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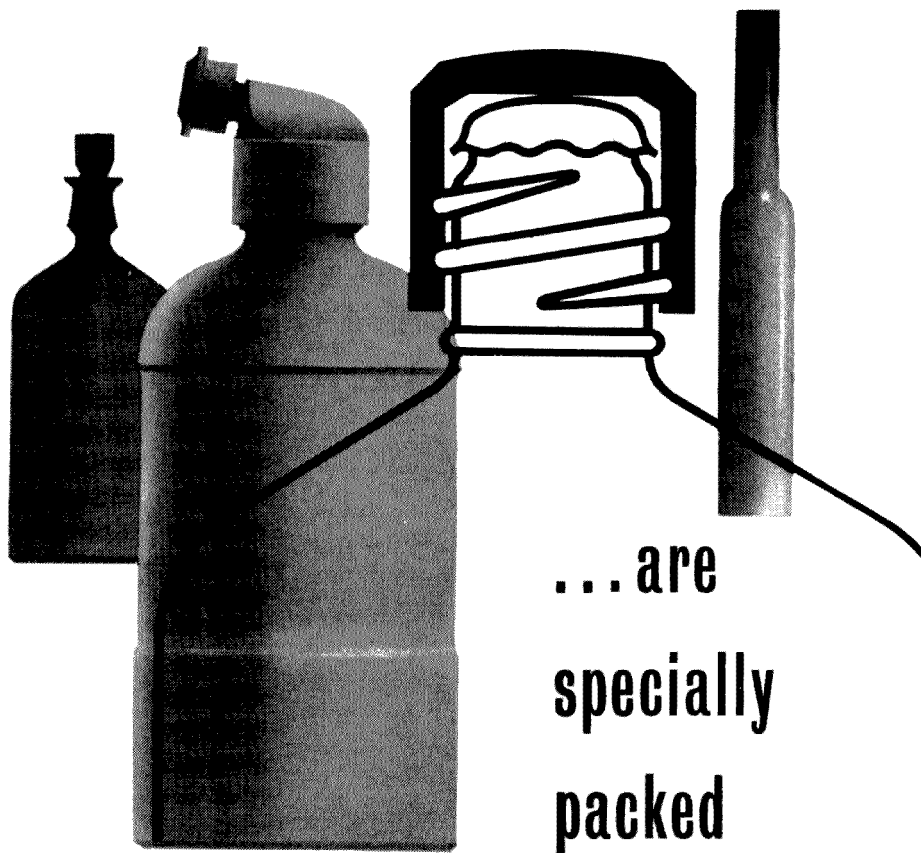
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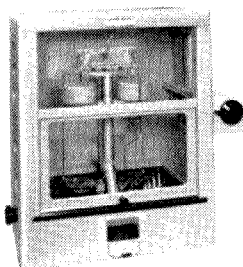
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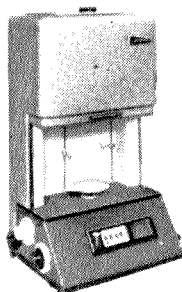
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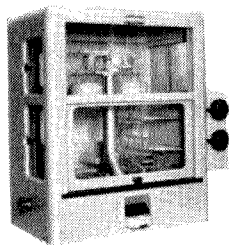
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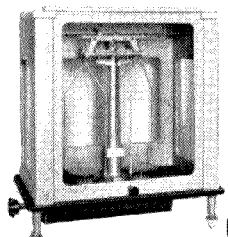
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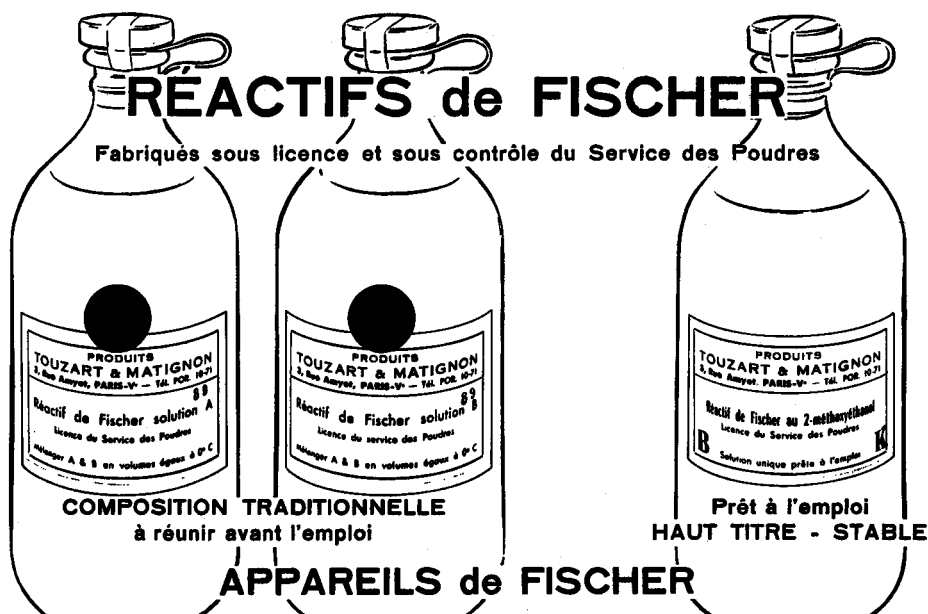
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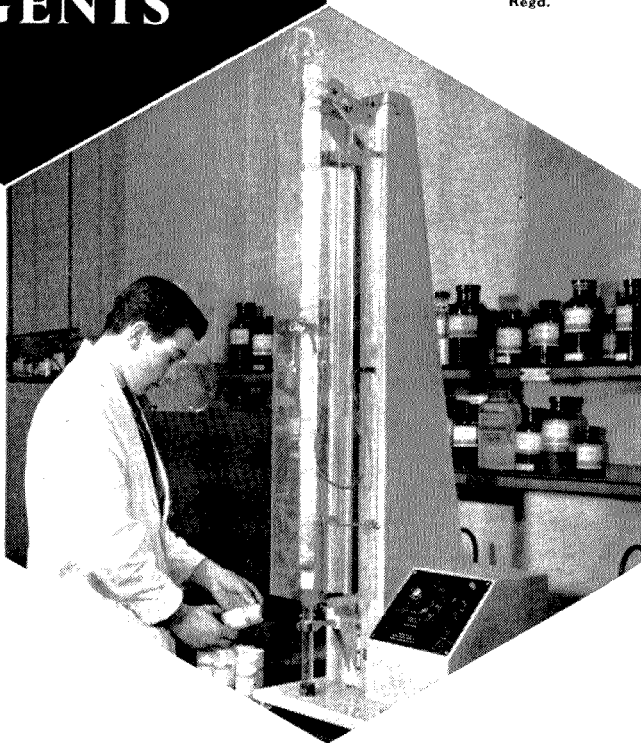
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TURBIDIMETRIC TITRATIONS*

ROBERT B. FISCHER, MARVIN L. YATES AND MARION M. BATTS

Department of Chemistry, Indiana University, Bloomington, Ind. (U.S.A.)

