitsvorschrift" angegebenen Bedingungen *eine* Sorptionsvorlage zur vollständigen Bindung des im N_2-Strom übergehenden H_2S auf jeden Fall aus. Es ist im Prinzip durchaus möglich, die Sorptionsvorlage selbst gleich als polarographische Zelle oder als Titrationsgefäss zu verwenden und so jedes Umfüllen zu vermeiden; nach unserer Erfahrung führt jedoch ein einmaliges Umfüllen aus der unter

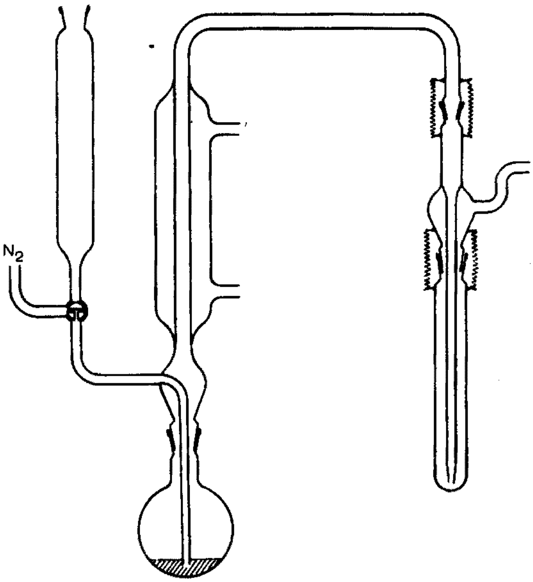

Fig. 1. Reduktionsapparatur.

N_2-Atmosphäre stehenden Vorlage in die polarographische Zelle zu keiner Änderung der polarographischen Stufenhöhe, wenn anschliessend sofort wieder entlüftet und dann gleich polarographiert wird. Für die praktische Anwendung der Methodik sei an dieser Stelle der an sich triviale Hinweis gegeben, dass die Apparatur auf keinen Fall entsprechend der üblichen Laborpraxis mit Chromschwefelsäure gereinigt werden darf, da sonst auch nach gründlichem Nachwaschen mit Wasser über längere Zeit hohe, unreproduzierbare Blindwerte auftreten. Bewährt hat sich ein Auswaschen mit destilliertem Wasser und Nachspülen mit entionisiertem Wasser.

Die Polarogramme wurden mit dem Heyrovský-Polarographen "LP 55" der Firma Pristroje, Praha, MPSt aufgenommen, wobei eine gesättigte Calomelelektrode als Gegenelektrode diente und die Tropfzeit 3 Sek betrug. Vermessen wurde die anodische Sulfidstufe (vergl.[5]) gegen die Galvanometergrundlinie bei — 0.6 V.

Vorversuche zeigten, dass auch nach 30 Min langem Kochen der aus Eisessig, Jodwasserstoffsäure und Hypophosphit bestehenden "Reduktionsmischung" durch die mit dem N_2-Strom übergehenden Dämpfe der Grundstrom der NaOH-Lösung in dem zur Auswertung herangezogenen Potentialbereich praktisch unbeeinflusst blieb und auch keine Änderung der Sulfidstufenhöhen erfolgte. Nur in einzelnen Fällen (nach längerem Kochen oder bei direkter Zugabe von Reduktionsgemisch zur Lauge) wurde eine bei positiveren Potentialen (— 0.3 bis — 0.4 V) beginnende und auf die Sulfidstufe aufbauende anodische Stufe beobachtet, die offenbar eine Jodid-Fällungsstufe darstellt, aber die Auswertung der Sulfidstufe in keiner Weise beeinträchtigte. Zur Prüfung unserer Methodik wurden zunächst definierte Mengen einer Sulfidlösung bekannten Gehaltes sowohl direkt polarographiert, als auch mit "Reduktionsmischung" gekocht und der H_2S im N_2-Strom in die Vorlage übergetrieben und dann polarographiert, wobei das Sulfid quantitativ wiedergefunden wurde. Nun führten wir eine Messreihe mit verschiedenen Mengen an Sulfat durch, indem 15–80 μg Schwefel entsprechende Volumina einer Na_2SO_4-Standardlösung in das Reduktionskölbchen gebracht und in einem kräftigen Stickstoffstrom völlig zur Trockene eingeengt wurden. Nach Abkühlen wurde, ebenfalls unter dauerndem Durchspülen mit N_2, 5 ml Reduktionslösung mittels Gummigebläse in das nun an die Apparatur angeschlossene Kölbchen gedrückt und nach 5 Min langem Entlüften bei einem N_2-Strom von 2–3 Blasen/Sek 25 Min gekocht, was zur quantitativen Reduktion des Sulfats und zum Übertreiben des H_2S in die vorgelegte NaOH auf jeden Fall ausreichte. Die Absorptionslösung war dann, je nach eingesetzter Sulfatmenge, $2 \cdot 10^{-5}$ bis $2 \cdot 10^{-4}$ M an Sulfid und wurde stets sofort polarographiert. Wie Fig. 2 zeigt, ist zwischen der "direkten Eichkurve für Sulfid" und den durch Reduktion definierter Sulfatmengen gefundenen Schwefelwerten eine systematische Abweichung mit Sicherheit nicht vorhanden, so dass die vorgeschlagene Methode zur Bestimmung von als Sulfat vorliegenden Schwefelmengen zwischen etwa 15 und 80 μg brauchbar erscheint.

Wir prüften ausserdem die Möglichkeit, das Sulfid in den hier vorliegenden Konzentrationen und Mengen potentiometrisch zu titrieren. Im Prinzip behielten wir die zur Bestimmung einer Reihe sulfidischer Anionen (Sulfid, Thiocarbonate[6], Xanthogenate[7], Thiocarbaminate[8]) bewährte Titrationsmethode mit $HgCl_2$ als Masslösung und einem amalgamierten Silberdraht als Indikatorelektrode bei. Als Masslösung diente eine durch Verdünnen einer gegen KJ eingestellten 0.01 M Lösung bereitete 0.001 M Lösung von Mercurichlorid, die aus einer 2-ml Bürette zugegeben wurde. Um das Elektrodensystem auf recht kleinem Raum unterzubringen und mögliche

Störungen durch Diffusionsvorgänge zu vermeiden, wurde als Bezugselektrode nicht die sonst übliche Calomelelektrode verwendet, sondern ein in die Lösung tauchender Draht aus Edelstahl V 2 A (ø 2 mm, Eintauchtiefe 4 cm). Wie die Titrationskurven in Fig. 3 zeigen, ändert sich in dem hier vorliegenden alkalischen und im pH-Wert

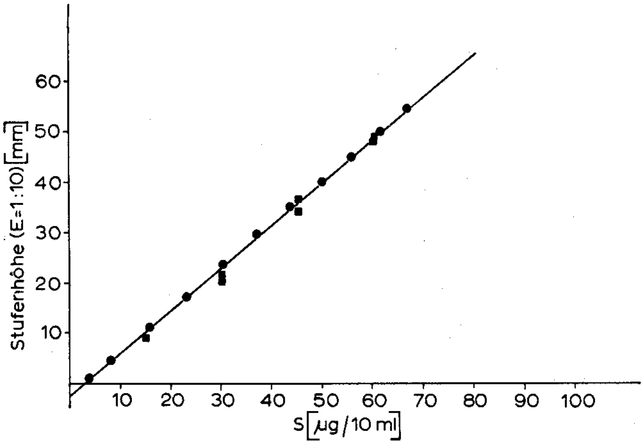

Fig. 2. Eichkurve für die polarographische Sulfidbestimmung (● Sulfid direkt; ■ Reduktion von Sulfat).

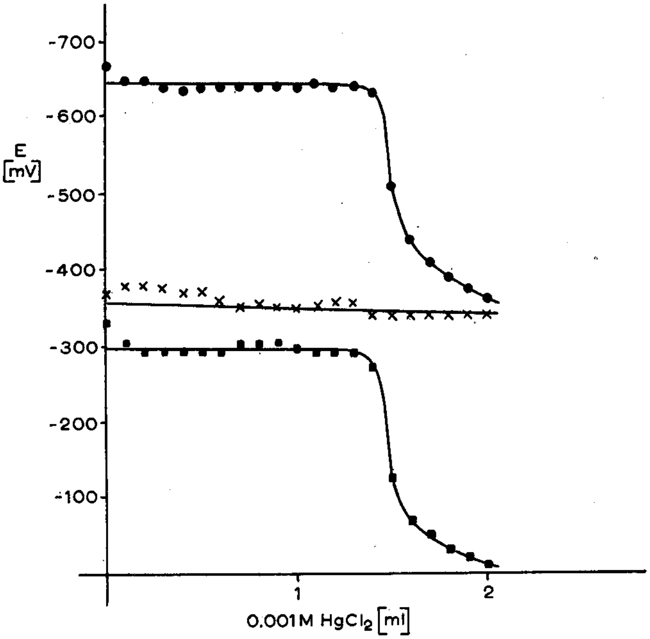

Fig. 3. Potentialverlauf während einer Titration von S^{2-} mit 0.001 *M* $HgCl_2$-Lösung für verschiedene Elektrodensysteme (● Ag-Hg gegen Calomelelektrode; × Stahl gegen Calomelelektrode; ■ Ag-Hg gegen Stahl).

praktisch konstanten Medium das Potential einer solchen Stahlelektrode während einer Sulfidtitration nur verhältnismässig wenig und ohne ausgeprägten Sprung, obwohl die Ausfällung des Sulfids mit einer starken Änderung des pH-Wertes verbunden ist. Mit der Kette Ag–Hg/Lösung/Stahldraht wird daher ein sehr steiler, durch die Potentialänderung der Silberelektrode bestimmter Potentialsprung erhalten.

Zur Bestimmung des in der vorgelegten 1 *N* NaOH vorhandenen Sulfids wurde nach beendeter Reduktion das Absorptionsgefäss ohne Umfüllen der Lösung auf einen nach Mass hergestellten Stopfen aus Polytetrafluoräthylen ("Heydeflon") geschoben, der zwei Bohrungen für die Elektroden, eine für das ausgezogene Hahnküken der Mikrobürette und eine für das Stickstoffeinleitungsrohr enthielt. Die Titration erfolgte unmittelbar nach der Reduktion unter Rührung mit einem lebhaften Stickstoffstrom. Als Anzeigeinstrument diente ein pH-Messverstärker MV 11 der Firma Clamann und Grahnert, Dresden. Die Potentialänderung im Äquivalenzpunkt betrug *ca.* 150 mV bei Zusatz von 0.05 ml 0.001 *M* $HgCl_2$ und einem Verbrauch von *ca.* 1.5 ml, sowohl nach Reduktion reiner Sulfatlösung, als auch nach dem Aufschliessen und Reduzieren schwefelhaltiger Polymerisate. Ein geringfügiger Reagentienblindwert ist gegebenenfalls zu berücksichtigen. Tabelle I zeigt anhand eines Vergleichs die gute Übereinstimmung zwischen polarographischer und potentiometrischer Sulfidbestimmung, wobei für diese Messungen von *einer* sulfidhaltigen NaOH-Vorlage definierte Mengen sowohl für die Polarographie wie für die Potentiometrie abpipettiert und sofort untersucht wurden.

TABELLE I

VERGLEICH DER POLAROGRAPHISCHEN UND DER POTENTIOMETRISCHEN SULFIDBESTIMMUNG

µg S (polarographisch)	*µg S (potentiometrisch)*
44.2	47.4
49.6	50.0
97.0	98.6
65.2	64.8
67.1	65.5
64.7	64.2
59.3	60.5

ZUR FESTLEGUNG EINER GEEIGNETEN AUFSCHLUSSMETHODE FÜR DIE POLAROGRAPHISCHE BZW. POTENTIOMETRISCHE SCHWEFELBESTIMMUNG IN ACRYLNITRIL

Vorversuche ergaben, dass Acrylnitrilpolymerisate mit "Reduktionsmischung" zwar weitgehend gelöst wurden, jedoch polarographisch nur etwa die Hälfte des komplexometrisch oder gravimetrisch nach nassem, oxydativem Aufschluss ermittelten Schwefelgehaltes gefunden wurde. Die Anwendung des bewährten oxydativen Nassaufschlusses mit HNO_3–$HClO_4$ erschien unzweckmässig, da vor der Reduktion eine vollständige Entfernung des überschüssigen Oxydationsmittels erforderlich wäre, ohne dass dabei die entstandenen geringen Schwefelsäuremengen mit abdestillieren dürfen, was sich experimentell kaum verwirklichen lässt. Versuche, die Verbrennung im sauerstoffgefüllten Kolben nach SCHÖNIGER mit der Hypophosphitreduktion und der polarographischen Endbestimmung zu kombinieren, führten bei den hier infrage kommenden geringen Schwefelmengen zu demselben unbefriedigenden Ergebnis wie die eingangs erwähnte Kombination SCHÖNIGER-Verbrennung–Methylenblaumethode: Während die "Chemikalienblindwerte" bei direktem Zusatz zur Reduktionsmischung nur Schwefelmengen zwischen 0 und 5 µg entsprachen, wurden bei Durchführung einer Leerverbrennung und üblicher Aufarbeitung der im Verbrennungskolben vorgelegten Sorptionsflüssigkeit stark schwankende Schwefelmengen zwischen 0 und *ca.* 40 µg vorgetäuscht. Werte mit der gleichen grossen Spannweite wurden übrigens auch gefunden beim Verbrennen eines Reinpolymerisats, dessen Schwefelgehalt aufgrund der Herstellungsbedingungen unter 0.01%, d.h. bei den hier angewandten Einwaagen unter 10 µg liegen musste.

Es erschien also zweckmässig, eine separate Verbrennung überhaupt zu vermeiden, und wir versuchten daher, die Analysensubstanzen durch eine Art "Ätzalkalischmelze" unmittelbar im Reduktionskolben aufzuschliessen: Unter Verwendung von Polymerisaten mit höherem, bekanntem Schwefelgehalt wurden *ca.* 50 µg S entsprechende Einwaagen im Reduktionskölbchen mit *ca.* 0.2 g festem KOH, *ca.* 3 ml entionisiertem Wasser und 20 Tropfen H_2O_2 (30%ig) versetzt. Unter N_2-Atmosphäre wurde dann zur Trockene gedampft und anschliessend 10 Min scharf erhitzt, wobei die Substanz weitgehend verkohlte. Nach Abkühlen unter N_2 erfolgten Reduktion und polarographische Bestimmung in der schon erwähnten Weise, wobei gegen die in Fig. 2 gezeigte, mit Na_2SO_4-Lösungen aufgestellte Eichkurve ausgewertet wurde.

Wie Tabelle II zeigt, wurden schon bei diesen Vorversuchen zwar stark streuende, aber mit den komplexometrischen Ergebnissen einigermassen übereinstimmende Werte erhalten. Unter Heranziehung des "schwefelfreien Reinpolymerisats" wurde nun zunächst wieder die Frage des "Blindwertes" geprüft und festgestellt, dass dieser in Grössenordnung und Spannweite mit Werten entsprechend 0 bis 7 µg Schwefel etwa den reinen Chemikalienblindwerten entsprach. Wenn damit auch nach wie vor die Genauigkeit der Methode durch die Schwankungen im Blindwert begrenzt wurde, so erschienen diese doch für das gesetzte Ziel einer Schwefelbestimmung im Bereich zwischen 0.01 und 0.2% bei Einwaagen in der Grössenordnung 50–100 mg noch akzeptabel. Anhand eines Polymerisats mit bekanntem, höherem S-Gehalt legten wir die geeignetsten Aufschlussbedingungen fest und ermittelten gleichzeitig die Reproduzierbarkeit unserer Methode, wobei die in Tabelle III angegebenen Schwefelgehalte über die in Fig. 4 dargestellte "Eichkurve bei Zusatz von S-freiem Polymeren" erhalten wurden.

TABELLE II

VERGLEICH VON KOMPLEXOMETRISCHER UND POLAROGRAPHISCHER S-BESTIMMUNG IN ACRYLNITRILPOLYMERISATEN

Probe Nr.	*% S (komplexometrisch)*		*% S (polarographisch)*			
1	0.304		0.382	0.336	0.278	0.265
2	0.124	0.151	0.178	0.170	0.137	0.122

Offensichtlich besteht zwischen den Mittelwerten der einzelnen Wertegruppen der Tabelle III kein signifikanter Unterschied. Der entscheidende Schritt beim Aufschluss ist auf jeden Fall das Erhitzen mit KOH bis zur Schmelze. Ein H_2O_2-Zusatz ist nicht unbedingt erforderlich, wurde jedoch von uns beibehalten, weil sich dann das Polymerisat beim Erwärmen mit der KOH stets glatt auflöste. Ebenso ist ein längeres Erhitzen der Analysenproben nach dem Einengen mit KOH bis zur Trockene bzw. Schmelze nicht unbedingt notwendig und wurde von uns auch bei den späteren Reihenversuchen mit normalen Einwaagen von *ca.* 30–80 mg unterlassen. Hingegen empfiehlt sich diese stärkere Pyrolyse, wenn zur Bestimmung sehr niedriger S-Gehalte unter 0.01% höhere Einwaagen von 200–500 mg aufgeschlossen wurden, da sonst in manchen Fällen aus der Reduktionsmischung in merklichem Umfange Jod frei wurde, was eine Bestimmung des Schwefels als Sulfid ausschliesst. Ein nochmaliges Auf-

TABELLE III

EINFLUSS DER AUFSCHLUSSBEDINGUNGEN AUF DEN POLAROGRAPHISCH ERMITTELTEN SCHWEFELGEHALT

(*Ca.* 35 mg Polymerisat + 0.3 g KOH + 3 ml entionisiertes Wasser)

Aufschlussbedingungen	*% S gefunden*			*Mittelwert*
Zur Trockene eingeengt	0.158	0.141		0.150
+ 20 Tropfen H_2O_2, zur Trockene eingeengt	0.157 0.128	0.144 0.158	0.156 0.145	0.148
+ 20 Tropfen H_2O_2, zur Trockene eingeengt, 10 Min scharf erhitzt	0.168	0.137	0.138	0.148
+ 20 Tropfen H_2O_2, zur Trockene eingeengt, 10 Min scharf erhitzt nochmals mit wenig Wasser und H_2O_2 aufgenommen und vorsichtig eingedampft	0.140 0.162	0.152	(0.181)	0.158
	Mittelwert = 0.151%			*s* = 0.014%