Turbidimetric measurements can be used in two general ways in analytical chemistry. In one method, the unknown component is put into suspension by precipitation with an appropriate reagent, and the turbidity of the suspension is compared by one of several possible techniques with that of one or more standard suspensions. In the other method, a solution of the unknown is titrated by a solution of a precipitating agent, and the end-point is obtained by means of a plot of measured turbidity *vs.* volume of added reagent.

One chief limiting factor in all analytical turbidimetric procedures has been the irreproducibility of the physical form of the precipitate. This factor is more serious when comparison must be made with standards than in titrations, because it is not possible to precipitate the unknown and the standards under identical conditions. Extensive experimentation in this laboratory has revealed that the physical form of a precipitate is determined largely by the first batch of precipitated particles, even though there is considerable random variation among a series of initial batches of precipitate in supposedly identical trials. It seems, therefore, that titration procedures should be distinctly superior to those turbidimetric procedures which are based upon comparisons with standards. The turbidimetric method of detecting titration end-points with precipitation reactions is of particular interest because no general type chemical indicators have been developed for precipitation titrations as has been done for neutralization and oxidation-reduction titrations.

Several specific applications of turbidimetric titrations have been reported in the literature, including those in a number of papers by BOBTELSKY *et al.*¹⁻³, and others. It is the purpose of the present study to examine the roles of nucleation and crystal growth in the precipitation reaction by the preparation of calculated titration curves and, from these curves, to make and to test certain predictions concerning turbidimetric titrations.

CALCULATED TITRATION CURVES

The first portion of precipitating agent forms the first batch of particles by both nucleation and crystal growth. This growth may be designated "initial growth." It is conceivable that the next equal increment of mass of precipitate could form in one of four ways: (A) it could consist of further nucleation and initial growth just as did the first increment; (B) it could consist of uniform growth on all crystal faces of the particles already present; (C) it could consist of preferential growth on certain crystal face(s) of the precipitate already present; (D) it could consist of some new nucleation

* Contribution 871, Chemistry department, Indiana University. Work supported by the U.S. Atomic Energy Commission under Contract AT(11-1)-497.

but primarily of further growth. Situation (D) is intermediate between situations (A) and either (B) or (C). Calculated curves of total surface area *vs.* mass of precipitate are shown in Fig. 1 for situations (A) and (B); the area and the mass of the initial batch of particles are both assigned the arbitrary values of 0.1. The curve for situation (B) applies whatever the particle shape is, *i.e.*, whether spheres, cubes, etc. Curves calculated for situation (C) lie intermediate between (A) and (B), with the exact placement relative to (A) and (B) determined by the particle shape and by which face(s) bear the additional growth. Situation (D) is also an intermediate one, so the two curves of Fig. 1 are the extremes with all other possibilities lying between.

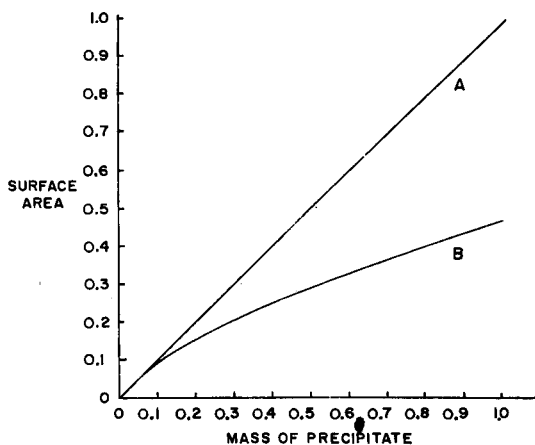


Fig. 1. Calculated curves for conditions of (A) continual new nucleation and initial growth with each increment of mass of precipitate and (B) crystal growth only beyond first increment of mass of precipitate (both axes in arbitrary units).

It is now necessary to relate the curves of Fig. 1 to titration curves. By analogy to the Lambert-Beer law for light-absorbing systems, it can be expected that the "apparent optical density" (log of the ratio of intensity of incident light to intensity of transmitted light) of a light-scattering system should be a linear function of the total surface area of the suspended particles. This expectation was verified experimentally by measurements upon aqueous suspensions of known, but varied, numbers of uniform-sized spheres of a polystyrene latex. Furthermore, the mass of precipitate present in a turbidimetric titration is a linear function of the volume of added reagent, assuming only that the precipitate has a negligible solubility. Therefore, the plots of Fig. 1 are in fact calculated titration curves of optical density *vs.* volume of added titrant, both in arbitrary units, up to the equivalence point. Beyond the equivalence point, no further precipitate is formed, so the titration curve should be a horizontal line from this point on. Thus each end-point is marked by the transition from a rising to a constant optical density. For situation (A) there is a linear increase in optical density up to the equivalence point, while situation (B) is marked both by curvature and by a lower optical density. Selective growth without further nucleation, situation (C) is characterized by a titration curve between (A) and (B), and situation (D) is also an intermediate one.

There are several reasons why actual titrations curves may be expected to differ

from the calculated ones. First, a precipitate tends to recrystallize, coagulate and settle, at a rate which is neither constant nor uniformly varying throughout the titration. This factor tends to decrease the optical density, to make the end-point transition less distinct, and if the precipitate settles below the level at which the light beam traverses the sample to make it impossible to obtain meaningful measurements of optical density. Second, as the titration proceeds toward the equivalence point, the tendency to nucleate may be expected to decrease gradually and the corresponding tendency toward crystal growth to increase. This factor consists of a gradual shift from situation (A) to situation (B) during the titration, so also renders less distinct the transition from a rising to a constant optical density. Third, the precipitates are never completely insoluble, and the solubility is generally greatest right at the equivalence point when neither ion is present in excess. This factor also tends to make the end-point "break" on the titration curve less distinct. Fourth, some scatter of points may be expected from random, unknown and/or uncontrolled, factors, even though the randomness is much less in titrations than when turbidities must be compared to standards.