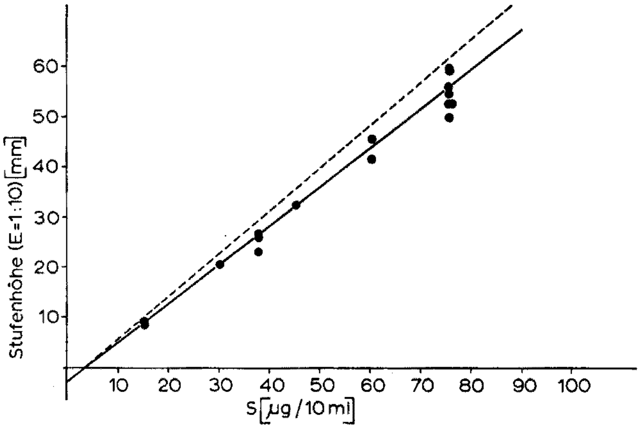

Fig. 4. Eichkurve für die polarographische Sulfidbestimmung (● mit Reinpolymerisatzusatz; – – – von Fig. 2).

nehmen mit Wasser und H_2O_2 nach der Pyrolyse ist bei solch hohen Einwaagen zweckmässig. Gerade zum Erkennen solcher Störungen, die sowohl bei hohen Einwaagen durch Zersetzungsprodukte des Polyacrylnitrils wie auch bei unsachgemässem Arbeiten durch Eindringen von Luftsauerstoff in die Apparatur gelegentlich auftraten, erweist sich die polarographische Endbestimmung als vorteilhaft, da dann der kathodische Teil des Polarogramms anders verläuft, weil die infrage kommenden Oxydationsprodukte des Sulfids (S bzw. S_x^{2-}) im Gegensatz zu Sulfid selbst kathodische Stufen liefern (vergl. Fig. 5). Der Mittelwert aller in Tabelle III angegebenen

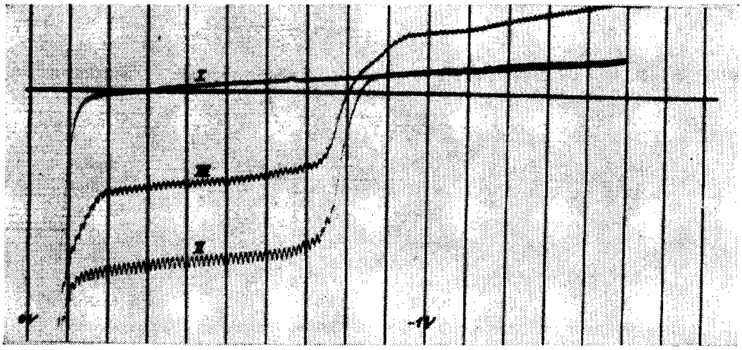

Fig. 5. Änderung der Sulfidstufe und des kathodischen Teils des Polarogramms durch Einwirkung von Luftsauerstoff (I, Grundstrom; II, Sulfidstufe; III, Sulfidstufe nach Einwirkung von Luftsauerstoff).

polarographischen Einzelbestimmungen betrug 0.151% S in recht guter Übereinstimmung mit dem durch nassen Aufschluss und gravimetrische Endbestimmung erhaltenen Wert von 0.159% S. Die relative Standardabweichung (Varianz) lag bei der hier entwickelten Methode unter Verwendung der Werte von Tabelle III bei $V = 9.2\%$ gegenüber 8.5% bei nassem Aufschluss und komplexometrischer Endbestimmung für S-Gehalte von *ca.* 0.15%. Hierbei ist allerdings zu berücksichtigen, dass bei unserer Reduktionsmethode mit *ca.* 35 mg Einwaage, beim nassen Aufschluss dagegen mit 200–250 mg Einwaage gearbeitet wurde, somit die sehr wahrscheinlich vorhandenen Inhomogenitäten im Polymerisat selbst bei der Reduktionsmethode stärker ins Gewicht fielen und die Standardabweichung erhöhen.

Zur Festlegung einer endgültigen Arbeitsvorschrift mit polarographischer Endbestimmung war die nochmalige Aufstellung einer Eichkurve durch Reduktion definierter Mengen an Na_2SO_4 erforderlich, diesmal jedoch unter Zugabe von jeweils 100 mg an schwefelfreiem Reinpolymerisat, das wir in Form einer DMF-Lösung ins Kölbchen gaben, die dann unter N_2-Atmosphäre zur Trockene eingeengt wurde. Nach Erkalten wurden steigende Mengen Na_2SO_4 zwischen 7 und 80 μg S in Form einer Lösung mit 7.6 μg S/ml zugesetzt, 0.3 g KOH in Plätzchen und 20 Tropfen H_2O_2 (30%ig, SO_4^{2-}-frei) zugegeben und dann, wie in der "Arbeitsvorschrift" (vergl. Festlegung der Arbeitsvorschrift und deren Erprobung an einer Analysenserie) nochmals ausführlich beschrieben, aufgeschlossen, reduziert und polarographiert. Die erhaltene Eichkurve (vergl. Fig. 4) verläuft etwas flacher als die aus Fig. 2 übernommene "direkte Eichkurve für Sulfid", wobei die Abweichung in den Stufenhöhen beider Kurven bei gleichen vorgegebenen Schwefelmengen *ca.* 6 % beträgt und damit etwas ausserhalb der apparativen Fehlergrenzen der polarographischen Methode liegt. Unserer Auffassung nach ist es auf jeden Fall empfehlenswert, eine Eichkurve unter unmittelbaren Aufschlussbedingungen aufzunehmen, falls ein schwefelfreies Polymerisat zur Verfügung steht, und sich nicht mit Zusätzen definierter Sulfatmengen zur Reduktionslösung zu begnügen.

Unter Anwendung der mit schwefelfreiem Polymerisat und Na_2SO_4-Vorgaben erhaltenen Eichkurve (Fig. 4) prüften wir an einem Polymerisat mit *ca.* 0.1% S, inwieweit der gefundene Schwefelwert von der Einwaage unabhängig ist (Tabelle IV). Nur bei sehr niedrigen Einwaagen unter 30 mg entsprechend $< 20\ \mu g$ S und einer Stufenhöhe unter 15 mm ist eine leichte Tendenz zu ansteigenden Werten mit sinkender Einwaage zu beobachten, die aber statistisch nicht gesichert ist. Bei Einwaagen zwischen 30 und 100 mg ist der gefundene Schwefelwert mit Sicherheit von der Einwaage unabhängig.

TABELLE IV

POLAROGRAPHISCH BESTIMMTE S-GEHALTE EINES POLYMERISATS BEI VERSCHIEDENER EINWAAGE

Einwaage (mg)	*% S gefunden*				*Mittelwert*
20	0.139	0.100	0.096	0.089	0.095
25	0.099	0.100	0.092	0.083	0.093
30		0.082	0.093		0.088
40			0.090		0.090
50			0.087		0.087
60			0.088		0.088
80			0.083		0.083
100	0.082	0.083	0.083	0.091	0.085

FESTLEGUNG DER ARBEITSVORSCHRIFT UND DEREN ERPROBUNG AN EINER ANALYSENSERIE

In Auswertung der bisher beschriebenen Versuchsergebnisse schlagen wir folgende Arbeitsvorschrift zur Schwefelbestimmung in Acrylnitrilpolymerisaten vor.

Die Einwaage von 15–300 mg entsprechend einer Schwefelmenge zwischen 20 und 80 μg S wird in den Reduktionskolben gebracht, mit 3 Plätzchen KOH (*ca.* 0.3 g), 3 ml entionisiertem Wasser und 20 Tropfen H_2O_2 versetzt. Nach 5 Min Einwirken in der Kälte (unter N_2) wird unter weiterem Überleiten eines kräftigen N_2-Stromes bis zur Trockene eingeengt und die Temperatur bis zur Schmelze des KOH gesteigert. Muss die Einwaage bei sehr geringen Schwefelgehalten höher als 150 mg liegen, so erhöht man die KOH-Menge auf 0.5 g und erhitzt die Schmelze noch etwa 15 Min, bis das Polymerisat weitgehend thermisch zersetzt ist. Nach Erkalten nimmt man in diesem Falle nochmals mit wenig Wasser und einigen Tropfen H_2O_2 (30%ig) auf und engt erneut zur Trockene ein. Nach Erkalten wird der Kolben an die Reduktionsapparatur angeschlossen, und nach Anstellen eines Stickstoffstromes von 2–3 Blasen/Sek gibt man 5 ml Reduktionslösung (100 ml Jodwasserstoffsäure ($d = 1.70$) + 25 ml Eisessig + 2.5 g Natriumhypophosphit, $NaH_2PO_2 \cdot H_2O$) zu. Die Absorptionsvorlage wird mit 10.00 ml 1 *N* NaOH gefüllt. Nach 5 Min langem Durchleiten von

Stickstoff zur Entlüftung der Lauge wird 25 Min bei Siedehitze reduziert und anschliessend in der sulfidhaltigen Absorptionslösung sofort der Schwefel polarographisch oder potentiometrisch bestimmt.

Zur polarographischen Bestimmung werden 8 ml der Lösung in eine polarographische Zelle gegeben und die anodische Sulfidstufe bei Raumtemperatur unter Verwendung einer Calomelelektrode als Gegenelektrode im Potentialbereich von 0 bis −1 V aufgenommen. Bewährt hat sich eine Tropfzeit von 3 Sek und bei dem von uns benutzten Gerät eine Galvanometerempfindlichkeit von 1 : 10. Zur Auswertung wird die Stufenhöhe bei −0.6 V gegen die Galvanometernull-Linie vermessen und dann die zugehörige Schwefelmenge einer entsprechend Fig. 4 unter Verwendung eines schwefelfreien Polymerisats aufgestellten Eichkurve entnommen.