Several predictions can be made on the basis of the considerations thus far, including the following:

a. Any experimental factor which enhances continual nucleation at the expense of further crystal growth should be desirable, because the end-point transition from a rising to a constant optical density is most distinct in situation (A).

b. Any experimental factor which tends to minimize coagulation and settling of the precipitate should render the end-points more distinct.

c. Any experimental factor increasing the extent of initial nucleation should increase the optical density and make titrations of lower concentrations of unknown possible.

d. Any experimental factor exerting considerable control over the nucleation-growth phenomena should make less significant those random factors which cause scatter of points on the titration curve.

EFFECTS OF NON-IONIC DETERGENTS

It has been found that, in some instances, the presence of a small amount of a non-ionic detergent in the titrated solution, serves as an experimental factor which fulfills to an appreciable extent all four of the desiderata of the preceding paragraph. Possibly the detergent molecules are adsorbed upon the surfaces of the particles of precipitate in such a way as to prevent or to minimize further growth of those particles.

Many measurements have been made on numerous systems. The action of the non-ionic detergents is quite selective, being quite pronounced with some precipitation reactions and of no significance whatever in others. For each system, titrations were performed without and with each of several added agents, and other experimental factors were varied as seemed desirable. The optical density, as measured on a Bausch and Lomb Spectronic Colorimeter or a Coleman Nefluorophotometer, was plotted *vs.* volume of added titrant, and the plots were examined for such factors as scatter of points from a smooth curve, magnitude of optical density, linearity prior to end-point, whether strictly horizontal beyond end-point or not, sharpness of transition from rising to constant optical density, and agreement between observed and known end-points.

Precipitation of barium sulfate

Two non-ionic detergents, Tergitol and Triton, were found to influence the precipitation process quite markedly. They increased the optical density considerably, speeded up the precipitation reaction so that a constant reading was reached more quickly after each increment of titrant, and minimized the tendency for the precipitate to coagulate and to settle to the bottom of the vessel. However, the titration curves are sufficiently rounded at and near the equivalence points, even with the surfactants present, to make accurate recognition of end-points difficult.

Precipitation of lead chromate

The non-ionic detergents exerted practically no influence on the nucleation-growth characteristics of lead chromate.

Precipitation of lead molybdate

The non-ionic surfactants failed to influence the precipitation process. However, another addition agent, dextrin, did enhance nucleation, as evidenced by an increased optical density, and it also prevented coagulation of the precipitate.

Precipitation of lead carbonate

In the titration of lead nitrate by sodium carbonate, the effects of non-ionic detergents were quite pronounced. The agents served to increase the optical density, to minimize settling of the precipitate during the titration, and to make the end-point transition from a rising optical density to a constant one somewhat sharper and more distinct. In this system, as in some others, the end-point is more distinct with more concentrated reagents than with extremely dilute ones, but the total optical density is difficult to measure accurately if it becomes too high.

Precipitation of calcium oxalate

In some titrations of calcium ion by oxalate ion, the presence of non-ionic surfactants, either Tergitol or Triton, served to result in higher optical densities, thereby making determinations of quite low concentration of calcium possible. However, the effect is not consistently reproducible, for the agents exerted no influence in many experiments. Other random variables, such as rate of mixing and size of increment of titrant, are much more significant. The agents do minimize coagulation, but this is not a serious problem in this determination anyway.

Precipitation of silver chloride

Both non-ionic surfactants, Tergitol and Triton, caused a slight decrease in optical density, perhaps due to a slightly enhanced coagulation rather than to actual increase in crystal growth, but the agents did not influence the accuracy or the precision of this turbidimetric titration determination. Gelatin, a common dispersing agent, made the end-point transition completely non-recognizable. Dextrin had negligible influence.

Precipitation of nickel dimethylglyoxime

Triton or Tergitol, particularly when gelatin was also present, resulted in reasonably

good titration curves. Without any addition agents, the random scatter on the titration curves was considerable. It was observed that the precipitate of nickel dimethylglyoxime tended to stick to the glass walls and to float to the surface when no surfactant was present, but that the suspension was made much more stable and uniform in the presence of the addition agents.

Precipitation of calcium fluoride

A turbidimetric titration procedure involving the precipitation of calcium fluoride has recently been published⁴. It was found in the present study that both Tergitol and Triton cause an increase in optical density of the suspended precipitate, thus signifying enhanced nucleation at the expense of crystal growth. The agents also made the titration curves more linear prior to the end-points, and the accuracy of the determination was improved appreciably.

SUMMARY

The physical form of a precipitate is subject to considerable random variation but is determined largely by the first batch of precipitated particles. So turbidimetric titration procedures are generally preferable to turbidimetric determinations based upon comparisons to standards. Titration curves of optical density *vs.* volume of titrant have been calculated for various conditions of nucleation and crystal growth. It is predicted from the calculated curves that any factor which enhances nucleation at the expense of crystal growth should improve the analytical usefulness of turbidimetric titrations. One such factor is the presence of a non-ionic surfactant which is apparently adsorbed on crystal surfaces, thereby minimizing further crystal growth. The prediction is verified with some precipitation reactions, but the surfactant is of no effect on others.

RÉSUMÉ

Les méthodes de titrage turbidimétrique (consistant à mesurer la densité optique en fonction du volume de réactif) se montrent généralement préférables aux dosages par comparaison avec des étalons. Des courbes de titrage ont été calculées dans diverses conditions.

ZUSAMMENFASSUNG

Turbidimetrische Titraktionen (Messung der optischen Dichte als Funktion der Menge zugesetzter Reagenzlösung) sind im allgemeinen den Vergleichsmethoden mit einer Standard-Trübung überlegen. Die Änderung der optischen Dichte in Abhängigkeit von der Menge Reagenzlösung unter verschiedenen Bedingungen wurde errechnet und in Kurven dargestellt.

REFERENCES

- ¹ M. BOBTELSKY, *Anal. Chim. Acta*, 13 (1955) 172.
- ² M. BOBTELSKY AND J. EISENSTADTER, *Anal. Chim. Acta*, 16 (1957) 479.
- ³ M. BOBTELSKY AND I. BAR-GADDA, *Anal. Chim. Acta*, 9 (1953) 168.
- ⁴ W. W. BRANDT AND A. A. DUSWALT, JR., *Anal. Chem.*, 30 (1958) 1120.

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DETERMINATION OF STRONG ACID MIXTURES

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The recently proposed tetraalkylammonium hydroxides¹⁻⁴ are gaining wide acceptance as titrants for the determination of acidic compounds and acid mixtures because their use supplants a large number of other diverse titrimetric methods. Among the applications recommended for these quaternary ammonium hydroxides are several procedures for differentiating titrations of both weak and strong acids^{3, 5, 6}. None of these offer supporting data for quantitative analysis of mixtures containing strong acids.

The authors have proposed an improved quaternary ammonium hydroxide titrant for the determination of strong acids⁷ and in another report discussed solvent-solute reactions which occur in the titration of strong acids in a number of nonaqueous solvents⁸. These studies provided the basis for the exact quantitative determination of acid mixtures containing strong acids. In this work, differentiating titrations of several acid mixtures are described with supporting quantitative data. Although emphasis is placed on mixtures containing sulfuric acid, the analysis of other acid mixtures is outlined to illustrate the potential of this procedure, and to demonstrate further the exceeding versatility of quaternary ammonium hydroxide titrants.

PROCEDURE

The apparatus and preparation of reagents were described previously⁷.

Dissolve 0.7-0.9 mequivs. of total acid in 50 ml of pyridine and titrate potentiometrically with 0.1*N* tetrabutylammonium hydroxide under a nitrogen atmosphere. Determine the end-points from a plot of potential *vs.* volume of titrant. Correct the final end-point for the solvent blank. When two or more inflections are present in the curve, use the difference between successive end-points to calculate the volume of titrant equivalent to the acids represented.

If any of the acids are pyridine insoluble, dissolve in 1.5 ml water prior to adding the pyridine. The addition of three drops of azo-violet indicator solution is often beneficial in the discernment of one or more of the end-points.

EXPERIMENTAL

Titration of strong acid mixtures

Fig. 1 typifies the potentiometric curve obtained when titrating a mixture of sulfuric acid and another monobasic strong acid. In this curve the first inflection includes the neutralization of nitric acid and the first equivalent of sulfuric acid, the second inflection represents the neutralization of the second equivalent of sulfuric

TABLE I
ANALYSIS OF NITRIC-SULFURIC ACID MIXTURES

Nitric acid			Sulfuric acid		
Added mg	Found mg	Recovery %	Added mg	Found mg	Recovery %
42.58	42.64	100.1	16.13	16.13	100.0
8.52	8.53	100.1	32.26	32.16	99.7
53.23	53.14	99.8	9.68	9.70	100.2
12.77	12.79	100.2	25.81	25.73	99.7
42.58	42.58	100.0	6.45	6.43	99.7

acid. Table I shows data on the analysis of known mixtures of sulfuric and nitric acids.

Titration of sulfuric-phosphoric acid mixtures yielded a potentiometric curve with three inflections, the first representing the neutralization of the first equivalent of sulfuric acid, the second representing the neutralization of the second sulfuric and first phosphoric acid equivalents, and the third representing the neutralization of the second phosphoric acid equivalent. The third phosphoric acid equivalent does not titrate in this mixture. This curve is illustrated in Fig. 2.

Table II lists the results obtained in the analysis of sulfuric-phosphoric acid mixtures.

Mixtures of phosphoric acid with *p*-toluenesulfonic, nitric and hydrochloric acid, respectively, on titration yielded a potentiometric curve similar to that illustrated in Fig. 2. Three inflections were obtained, the first representing the neutralization of the *p*-toluenesulfonic, nitric or hydrochloric acid, the second and third representing

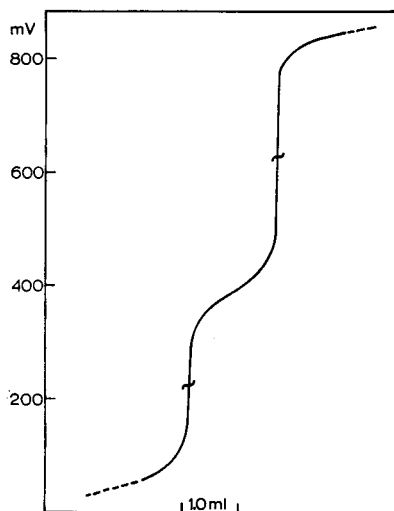


Fig. 1. Titration of nitric-sulfuric acid mixture.

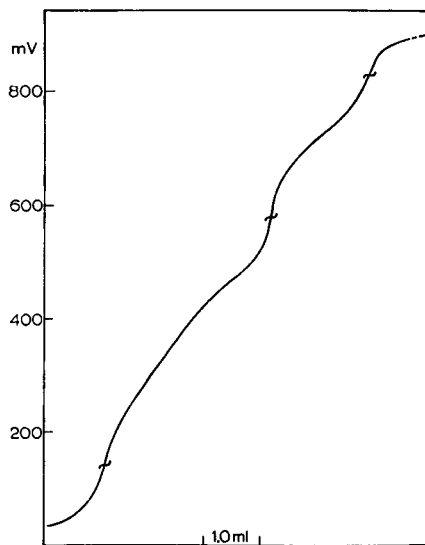


Fig. 2. Titration of phosphoric-sulfuric acid mixture.

TABLE II
ANALYSIS OF SULFURIC-PHOSPHORIC ACID MIXTURES

Phosphoric acid			Sulfuric acid		
Added mg	Found mg	Recovery %	Added mg	Found mg	Recovery %
17.94	17.84	99.4	11.02	10.91	99.0
29.15	28.95	99.3	15.20	15.30	100.7
35.87	36.08	100.6	22.03	22.03	100.0
18.24	18.24	100.0	25.09	25.09	100.0
17.94	17.94	100.0	25.09	24.99	99.6

TABLE III
ANALYSIS OF *p*-TOLUENESULFONIC-PHOSPHORIC ACID MIXTURES

<i>p</i> -Toluenesulfonic acid			Phosphoric acid		
Added mg	Found mg	Recovery %	Added mg	Found mg	Recovery %
50.94	50.94	100.0	28.48	28.58	100.4
84.90	85.07	100.2	14.24	14.14	99.3
135.84	134.41	98.9	22.78	22.79	100.0
33.96	34.14	100.5	42.72	42.52	99.5

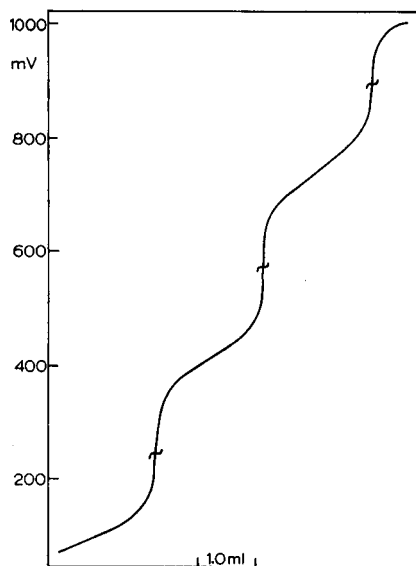


Fig. 3. Titration of *p*-toluenesulfonic acid, propionic acid and *p*-benzylphenol mixture.

the neutralization of the first two equivalents of phosphoric acid. Table III gives the results from analysis of *p*-toluenesulfonic-phosphoric acid mixtures.