TABELLE V

VERGLEICH DER POLAROGRAPHISCH UND POTENTIOMETRISCH ERMITTELTEN S-GEHALTE VON REINPOLYMERISATEN

Probe Nr.	*% S polarographisch*				*% S potentiometrisch*		
	Einzelwerte			*Mittelwerte*	*Einzelwerte*		*Mittelwerte*
1	0.033	0.028	0.031	0.031	0.027	0.026	0.027
2	0.028	0.024		0.026	0.030	0.030	0.030
3	0.063	0.063		0.063	0.058	0.056	0.057
4	0.100	0.103	0.089	0.097	0.094	0.092	0.093
5	0.085	0.090	0.087	0.088	0.093	0.091	0.092
6	0.141	0.163		0.152	0.138	0.142	0.141
7	0.331	0.328		0.330	0.324	0.319	0.322

Zur potentiometrischen Bestimmung des Sulfids schiebt man das Absorptionsgefäss mit der gesamten Vorlage auf den passend hergestellten Stopfen, durch den die beiden Elektroden (Silberamalgam/V 2 A-Stahl), das Stickstoffeinleitungsrohr und der Bürettenhahn geführt sind. Unter Rührung mit Stickstoff erfolgt die Titration mit 0.001 *M* $HgCl_2$-Lösung, die aus einer Mikrobürette zugesetzt wird. Bei der Berechnung des Schwefelgehaltes ist gegebenenfalls ein Blindwert zu berücksichtigen.

In Tabelle V sind die für eine Analysenserie sowohl durch polarographische als auch durch potentiometrische Endbestimmung des Sulfids erhaltenen Werte zusammengestellt, wobei der Aufschluss und die Reduktion in der beschriebenen Weise durchgeführt wurden.

Fräulein HELMA ROSENOW und Herrn WALTER SCHULZ danken wir für die umsichtige und sorgfältige Mitarbeit bei den experimentellen Untersuchungen.

ZUSAMMENFASSUNG

Zur Ermittlung des Schwefelgehaltes von Acrylnitrilpolymerisaten im Bereich von 0.01–0.2% S bei Einwaagen von *ca.* 50–100 mg wird vorgeschlagen: ein Aufschluss durch Erhitzen mit KOH, anschliessende Reduktion des entstandenen Sulfats mit einer Mischung aus Eisessig, Jodwasserstoffsäure und Hypophosphit und schliesslich zur Endbestimmung des in 1 *N* NaOH als Sulfid gebundenen H_2S die Aufnahme eines Polarogramms und Auswertung der anodischen Sulfidstufe bzw. die potentiometrische Titration mit 0.001 *M* $HgCl_2$-Lösung unter Verwendung einer Mess-

kette aus amalgamierter Silberelektrode als Indikatorelektrode und einer Edelstahlelektrode als Bezugselektrode. Da sämtliche Arbeitsgänge unter einem N_2-Strom erfolgen, kann die Methode auch unter den Bedingungen einer durch S-Verbindungen (H_2S, SO_2, CS_2) verunreinigten Atmosphäre angewandt werden.

SUMMARY

Sulphur contents (0.01–0.2% S) in polyacrylonitriles (50–100 mg samples) can be estimated by decomposition of the polymer by heating with KOH, reduction of the sulphate formed (with acetic acid, hydriodic acid, and hypophosphite) and absorption of hydrogen sulphide in 1 *N* sodium hydroxide. Sulphide is then determined polarographically utilizing the anodic sulphide wave, or potentiometrically with 0.001 *M* mercuric chloride as titrant and amalgamated silver wire and stainless steel wire as electrodes. The whole procedure is done easily in a stream of nitrogen and can therefore be applied even when the atmosphere is contaminated with sulphur-containing substances.

RÉSUMÉ

Une méthode est proposée pour le dosage de faibles teneurs en soufre (0.01 à 0.2% S) dans des polyacrilonitriles. On procède par décomposition du polymère par chauffage en présence d'hydroxyde de potassium, réduction du sulfate formé et absorption de l'hydrogène sulfuré obtenu dans l'hydroxyde de potassium 1 *N*. On termine le dosage, soit par polarographie (oxydation anodique du sulfure formé), soit par potentiométrie (titrage au moyen de chlorure mercurique). Lorsque l'atmosphère est contaminée par des substances sulfurées, toute la détermination peut s'effectuer dans un courant d'azote.

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SPECTROPHOTOMETRIC DETERMINATION OF TANTALUM AS REDUCED 12-MOLYBDOTANTALIC ACID

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Because of its corrosion resistant characteristics, tantalum is increasing in industrial importance. Accurate and sensitive methods for its determination are thus necessary. Although a variety of chromogenic reagents has been utilized for the spectrophotometric measurement of tantalum[1-8], no reference to a heteropoly acid technique was found. The purpose of this investigation was to examine the possibility of developing a heteropoly acid method for the determination of tantalum, and to gain information concerning the heteropoly compound formed.

EXPERIMENTAL

Apparatus

All spectrophotometric measurements were made on a Cary Model 12 recording spectrophotometer using 1.000 ±0.002 cm quartz cells. Measurements of pH were made with a Beckman Zeromatic pH meter.

Reagents

Standard tantalum solution. Standard tantalum solutions were prepared from two different reagents. Sufficient tantalum potassium fluoride (K_2TaF_7, 96% minimum) to prepare a solution containing approximately 0.5 g/l of tantalum was dissolved in 20 ml of concentrated sulfuric acid and the resulting solution diluted to 1 l. The solution was subsequently standardized gravimetrically. Spectrographic analysis of the tantalum potassium fluoride showed no impurities that would yield heteropoly compounds. This solution was used for the majority of the experiments. In addition, 0.5000 g of surgical tantalum foil was dissolved in hydrofluoric acid and the excess hydrofluoric acid removed by addition of sulfuric acid and evaporation. The resulting solution was diluted to 1 l.

Sodium molybdate solution. A 1% sodium molybdate solution was prepared by dissolution of 10 g of $Na_2MoO_4 \cdot 2H_2O$ in water and dilution to 1 l.

Chlorostannous acid solution. A 0.85% chlorostannous acid solution was prepared by dissolving 1 g of $SnCl \cdot 2H_2O$ in 1 ml of concentrated hydrochloric acid and diluting to 100 ml with water. Tis solution was prepared fresh daily.

Recommended procedure

Based on preliminary experiments and a study of the effect of variables the following recommended procedure was developed. To a solution containing 1–20 p.p.m. of tantalum, 10 ml of 1% sodium molybdate was added and the volume was adjusted to approximately 60 ml. The pH was adjusted to 1.5–2.0 with sulfuric acid, and the resulting yellow solution was transferred to a 100-ml volumetric flask. Ten ml of 1:1 sulfuric acid was added to the flask, followed by 1 ml of 0.85% chlorostannous acid. After dilution to the mark, the absorbance of the resulting blue solution was measured at 820 mμ.

STUDY OF VARIABLES

Stability

It was obvious early in the study that the reaction between the tantalum and the sodium molybdate resulted in a species of considerable stability. When the reagents were mixed and the pH was adjusted, the yellow color of the unreduced heteropoly acid formed almost immediately. The absorption spectrum of this species is given in Fig. 1. This yellow color persisted for 5 to 10 min even with such drastic changes as the addition of 10 ml of 1:1 sulfuric acid just prior to reduction.

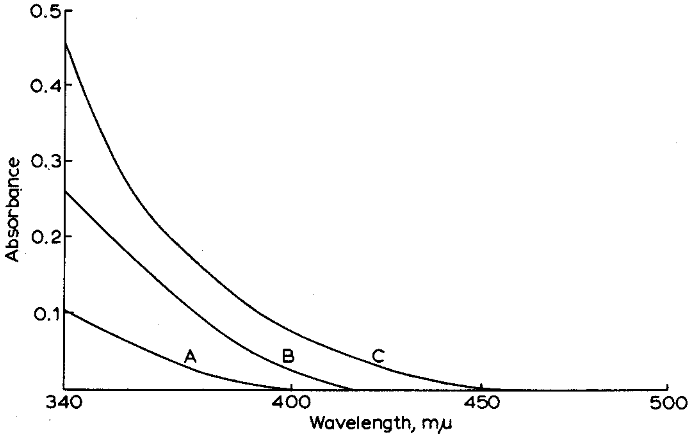

Fig. 1. Absorption spectra of 12-molybdotantalic acid. (A) 0 p.p.m. Ta; (B) 25 p.p.m. Ta; (C) 50 p. p. m. Ta.

Upon addition of the chlorostannous acid the blue color of the reduced heteropoly acid was fully developed in less than 1 min, and remained stable for approximately 1 h, after which slow fading occurred. The absorption spectrum of the reduced tantalum heteropoly species is given in Fig. 2.

Effect of pH

Solutions containing 5 p.p.m. of tantalum were treated as in the recommended procedure except that the pH was varied. The results of this study are given in Table I. Although a slightly greater sensitivity was obtained at pH 1.4, a pH range of 1.5–2.0 was chosen for use because of the small dependence of absorbance on pH in this range.

Effect of molybdate concentration

Solutions containing 5 p.p.m. of tantalum were treated as in the recommended procedure except that the sodium molybdate concentration was varied. The results of this study are given in Table II. A volume of 10 ml of 1% sodium molybdate was chosen for subsequent work.