Results for the analysis of several other strong acid mixtures are given in Table IV.

The potentiometric curve for each of the mixtures containing sulfuric acid was similar to that illustrated in Fig. 1, the curves for the mixtures containing phosphoric acid were similar to that illustrated in Fig. 2.

TABLE IV
ANALYSIS OF STRONG ACID MIXTURES

Compounds	Added mg	Found mg	Recovery %
Perchloric acid	52.24	52.35	100.2
Sulfuric acid	25.86	25.96	100.4
Hydrochloric acid	16.76	16.76	100.0
Sulfuric acid	17.50	17.50	100.0
Benzenesulfonic acid	55.94	55.36	99.0
Sulfuric acid	25.96	26.06	100.4
3-Amino- <i>p</i> -toluenesulfonic acid	94.58	93.52	98.9
Sulfuric acid	25.96	26.16	100.8
Naphalene- β -sulfonic acid	53.07	52.60	99.1
Sulfuric acid	28.25	28.40	100.5
Sulfamic acid	57.17	57.37	100.4
Sulfuric acid	29.63	29.52	99.6
<i>p</i> -Toluenesulfonic acid	80.95	80.95	100.0
Sulfuric acid	25.91	25.86	99.8
Methanesulfonic acid	20.15	20.05	99.5
Sulfuric acid	25.86	25.86	100.0
Benzenesulfonyl chloride	71.68	72.05	100.5
Sulfuric acid	26.16	26.06	99.6
Nitric acid	25.90	25.84	99.8
Phosphoric acid	28.48	28.48	100.0
Hydrochloric acid	14.19	14.27	100.6
Phosphoric acid	42.72	42.82	100.3

Titration of a mixture containing a strong, weak, and very weak acid

Fig. 3 shows the potentiometric curve for titration of *p*-toluenesulfonic, propionic acid, and *p*-benzylphenol, which typify the strong, weak and very weak acids classifications. The first inflection represents the neutralization of *p*-toluenesulfonic acid, the second, propionic acid, and the third, *p*-benzylphenol. Table V indicates the results obtained on analysis of mixtures of these three acids.

DISCUSSION

This work does not purport to be a complete study of the analysis of any specific acid mixture. It does indicate, however, the feasibility of determining all types of acid mixtures by the differentiating titrations described and should suggest simple

TABLE V

ANALYSIS OF *p*-TOLUENESULFONIC ACID, PROPIONIC ACID, AND *p*-BENZYLPHENOL MIXTURES

<i>p</i> -Toluenesulfonic acid		Recovery %	Propionic acid		Recovery %	<i>p</i> -Benzylphenol		Recovery %
Added mg	Found mg		Added mg	Found mg		Added mg	Found mg	
33.67	33.60	99.8	21.69	21.92	101.1	45.16	44.94	99.5
50.51	50.76	100.5	17.35	17.22	99.3	27.09	27.35	101.0
67.34	67.38	100.1	13.01	13.00	99.9	36.12	35.57	98.5
84.18	84.00	99.8	8.68	8.69	100.1	72.25	73.05	101.1
16.84	16.80	99.8	34.70	34.60	99.7	18.06	17.78	98.4

procedures for the analysis of acid mixtures now being determined by tedious and indirect methods.

Data on the differential titration of sulfuric acid–hydrochloric acid and sulfuric acid–nitric acid mixtures are not presented as a new alkalimetric method. The analysis of these acid mixtures with another titrant was reported by CRITCHFIELD AND JOHNSON⁹, who reviewed the literature on this subject to 1954. The purpose of this work, as previously emphasized, is to indicate further the great versatility of tetrabutylammonium hydroxide as a titrant for acids and acid mixtures.

ACKNOWLEDGEMENT

The authors express their appreciation to A. J. SENSABAUGH for preparation of the figures.

SUMMARY

Strong acid mixtures as well as acid mixtures containing all classifications of acids can be analyzed by differentiating titrations in pyridine solution with 0.1*N* tetrabutylammonium hydroxide as the titrant. Included in the study are analyses of mixtures of sulfuric acid and nitric, hydrochloric, perchloric, phosphoric and sulfonic acids, respectively, as well as the resolution of a typical strong acid, weak acid and very weak acid mixture.

RÉSUMÉ

Des mélanges d'acides forts ont pu être dosée, dans la pyridine, par titrage différentiel, au moyen d'hydroxyde de tétrabutylammonium. On a pu également effectuer l'analyse de mélanges renfermant un acide fort, un acide faible et un acide très faible.

ZUSAMMENFASSUNG

Mischungen von starken Säuren, in Pyridin gelöst, können durch eine differenzierte Titration mit einer Standard-Tetrabutylammoniumhydroxydlösung analysiert werden. Die Methode lässt sich auch auf Gemische von starken, schwachen und sehr schwachen Säuren anwenden.

REFERENCES

- 1 R. H. CUNDIFF AND P. C. MARKUNAS, *Anal. Chem.*, 28 (1956) 792.
- 2 V. Z. DEAL AND G. E. A. WYLD, *Anal. Chem.*, 27 (1955) 47.
- 3 J. S. FRITZ AND S. S. YAMAMURA, *Anal. Chem.*, 29 (1957) 1079.
- 4 G. A. HARLOW, C. M. NOBLE AND G. E. A. WYLD, *Anal. Chem.*, 28 (1957) 787.
- 5 B. B. BRUSS AND G. E. A. WYLD, *Anal. Chem.*, 29 (1957) 232.
- 6 G. A. HARLOW AND G. E. A. WYLD, *Anal. Chem.*, 30 (1958) 69.
- 7 R. H. CUNDIFF AND P. C. MARKUNAS, *Anal. Chem.*, 30 (1958) 1450.
- 8 R. H. CUNDIFF AND P. C. MARKUNAS, *Anal. Chem.*, 30 (1958) 1447.
- 9 F. E. CRITCHFIELD AND J. B. JOHNSON, *Anal. Chem.*, 26 (1954) 1803.

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HIGH FREQUENCY TITRATION AND ESTIMATION OF IONS

I. DETERMINATION OF SILVER

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Use of the high frequency titrimeter has attracted the attention of the analysts during the past few years and at present various types of chemical reactions are being studied with it. High frequency titrimetry has been found, as reported herein, to be a very useful technique for the estimation of silver with certain common organic and inorganic reagents. The end-point of the reactions has been found to be very sharp, stoichiometric and reproducible.

Apparatus

The apparatus used in the present investigation is a modification of that proposed by HALL¹. The complete assembly is shown in the attached diagram (Fig. 1).

The cell containing the electrolytic solution was placed in parallel with the capacitor circuit. The frequency of 5.774 mega cycles/sec was produced by a piezo-electric quartz crystal. A change in the composition of the solution produced a change in the frequency, as a result of which, the oscillations of the quartz crystal stopped. Thus a change in capacity was necessary to restore the oscillations to their original value and these changes in capacity, following the change in composition of the solution, were noted and plotted against the volume in ml of the reagent added. Since the condenser dial readings were found to decrease linearly with the capacity of the condenser, dial readings were plotted, for the sake of convenience, against ml of the added electrolyte. The dial used was a slow motion vernier (Ormond) divided into 100 divisions.

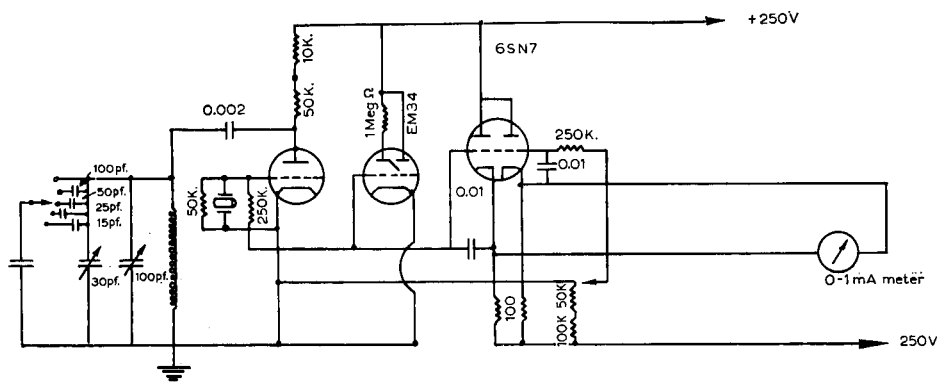


Fig. 1. High frequency titration apparatus.

EXPERIMENTAL

Materials

Doubly-distilled water is used throughout the course of the experiment. All chemicals used were of A.R. quality. Standard solutions of silver nitrate, potassium chloride, potassium bromide,

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potassium iodide, potassium chromate, ammonium thiocyanate and potassium cyanide were prepared by the usual methods.

A standard solution of bismuthiol I was prepared by dissolving a weighed quantity of this reagent in a definite volume of water, whereas those of bismuthiol II, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole were prepared in ethyl alcohol.

Procedure

Silver has been estimated with potassium chloride, potassium bromide, potassium iodide, potassium cyanide, ammonium thiocyanate, potassium chromate and some organic reagents as bismuthiol I, bismuthiol II, 2-mercaptobenzimidazole and 2-mercaptobenzothiazole. The results are highly accurate except for those methods involving chromate, bismuthiol I and 2-mercaptobenzimidazole. The requisite amount of silver nitrate solution was placed in the titration cell and then diluted with water to 70 ml at which the height of the water was just sufficient to fill the cell to a level slightly above the upper metal band. The standard solution of the reagent was then added in small increments, over a range of several ml on both sides of the end-point, and the change in the condenser dial readings, after each addition, was noted. Potas-

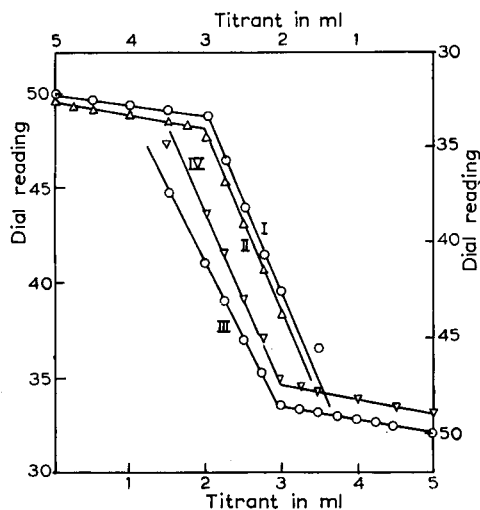


Fig. 2. Determination of silver. I: 10 ml $M/100$ $AgNO_3$ with $M/20$ KI ; II: 10 ml $M/100$ $AgNO_3$ with $M/20$ KCl ; III: 10 ml $M/100$ $AgNO_3$ with $M/20$ NH_4SCN ; IV: 10 ml $M/100$ $AgNO_3$ with $M/20$ KBr .

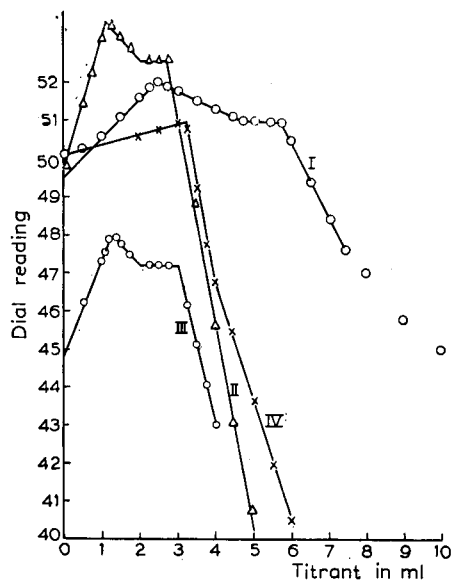


Fig. 3. Titration of I: 5 ml $M/20$ KCN with $M/20$ $AgNO_3$; II: 2.5 ml $M/20$ KCN with $M/20$ $AgNO_3$; III: 1.25 ml $M/20$ KCN with $M/40$ $AgNO_3$; IV: 20 ml $M/100$ $AgNO_3$ with $M/20$ KCN .