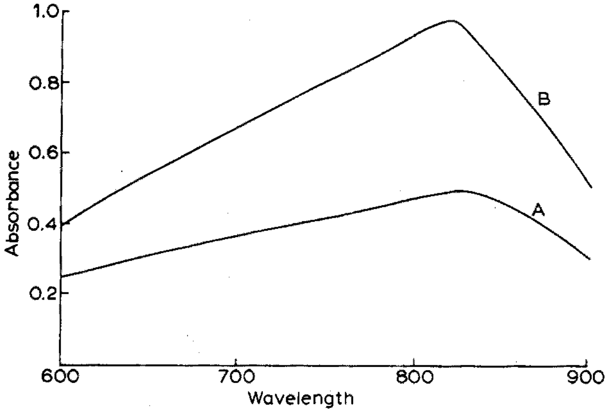

Fig. 2. Absorption spectra of reduced 12-molybdotantalic acid. (A) 5 p.p.m. Ta; (B) 10 p.p.m. Ta.

TABLE I

EFFECT OF pH

(5 p.p.m. Ta, 10 ml 1% sodium molybdate, 1 ml 0.85% chlorostannous acid)

pH	*Absorbance (820 mμ)*	*pH*	*Absorbance (820 mμ)*
0.5	0.445	1.5	0.490
1.0	0.455	1.6	0.490
1.1	0.460	1.7	0.490
1.2	0.465	1.8	0.491
1.3	0.470	1.9	0.490
1.35	0.500	2.0	0.489
1.4	0.525	2.5	0.485
1.45	0.498	3.0	0.375

TABLE II

EFFECT OF MOLYBDATE CONCENTRATION

(5 p.p.m. Ta, pH 1.5, 1 ml 0.85% chlorostannous acid)

ml 1% sodium molybdate	*Absorbance (820 mμ)*
1.0	0.051
3.0	0.092
5.0	0.180
8.0	0.410
10.0	0.490
12.0	0.491
15.0	0.490

Effect of sulfuric acid

Sodium molybdate solutions in the pH range 1.5–2.0 are readily reducible to a blue color. This would result in a very large blank correction in the tantalum determination. This problem can be eliminated by the addition of a large excess of sulfuric acid just before reduction. The sulfuric acid destroys the reducibility of the excess sodium molybdate but does not appreciably affect the tantalum heteropoly compound for several minutes. Ten ml of 1:1 sulfuric acid was found satisfactory for elimination of the blank correction.

Choice of reductant

Several compounds commonly used as heteropoly reducing agents were examined. Ascorbic acid gave an intense blue color but the reaction was slow. Iron(II) gave a pale green product. Hydrazine hydrochloride gave a very pale blue color. Tin(II) rapidly gave an intense blue color, and was chosen as the most desirable reductant.

Concentration of reductant

Solutions containing 5 p.p.m. of tantalum were treated as in the recommended procedure except that the concentration of chlorostannous acid was varied. The results of this study are given in Table III. One ml of 0.85% chlorostannous acid was chosen for subsequent work.

TABLE III

EFFECT OF CONCENTRATION OF REDUCTANT

(5 p.p.m. Ta, 10 ml 1% sodium molybdate, pH 1.5)

ml 0.85% chlorostannous acid	*Absorbance (820 mμ)*[a]
0.25	0.429
0.50	0.460
1.00	0.490
1.50	0.490
2.00	0.491
3.00	0.491

[a] Corrected for increasing blank.

TABLE IV

EFFECT OF DIVERSE IONS

(5 p.p.m. Ta, 10 ml 1% sodium molybdate, 1 ml 0.85% chlorostannous acid, pH 1.5)

Ion	*Amount tolerated (p.p.m.)*	*Ion*	*Amount tolerated (p.p.m.)*
Al^{3+}	100	Fe^{3+}	5
NH_4^+	100	I^-	100
Br^-	100	Mg^{2+}	100
BO_3^{3-}	100	Ni^{2+}	100
Cd^{2+}	100	Zn^{2+}	100
ClO_3^-	100	Zr^{4+}	25
ClO_4^-	100	Ti^{4+}	100
Cu^{2+}	50	Nb^{5+}	100

Effect of diverse ions

Solutions containing 5 p.p.m. of tantalum were treated as in the recommended procedure, and in addition, 100 p.p.m. of various ions were added. Ag^+, Ba^{2+}, Pb^{2+}, and Sr^{2+} form insoluble precipitates under the conditions of the experiments. As^{5+},

Co^{2+}, Cr^{3+}, Cr^{6+}, Fe^{2+}, IO_4^-, PO_4^{3-}, SiO_3^{2-}, CN^-, oxalate and citrate interfere seriously. Other substances investigated can be tolerated in the concentrations shown in Table IV. A 2% relative error was considered tolerable.

COMPOSITION OF THE REACTION PRODUCT

Continuous variations method

For application of the continuous variations technique, solutions $3 \cdot 10^{-3}$ *M* in tantalum and molybdenum were prepared. These solutions were mixed in various ratios, keeping the total molybdenum plus tantalum concentrations constant. The pH of these solutions was adjusted to 1.5, and 5 ml of 1:1 sulfuric acid and 1 ml of 0.85% chlorostannous acid were added. The solution was diluted to 25 ml and the absorbance was measured at 820 mμ. The results of this study (Fig. 3) indicate a ratio of 12 Mo : 1 Ta.

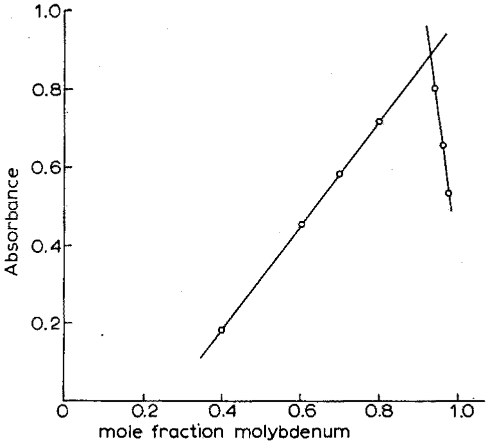

Fig. 3. Continuous variations plot for tantalum-molybdenum system.

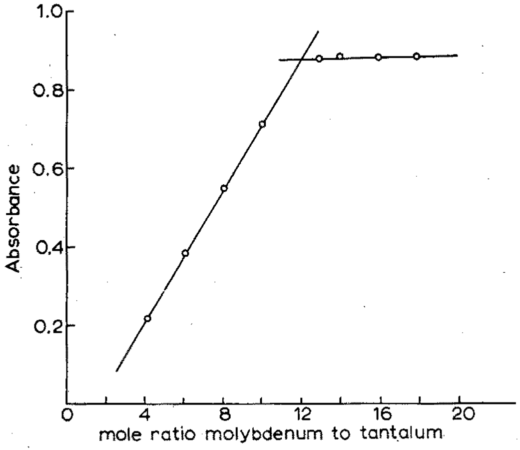

Fig. 4. Mole ratio plot for tantalum-molybdenum system.

Mole ratio method

In this study the same solutions as in the continuous variations method were used. Various ratios of molybdenum to tantalum were prepared, keeping the tantalum concentration constant. The results of this study (Fig. 4) again indicate a ratio of 12 Mo : 1 Ta.

DISCUSSION

The spectrophotometric method presented here is simple and sensitive but subject to a variety of interferences. Perhaps its chief advantage is that several-fold excesses of niobium and titanium do not interfere. Similar spectrophotometric procedures for titanium[9] and niobium[10] did not yield heteropoly species with the stability of the 12-molybdotantalic acid. When the excess of sulfuric acid used to eliminate the blank correction was added to the niobium and titanium systems, the reductant had to be added rapidly or the niobium and titanium heteropoly species were destroyed. The 12-molybdotantalic acid is stable for several minutes under these conditions, and thus the niobium and titanium interferences can be eliminated. The stability of the tantalum heteropoly species is similar to that of the zirconium species previously described[11].

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SUMMARY

A simple sensitive spectrophotometric method for the determination of tantalum is described. The method is based on the reaction of sodium molybdate with tantalum at pH 1.5–2.0. The resulting 12-molybdotantalic acid is reduced and the absorbance measured at 820 mμ. The method is subject to a number of interferences but is applicable in the presence of several-fold excesses of niobium and titanium.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du tantale. Elle est basée sur la réaction du molybdate de sodium avec le tantale, au pH 1.5–2.0. L'acide molybdotantalique formé est réduit; son absorption est mesurée à 820 mμ. Ce dosage peut s'effectuer en présence de niobium et de titane.

ZUSAMMENFASSUNG

Eine einfache, empfindliche, spektralphotometrische Methode zur Bestimmung von Tantal wird beschrieben. Die Methode beruht auf der Reaktion von Natriummolybdat mit Tantal beim pH-Wert 1.5–2.0. Die entstehende Molybdatotantalsäure wird reduziert und die Absorption bei 820 mμ gemessen. Die Methode ist einer Reihe von Störungen unterworfen; sie ist in Gegenwart eines mehrfachen Überschussen von Niob und Titan anwendbar.

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Short Communications

Titrimetrische Bestimmung von Nd^{3+} mittels Natriumwolframat in Gegenwart von Adsorptionsindikatoren

Neodym zeichnet sich, ähnlich wie andere Elemente der seltenen Erden, durch ein charakteristisches Emissionsspektrum aus. Auf Grund dieser Erscheinung wurde eine Reihe spektrophotometrischer beziehungsweise spektroskopischer[1–5] Methoden ausgearbeitet. Als Ausgangspunkt für die neu erarbeitete Bestimmungsmethode von Nd^{3+} diente die Feststellung, dass Neodymsalze mit Natriumwolframat einen schwerlöslichen Niederschlag von Neodymwolframat[6] gemäss nachstehender Reaktion bilden:

$$2\ Nd^{3+} + 3\ WO_4^{2-} = Nd_2(WO_4)_3$$

Reagentien

(*1*) 0.1 und 0.05 *M* $Na_2WO_4 \cdot 2H_2O$ p.a.(Merck). (*2*) 0.05 *M* $NdCl_3 \cdot 6\ H_2O$ chem. rein (Fluka AG, Switzerland). (*3*) Gesättigte alkoholische Methylrotlösung. (*4*) 0.04%-ige wässrige Bromkresolgrünlösung.