sium chloride, potassium bromide, potassium iodide and ammonium thiocyanate were found to behave similarly in that silver (1 to 50 mg) was accurately determined by their use (Fig. 2). However, low results were obtained when silver nitrate was titrated with potassium cyanide (see curves of Fig. 3). When the cyanide solution

was taken in the titration cell and silver nitrate added the end-point corresponding to the formation of $K[Ag(CN)_2]$ was found to be highly accurate. The second break in the curves was suggested to be due to the dissociation of the complex simply to $AgCN$; during direct titration, an end-point corresponding to the formation of simple $AgCN$ was not obtained. Among the organic reagents employed, bismuthiol II and 2-mercaptobenzothiazole were found to give good results only when less than 15 mg of silver were present (Fig. 4). With higher amounts, results were not very good. Very low results were obtained with the reagents bismuthiol I and 2-mercaptobenzimidazole, since with their use precipitation of silver was not very rapid.

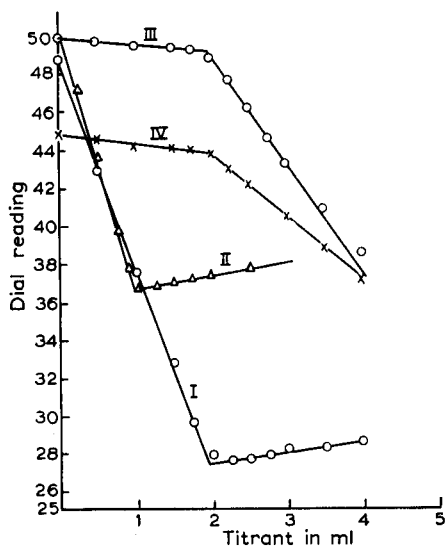


Fig. 4. Titration of I: 10 ml $M/100$ $AgNO_3$ with $M/20$ 2-mercaptobenzothiazole; II: 5 ml $M/100$ $AgNO_3$ with $M/20$ 2-mercaptobenzothiazole; III: 10 ml $M/100$ $AgNO_3$ with $M/20$ bismuthiol II; IV: 5 ml $M/100$ $AgNO_3$ with $M/40$ bismuthiol II.

ACKNOWLEDGEMENTS

Our grateful thanks are due to University Grants Commission, Government of India, for providing us with the funds for the construction of the high frequency titration apparatus.

SUMMARY

High frequency titration has been found to be a highly suitable technique for the volumetric estimation of silver with potassium chloride, potassium bromide, potassium iodide, ammonium thiocyanate, 2-mercaptobenzothiazole and bismuthiol II. The results have been accurate when the amount of silver present was not more than 15 mg. Titration of potassium cyanide with silver nitrate gives an end-point corresponding to the complex $K[Ag(CN)_2]$. Reverse titration fails to give any sharp break. Mercaptobenzimidazole, bismuthiol I and potassium chromate were not suitable reagents in these determinations.

RÉSUMÉ

La technique de titrage à haute fréquence convient très bien au dosage volumétrique de l'argent au moyen de chlorure de potassium, de bromure de potassium, d'iode de potassium, de thio-

cyanate d'ammonium, le mercapto-2-benzothiazole et le bismuthiol II. Pour des quantités d'argent inférieures à 15 mg, la précision des résultats est excellente.

ZUSAMMENFASSUNG

Die Methoden der Hochfrequenztitration eignen sich sehr gut zur volumetrischen Bestimmung von Silber mit Hilfe einer Lösung von Kaliumchlorid, Kaliumbromid, Kaliumjodid, Ammoniumthiocyanat, 2-Mercaptobenzothiazol und Wismuthiol II. Bei Mengen von weniger als 15 mg Silber werden sehr gute Resultate erhalten.

REFERENCE

¹ J. L. HALL, *Anal. Chem.*, 24 (1952) 1244.

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SEPARATIONS INVOLVING SULPHIDES

III. SEPARATION OF MOLYBDENUM AND TELLURIUM FROM BARIUM

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In a previous publication¹ in this series, methods were proposed for the quantitative separation of selenium, arsenic, antimony and mercury from barium. These methods are based upon the formation and subsequent decomposition of thiosalts. In this paper a description is given of the successful separation of molybdenum and tellurium from barium by means of this method.

EXPERIMENTAL

Reagents

Ammonium molybdate (Kahlbaum), barium chloride (AnalaR), potassium tellurite, sodium sulphide 2*N*, hydrochloric acid 2*N*.

Separation of molybdenum from barium

The mixture (in HCl) was treated with a large excess of sodium sulphide reagent (the reagent must be added in small quantities at a time with constant shaking to avoid the formation of molybdenum blue), acidified with hydrochloric acid, heated to boiling, and allowed to cool to room temperature. The precipitate of molybdenum trisulphide was filtered through a weighed sintered glass crucible (porosity 4) washed thoroughly with water, and then with alcohol and ether, sucked dry at the filter pump for 15 min, dried in a vacuum desiccator for an hour and weighed as $\text{MoS}_3 \cdot 2\text{H}_2\text{O}$. In the filtrate barium was estimated as sulphate. The results are given in Table I.

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TABLE I
SEPARATION OF MOLYBDENUM FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

<i>Wt. of Mo as found in the ppt. MoS₃·2H₂O</i>	<i>Wt. of Mo actually present</i>	<i>Wt. of Ba as found in the ppt. BaSO₄</i>	<i>Wt. of Ba actually present</i>
g	g	g	g
0.04758	0.04760	0.1756	0.1756
0.03811	0.03808	0.09640	0.09656
0.05163	0.05154	0.1353	0.1352

Separation of tellurium from barium

The mixture was treated as for the separation Mo–Ba. The precipitate of tellurium sulphide was dried at 100–105° for an hour and weighed as TeS₂. In the filtrate barium was estimated as sulphate. The results are given in Table II.