Zur Herstellung der Grundlösungen wie auch zu ihrer Verdünnung wurde bidestilliertes Wasser gebraucht.

TABELLE I

TITRATIONEN MIT 0.1 *M* Na_2WO_4-LÖSUNG

Menge 0.1 M Na_2WO_4 (ml)[a]	*Neodymmenge*		*Unterschied (%)*
	Gefunden (mg)	*Errechnet (mg)*	
0.05 *M* $NdCl_3$			
3.746	36.02	36.07	−0.13
7.480	71.93	72.13	−0.27
11.220	107.89	108.20	−0.28
14.890	143.18	144.27	−0.75
18.653	179.37	180.34	−0.53
0.025 *M* $NdCl_3$			
1.870	17.98	18.03	−0.27
3.750	36.06	36.07	−0.02
5.606	53.91	54.10	−0.35
7.480	71.93	72.13	−0.27
9.353	89.94	90.17	−0.25
0.0125 *M* $NdCl_3$			
0.936	9.00	9.02	−0.22
1.873	18.01	18.03	−0.11
2.810	27.02	27.05	0.11
3.746	36.02	36.07	−0.13
4.7673	44.94	45.08	−0.31

[a] Mittelwerten der 3 Titrationen

Arbeitsvorschrift

Aus der Lösung 0.05 *M* $NdCl_3 \cdot 6\ H_2O$ wurden durch entsprechendes Verdünnen 0.05, 0.025, 0.0125 und 0.00625 *M* $NdCl_3 \cdot 6\ H_2O$-Lösungen hergestellt.

Anschliessend wurden Erlenmeyerkolben mit weitem Hals genau mit 5, 10, 15, 20 und 25 ml entsprechender Neodymchloridlösung angefüllt. Nach der Beigabe des Indikators wurde die Lösung bis auf etwa 90° erhitzt und unter ständigem Rühren mit Natriumwolframat titriert. Während dieses Vorgangs wurde die Lösung auf Siedetemperatur gehalten. Zum Titrieren bediente man sich einer Mikrobürette mit einer Genauigkeit der Skala bis zu 0.01 ml. Die erzielten Ergebnisse sind in den Tabellen zusammengestellt.

TABELLE II

TITRATION MIT 0.05 *M* Na_2WO_4-LÖSUNG

Menge 0.05 M Na_2WO_4 (ml)[a]	*Neodymmenge*		*Unterschied (%)*
	Gefunden (mg)	*Errechnet (mg)*	
0.025 *M* $NdCl_3$			
3.746	18.01	18.03	−0.11
11.226	53.97	54.10	−0.23
18.656	89.70	90.17	−0.52
0.0125 *M* $NdCl_3$			
1.873	9.01	9.02	−0.11
5.606	26.95	27.05	−0.36
9.356	44.98	45.08	−0.22
0.00625 *M* $NdCl_3$			
0.936	4.50	4.51	−0.22
2.813	13.52	13.53	−0.07
4.676	22.47	22.54	−0.30

[a] Mittelwerten der 3 Titrationen

Besprechung der Ergebnisse

Während des Titrierens wird ein weisser, amorpher Niederschlag von $Nd_2(WO_4)_3$ ausgefällt. Der bei dieser Methode angewandte Mischindikator hatte folgende Zusammensetzung: angesättigte alkoholische Methylrotlösung und 0.04%-ige wässrige Bromkresolgrünlösung. Als Adsorptionsindikator wirkt hierbei Methylrot. Bromkresolgrün bringt den Farbübergang im Gleichgewichtspunkt deutlicher zum Vorschein. Zu jeder 5 ml Neodymchloridlösung wurden jeweils 2 Tropfen Methylrot und 2 Tropfen Bromkresolgrün beigegeben. Nach Zugabe der Indikatoren nimmt die $NdCl_3$-Lösung eine bräunlich-violette Färbung an.

Während des Titrierens in heissem Zustand färbt sich die Lösung bereits nach den ersten Tropfen Natriumwolframatlösung rötlich-violett, in der Nähe des Gleichgewichtspunktes geht die Färbung in blau-violett über und im Gleichgewichtspunkt wird der Niederschlag grünlich-violett. Die Flüssigkeit oberhalb des Niederschlages ist deutlich grün. Der Farbübergang tritt umso deutlicher hervor, je mehr die Neodymchloridlösung verdünnt ist. Das Titrieren erfolgte tropfenweise und unter ständigem Rühren.

Das Titrieren im kalten Zustand gibt nicht den beabsichtigten Effekt, da sich bereits nach den ersten Tropfen Natriumwolframatlösung die Nd^{3+}-Lösung grünlich färbt.

Aus den Zahlenangaben, die in den Tabellen zusammengestellt sind, ersieht man, dass der Fehler nicht hoch liegt, bedeutend unter 1%.

Die neu ausgearbeitete Methode zeichnet sich durch grosse Genauigkeit aus und ist schnell in der Ausführung. Die Menge des bestimmten Nd^{3+} lag bei 5–25 ml Lösung zwischen 0,0045–0,18 g.

Oben besprochene Methode eignet sich jedoch nicht zur Bestimmung von Nd^{3+} in Gegenwart von Schwermetallen, wie auch den übrigen Metallen der seltenen Erden.

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Anal. Chim. Acta, 30 (1964) 401–403

Barium nitrate can be dried at 375° to constant weight

GORDON AND CAMPBELL[1] and, more recently, WENDLANDT[2] have studied the changes which barium nitrate undergoes on heating, by means of differential thermal analysis. Up to 587°, or 560° respectively, the curves which they have recorded do not differ much from horizontal straight lines. DUVAL[3], by thermogravimetric analysis, obtained up to 607° a horizontal straight line. By using a more sensitive method, we have found, however, that there is a narrow plateau in the weight-loss curve at the temperature range from 350 to 400°. In our experiments a relatively large quantity

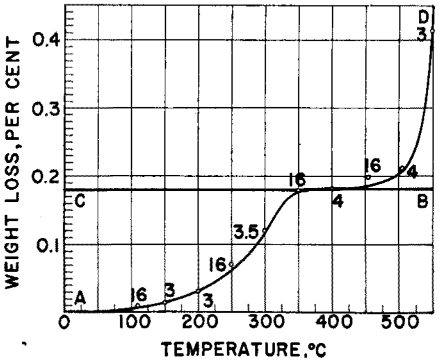

Fig. 1. The weight-loss curve of barium nitrate. The numbers at the points indicate the hours of heating at that temperature. The solid curves AB and CD have been drawn tentatively for 3 h of heating time at each temperature.

(4 g) of barium nitrate* was heated in a platinum crucible at a series of increasing temperatures for a number of hours and the weight loss was determined after each heating (Fig. 1). The weight-loss curve can be interpreted as a combination of two curves: the drying curve AB and the dissociation curve of (anhydrous) barium nitrate CD, the latter superposed on the former, but both curves still distinguishable as such. In a general case the fusion of both curves would be more complete. It occurred to us that at the midpoint of the plateau, 375°, barium nitrate could be dried to constant weight. This, however, could be decided only by experiment. For that purpose 65 g of barium nitrate, in a platinum crucible, was placed in a drying furnace at 100°. Then the voltage of the furnace was increased to such a predetermined value that overnight the temperature would reach a thermal soak condition at 375°. Next morning the sample was cooled in a desiccator for 1 h and weighed. This weight was taken as the initial value for the weight constancy test (zero weight loss). The sample was then returned to the furnace for several hours and weighed again. This was repeated 4 times. The results of the test are shown in Fig. 2. It can be seen that during 69.5 h of additional heating at 375°, the weight of barium nitrate remained constant within 0.002%. We believe that this interval of uncertainty is due to a desiccator gain and that with improved cooling technique it can be made smaller. On the basis of these data we submit that barium nitrate after 24 h of drying at 375° (± 25°) can be weighed as $Ba(NO_3)_2$.

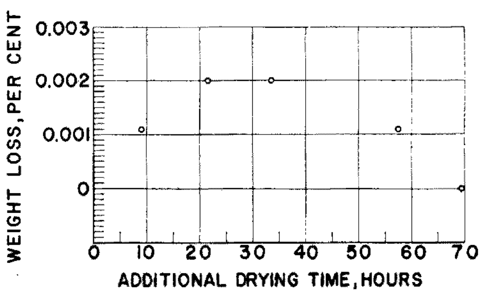

Fig. 2. The weight loss of barium nitrate on additional heating at 375°.

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* "Baker Analysed" Reagent; calcium and strontium salts (as SO_4) 0.10 %. In order to bring this impurity still lower the salt was recrystallized 7 times.

A new specific spot test for uranyl ions based on the behaviour of protonated Schiff bases of *p*-dimethylaminoaniline with aromatic aldehydes

In microanalytical chemistry extensive use is made of solutions of aromatic compounds in equilibrium with their coloured quinoidal form, where the anions to be detected stabilize the coloured species. For example, the equilibrium between lacto rhodamine B and its red quinoidal form makes possible the detection of antimony, gallium, gold, thallium and uranium, which all give voluminous anions which stabilize the intensively coloured species[1].

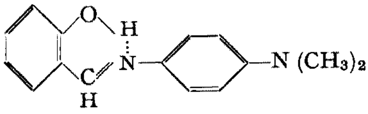
p-Dimethylaminoaniline salts give red protonated[2] Schiff bases with aromatic aldehydes. This reaction recently served for microdetection of aromatic aldehydes[3]:

$$\mathrm{ArCHO} + \mathrm{NH_3^+Ar'} \rightarrow [\mathrm{ArCH{=}NHAr'}]^+$$

If the red benzal derivative is treated with ammonia, it turns into the yellow non-protonated compound. This interesting equilibrium was investigated in the case of various aromatic aldehydes: benzaldehyde, salicylaldehyde, *p*-dimethylaminobenzaldehyde, nitro- and chlorobenzaldehydes, phthalaldehyde acid, and cinnamic and *p*-dimethylaminocinnamic aldehyde. Alcoholic solutions of the yellow Schiff bases were examined for their stability against acids. As was expected, all dilute mineral acids completely hydrolysed the benzal derivatives. However, a certain graduality of behaviour was observed towards dilute acetic acid. Generally, acetic acid shifts the equilibrium towards the red protonated form:

$$\underset{\text{yellow}}{\mathrm{Ar{-}CH{=}N{-}Ar'}} + \mathrm{H^+} \rightleftharpoons \underset{\text{red}}{[\mathrm{Ar{-}CH{=}NH{-}Ar'}]^+}$$

p-Dimethylaminobenzaldehyde, which contains a substituted positively inducing group, stabilizes the protonated form in such a manner that even atmospheric carbon dioxide affects the equilibrium. On the other hand, the yellow Schiff bases of *p*-chlorobenzaldehyde and salicylaldehyde are unaffected by acetic acid. In the former case, stabilization occurs owing to the negatively inducing *p*-chloro substituent, while in the latter the inner compound[4] (I) formed is responsible for the stability against acetic acid:



(I)

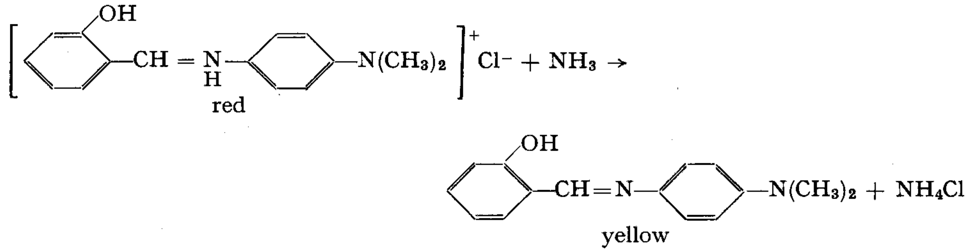
It was found that voluminous anions like $(\mathrm{CdI_4})^{2-}$, $[\mathrm{Hg(CNS)_4}]^{2-}$ and $[\mathrm{TlBr_4}]^-$ also stabilize the cationic form as in the case of rhodamine B[1]. Accordingly these complex anions produce red precipitates, when added to the yellow alcoholic solution of the Schiff base.

LUCAS[5] showed that alkali chlorides react with uranyl cations to give a compound in which the uranium appears in the anionic form:

$$2\,\mathrm{MCl} + \mathrm{UO_2Cl_2} \rightarrow (\mathrm{M})_2[\mathrm{UO_2Cl_4}] \qquad (1)$$

ITZIG[6] has also indicated the tendency of uranium to give anions, since it forms heteropoly acids.

In the preparation of our reagent and its subsequent treatment with ammonia, ammonium chloride is formed according to the reaction:



(II)

Thus, on the introduction of uranyl ions into the yellow reagent, conditions are present to produce a voluminous anion according to eqn. (1), and the basis is laid for the specific detection of uranium.

Procedure

The yellow freshly prepared reagent paper is spotted with a drop of the test solution. A positive response is indicated by the appearance of a red fleck, the intensity of which depends on the amount of uranyl ions.

Identification limit: 1 μg of uranium.
Dilution limit: 1 : 50,000.

Reagent paper

A concentrated alcoholic solution of *p*-dimethylaminoaniline hydrochloride is mixed in a test tube with a concentrated alcoholic solution of salicylaldehyde, and immersed for a few minutes in a boiling water bath. The blood red solution is then poured on to filter paper and partially dried with cold air. The red paper is placed on top of a beaker containing concentrated ammonia solution. After a few minutes the red paper turns yellow, and the drying is then completed.

It was found that the optimal pH range lies between 2 and 3. None of the available cations shows analogous behaviour. Iron(III), however, interferes because it reacts with one of the components — salicylaldehyde — giving a blue-violet inner complex. Owing to different rates of capillary diffusion on the dried reagent paper, a mixture of uranium and iron gives a central blue-violet spot surrounded by a well-defined red ring, thus overcoming interference and avoiding prior removal.

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Studies on adsorption indicators.

V. Application of metallochrome indicators as adsorption indicators

In a recent communication[1] from the authors' laboratories, the applicability of resorcinolsulphonphthalein (sulphonfluorescein) and its halogenated derivatives as adsorption indicators was described. It was considered of interest to investigate the suitability of some other sulphonphthalein dyes, *viz.* pyrocatecholsulphonphthalein (catechol violet) and pyrogallolsulphonphthalein (pyrogallol red) as adsorption indicators. These dyes are well-known metallochrome indicators[2–4] and as they were found suitable as adsorption indicators in the present work, it was considered worthwhile to extend the investigations to some other well-known metallochrome indicators (phthaleincomplexone[5], xylenol orange[6], calcein[7] and murexide[8]).

Evidence regarding the chemical nature of the mechanism of adsorption indicators has been furnished in recent communications[9] from the authors' laboratories. The applicability of dyes as metallochrome indicators in EDTA titrations depends on their ability to form a different coloured metal–dye complex which is less stable than the corresponding metal–EDTA complex. That these dyes can also function as adsorption indicators gives further support to the view that the mechanism of adsorption indicators is essentially of a chemical nature.

Experimental

Materials. The potassium iodide, bromide, chloride and thiocyanate used were B.D.H. (Analar) reagents; solutions of the required strength were prepared and standardised by well-known methods. Catechol violet, xylenol orange, calcein and murexide were used directly in 0.2% aqueous solution; solutions (0.2%) of pyrogallol red and phthaleincomplexone were prepared after the dyes had been converted to their ammonium salts.

General procedure. Halide or thiocyanate solutions of varying strength were titrated with solutions of silver nitrate of similar concentration; generally two drops of the indicator per 10 ml of the solution were added at the beginning of the titration and the titration was continued until a sharp colour change was observed. Titrations were repeated at least 3 times and were considered satisfactory only when the values obtained agreed with the theoretical values within ± 0.2%. The main characteristics and the range of applicability for the individual indicators are given below. In each case, the colour changes were found to be sharp and reversible.

Catechol violet (pyrocatecholsulphonphthalein) as adsorption indicator

The titrations are possible only in neutral medium. The colour change at the equivalence point is from yellow suspension to blue precipitate (green in the case of bromide or iodide). The titrations can be carried out up to dilutions of 0.02 *N* in the case of chloride, 0.005 *N* in the case of bromide and thiocyanate, and 0.001 *N* in the case of iodide.

Pyrogallol red (pyrogallolsulphonphthalein) as adsorption indicator

The titrations are carried out in neutral or slightly acidic medium in the pH range 4–7. The colour change at the equivalence point is from pink suspension to blue precipitate (green in the case of bromide or iodide). The colour change is sharp and reversible. Titrations of chloride, thiocyanate, bromide and iodide are possible up to dilutions of 0.01 *N*, 0.002 *N*, 0.002 *N* and 0.005 *N*, respectively.

Phthaleincomplexone (o-cresolphthaleindi(methyliminodiacetic acid)) as adsorption indicator

The titrations are possible only in slightly alkaline medium in presence of dilute sodium or ammonium hydroxide solution. The halide solution containing the indicator is treated with drops of 0.1 *N* alkali solution until a pink solution is produced. It is then titrated with silver solution. The colour change at the equivalence point is from pink suspension to blue precipitate (green in the case of bromide or iodide). Titrations are possible up to dilutions of 0.01 *N* for chloride, 0.002 *N* for bromide or thiocyanate, and 0.0005 *N* for iodide.

Xylenol orange (o-cresolsulphonphthaleindi(methyliminodiacetic acid)) as adsorption indicator

Like phthaleincomplexone, the indicator is applicable only in slightly alkaline medium. Dilute alkali is added to the halide solution containing the indicator until the pink colour appears and the solution is titrated with silver solution. The colour change at the equivalence point is from pink suspension to grey-blue precipitate (grey-green in the case of bromide or iodide). The indicator is unsuitable for chloride titrations because the grey-blue colour on the precipitate develops before the equivalence point. However, the indicator is suitable for titrations of thiocyanate, bromide and iodide up to dilutions of 0.01 *N*, 0.005 *N* and 0.001 *N*, respectively.

Calcein (fluoresceindi(methyliminodiacetic acid)) as adsorption indicator

The titrations can be carried out in slightly acidic, neutral or slightly alkaline medium (pH 2.5–8.5). The colour change at the equivalence point is from yellow or orange suspension to pink precipitate. Like xylenol orange, the indicator is unsuitable for the chloride titration because the pink colour develops on the precipitate before the equivalence point. However, it is possible to titrate thiocyanate, bromide and iodide up to dilutions of 0.01 *N*, 0.002 *N* and 0.0005 *N*, respectively.

Murexide (ammonium purpurate) as adsorption indicator

The titrations are possible only in neutral medium. The colour change at the equivalence point is from flesh-coloured suspension to violet precipitate. The titrations can be carried out up to dilutions of 0.02 *N* for chloride, 0.01 *N* for thiocyanate, 0.002 *N* for bromide and 0.001 *N* for iodide.

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Book Review

G. MILAZZO, *Electrochemistry, Theoretical Principles and Practical Applications*, Elsevier, Amsterdam, 1963, XV + 708 pp., price £ 5.10.0 d (D.fl. 55,—; DM 61.50).

In this book the author, with the cooperation of a number of specialists, covers a number of different aspects, which are more usually the subjects of several separate works. The first part deals with the introduction to, and the theoretical aspects of, electrochemistry. It includes chapters on the basic concepts, electrolytes and electrolytic conduction, galvanic cells, electrolysis and electrochemical kinetics. This is followed by a comprehensive treatment of analytical applications, after which comes a chapter on the electrochemistry of colloids and electrokinetic phenomena. This includes a section on electrophoresis and its analytical applications.

Most of the last third of the book is devoted to the principles and practical details of industrial electrochemical processes, in which electrometallurgy and non-metallic electrolytic processes are described and discussed. A special section is included in this part dealing in detail with processes involving electrolysis in molten electrolytes. Final chapters are concerned with practical primary cells and storage batteries, including fuel cells and with the electrochemistry of gases.

The book starts with a clear exposition of essential thermodynamics, in which a good balance is maintained and just about enough information is given for an understanding of what follows, but without excessive detail. This introduction is necessary as the approach of the author is strictly thermodynamic, even to the exclusion of discussion of the Nernst equation. This will not be favoured by many established electrochemists, who will also find the use of new and unfamiliar symbols confusing. All these symbols, which follow the latest international nomenclature, are given at the front of the book and are then, in general, introduced into the text without further explanation. This has assisted the production of a concise text and has made the book easier to write, but it makes it somewhat difficult to read in places and will cause irritation to the reader at times. A case in point is the use of "tension" throughout the book, especially as no explanation of the term is given. However, the author is a pioneer and complete acceptance and free use of these terms and symbols is only a matter of time. The section on thermodynamics ends rather abruptly and would have been improved by a few pages on the derivation and use of the various thermodynamic data, equations and relationships that have practical value in elucidating or predicting reactions. A great deal of this is, of course, present in the book, but it is scattered. The introductory and theoretical treatment is generally excellent and there are few parts which merit criticism. The difficult subject of migration is handled with care, but the result is rather inadequate.

The analytical applications described fall broadly into the groups, electrolytic analysis, potentiometry, conductometric methods including high frequency techniques, polarographic and voltammetric methods. The discussion of all these in the space of less than one hundred pages inevitably means that the treatment of each is brief. There are, however, again useful tables of data including lists of coulometrically generated reagents and the species which can be titrated with them, characteristics of the various electrodes used for the determination of pH, standard potentials of reference electrodes in practical use and the polarographic half-wave potentials of large numbers of inorganic and organic systems.

The section on colloids deals quite well with this rather specialised subject, not always thought of primarily as a branch of electrochemistry. Electrophoresis is briefly mentioned and useful details of analytical applications are given.

Considerations of industrial electrochemical processes start, very properly, with a general section which points out that every process has its own characteristics, which are reflected in the design of its plant and that economic and local conditions are important factors in design. Common features are then discussed very briefly, followed by details of applications to metallic and non-metallic species. This is followed by a useful section on molten electrolytes in which is described such industrially important processes as the preparation and refining of aluminium and the preparation of magnesium and sodium. This is undoubtedly a useful and valuable account of industrial practice, but it leaves the impression that it is rather too long and detailed to be an introduction to the subject and too short to be a handbook.

The account of cells and batteries is useful, especially that concerning fuel cells in which the principles are clearly given. The short final section on the electrochemistry of gases is informative and provides details not often available unless high specialised textbooks are consulted.

As indicated at the beginning of this review the author has attempted to compress the scope of several books into one. He is to be congratulated on the extent to which he has achieved this without falling between any of several stools. It is consequently recommended for use by a wide range of readers from undergraduates to postgraduate specialists. Many will wish to acquire a personal copy and others will require it to be available in reference libraries. It deserves to rival the earlier German and Italian editions in popularity.

G. F. Reynolds, Loughborough

Anal. Chim. Acta, 30 (1964) 410–411

Announcements

1965 INTERNATIONAL SYMPOSIUM ON MICROCHEMICAL TECHNIQUES

The Pennsylvania State University will conduct an International Symposium on Microchemical Techniques during August 22–27, 1965 at the Pennsylvania State University, University Park, Pennsylvania, U.S.A. The Symposium will be organized by The American Microchemical Society (formerly the Metropolitan Microchemical Society) and will be similar to the Symposium of 1961. The same committee is in charge. Details will be announced by the Society at a future date.

Anal. Chim. Acta, 30 (1964) 411

VERANSTALTUNGEN DER GESELLSCHAFT DEUTSCHER CHEMIKER 1964

KARLSRUHE, 1.–2. April, *GDCh-Fachgruppe "Kern-, Radio- und Strahlenchemie"*, Symposium über "Methoden zur Messung weicher β-Strahler".

BAD NAUHEIM, 13.–14. April, *GDCh-Fachgruppe "Kunststoffe und Kautschuk"*, Tagung über "Hochpolymere mit Hetero-Atomen".

EINDHOVEN, 20.–23. Mai, *GDCh-Fachgruppe "Analytische Chemie" und Sectie voor Analytische Chemie van de Koninklijke Nederlandse Chemische Vereniging*, Symposium über "Moderne Methoden der Analyse organischer Verbindungen".

HEIDELBERG, 20.–23. Mai, IUPAC-Symposium "Organo-Phosphorus Compounds" organized by the *Division of Organic Chemistry of the International Union of Pure and Applied Chemistry and by the Gesellschaft Deutscher Chemiker.*

BAD WIESSEE, 26.–27. Mai, *GDCh-Fachgruppe "Wasserchemie"*, Jahrestagung 1964.

FRANKFURT (M), 24. Juni, Festsitzung und Vortragstagung der *Gesellschaft Deutscher Chemiker* anlässlich der ACHEMA.

DÜSSELDORF, 5.–7. Oktober, *GDCh-Fachgruppe "Analytische Chemie"*, Vortragstagung "Moderne Methoden der anorganischen Analyse".

FRANKFURT (M), 20. November, *GDCh-Fachgruppe "Geschichte der Chemie"*, Vortragstagung.

LINDAU/BREGENZ, 30. September–2. Oktober, *GDCh-Fachgruppe "Lebensmittelchemie und gerichtliche Chemie"*, Jahrestagung mit dem Thema "Lagern und Haltbarmachen von Lebensmitteln".

MÜNCHEN, 12.–13. Oktober, *GDCh-Fachgruppe "Halbleiterchemie"*, Vortragstagung "Organische Halbleiter und anorganische Halbleiter mit Molekelgitter".

HEIDELBERG od. LUDWIGSHAFEN, 22.–23. Oktober, *GDCh-Fachgruppe "Angewandte Elektrochemie"*, Vortragstagung "Elektrochemische Verfahrenstechnik und Elektrochemie geschmolzener Salze".

BERLIN, 29.–30. Oktober, *GDCh-Fachgruppe "Anstrichstoffe und Pigmente"*, 28. Vortragstagung der Fachgruppe.

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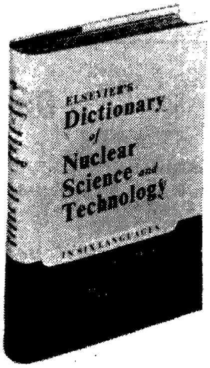
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2. Wheatley, N. B. and Cheney, L. C., *J. Amer. Chem. Soc.*, 1949, **71**, 64-6; 3795-7
3. Daub, G. H. and Johnson, W. S., *J. Amer. Chem. Soc.*, 1950, **72**, 501-4

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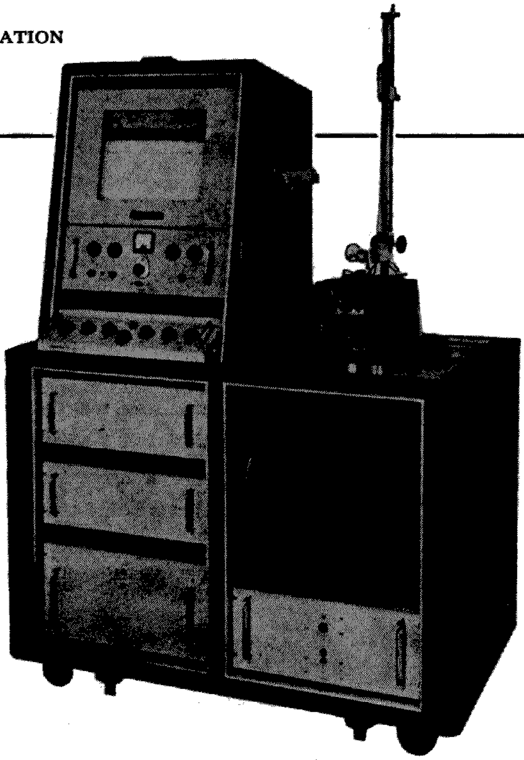

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