TABLE II
SEPARATION OF TELLURIUM FROM BARIUM WITH 2*N* SODIUM SULPHIDE REAGENT

<i>Wt. of Te as found in the ppt. TeS₂</i>	<i>Wt. of Te actually present</i>	<i>Wt. of Ba as found in the ppt. BaSO₄</i>	<i>Wt. of Ba actually present</i>
g	g	g	g
0.1180	0.1180	0.1412	0.1412
0.1181	0.1180	0.05637	0.05649
0.04736	0.04720	0.1411	0.1412

ACKNOWLEDGEMENTS

This work was carried out in the Chemical Laboratories, University of Allahabad. The author is grateful to Prof. Dr. S. GHOSH and Dr. I. K. TAIMNI for their kind interest.

SUMMARY

It has been shown that the method of separating of molybdenum and tellurium from barium, based on the decomposition of thioalts, gives fairly correct results in quantitative analysis.

RÉSUMÉ

Les séparations du molybdène et du tellure, d'avec le baryum, basées sur la décomposition des thioisels donnent de bons résultats en analyse quantitative.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass die Trennungen von Molybdän und Tellur vom Barium auf Grund der Zersetzung der Thioalze bei der quantitativen Analyse recht gute Resultate ergeben.

LITERATUR

- ¹ I. K. TAIMNI AND M. N. SRIVASTAVA, *Anal. Chim. Acta*, 15 (1956) 517.

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SEPARATIONS INVOLVING SULPHIDES

IV. SEPARATION OF ARSENIC, ANTIMONY, TELLURIUM AND MERCURY FROM ZIRCONIUM

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In earlier publications^{1,2} in this series, methods were proposed for the quantitative separation of the metals of the arsenic group from barium. These methods are based upon the formation and subsequent decomposition of thioalts. In this paper, a description is given of the successful separation of arsenic, antimony, tellurium and mercury from zirconium by means of this method.

In the following series of experiments the mixture containing the two metals is treated, if necessary, with sodium hydroxide and tartrate to keep zirconium in solution, and then an excess of the alkali sulphide reagent is added, whereby the metals of the arsenic group form thioalts. These are decomposed with a measured volume of hydrochloric acid, sufficient to make the concentration of acid in the resulting mixture higher than 1*N*. The metals are then separated and estimated as sulphides. Zirconium is precipitated from the filtrate with cupferron and estimated as ZrO₂.

EXPERIMENTAL

Reagents

Sodium arsenate, zirconium oxychloride, sodium hydroxide, sodium tartrate (AnalaR), sodium sulphide 2*N*, hydrochloric acid, antimony potassium tartrate (AnalaR), potassium tellurite, mercuric chloride (AnalaR).

Separation of arsenic from zirconium

Measured portions of standard solutions of salts of these metals are mixed together, and, in order to keep zirconium in solution, the precipitate of zirconium arsenate is dissolved by treatment with sodium hydroxide and tartrate. Then the mixture is treated with a large excess of sodium sulphide reagent and acidified with a measured quantity of conc. hydrochloric acid sufficient to make the concentration of acid in the resulting mixture approximately 6*N*. The mixture is heated to boiling, stirred and allowed to cool to room temperature. The precipitate of As₂S₅ is filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with *N* HCl, water, and alcohol, dried at 100–110° for an hour and weighed as As₂S₅.

After expelling the hydrogen sulphide gas from the filtrate and adding sulphuric acid to a concentration of about 10%, zirconium is precipitated by cupferron, ignited, and weighed as ZrO₂.

The results are given in Table I.

TABLE I
SEPARATION OF ARSENIC FROM ZIRCONIUM WITH 2*N* SODIUM SULPHIDE REAGENT

<i>Wt. of As as found in the ppt. As₂S₃</i> g	<i>Wt. of As actually present</i> g	<i>Wt. of Zr as found in the ppt. ZrO₂</i> g	<i>Wt. of Zr actually present</i> g
0.05694	0.05694	0.04130	0.04109
0.04564	0.04555	0.04116	0.04109
0.02046	0.02050	0.03279	0.03287

Separation of antimony from zirconium

Proceed as for As-Zr but acidify with a measured quantity of 3*N* hydrochloric acid sufficient to make the concentration of acid in the resulting mixture 1-1.2*N*. The precipitate of antimony sulphide thus obtained is filtered and weighed as Sb₂S₃. In the filtrate zirconium is precipitated by cupferron, ignited and weighed as ZrO₂. The results are given in Table II.

TABLE II
SEPARATION OF ANTIMONY FROM ZIRCONIUM WITH 2*N* SODIUM SULPHIDE REAGENT

<i>Wt. of Sb as found in the ppt. Sb₂S₃</i> g	<i>Wt. of Sb actually present</i> g	<i>Wt. of Zr as found in the ppt. ZrO₂</i> g	<i>Wt. of Zr actually present</i> g
0.08876	0.08875	0.04102	0.04109
0.08876	0.08875	0.03287	0.03287
0.03556	0.03550	0.03301	0.03287

Separation of tellurium from zirconium

Treat the mixture as for Sb-Zr in order to precipitate tellurium as the sulphide; this is filtered and weighed as TeS₂. In the filtrate zirconium is precipitated by cupferron, ignited, and weighed as ZrO₂. The results are given in Table III.

TABLE III
SEPARATION OF TELLURIUM FROM ZIRCONIUM WITH 2*N* SODIUM SULPHIDE REAGENT

<i>Wt. of Te as found in the ppt. TeS₂</i> g	<i>Wt. of Te actually present</i> g	<i>Wt. of Zr as found in the ppt. ZrO₂</i> g	<i>Wt. of Zr actually present</i> g
0.06247	0.06250	0.04102	0.04109
0.06261	0.06250	0.03279	0.03287
0.04982	0.0500	0.03287	0.03287

Separation of mercury from zirconium

The mixture is treated as usual to precipitate mercury as sulphide, which is then

filtered and weighed as HgS. In the filtrate zirconium is precipitated by cupferron, ignited and weighed as ZrO₂.

The results are given in Table IV.

TABLE IV
SEPARATION OF MERCURY FROM ZIRCONIUM WITH 2N SODIUM SULPHIDE REAGENT

<i>Wt. of Hg as found in the ppt. HgS</i> g	<i>Wt. of Hg actually present</i> g	<i>Wt. of Zr as found in the ppt. ZrO₂</i> g	<i>Wt. of Zr actually present</i> g
0.1876	0.1875	0.04116	0.04109
0.1741	0.1740	0.04109	0.04109
0.1740	0.1740	0.03279	0.03287

Notes on negative results

Negative results have been obtained in the following cases:

- (A) Selenium and zirconium,
- (B) Tin and zirconium.

(A) *Selenium and zirconium*: When attempts are made to separate selenium from a mixture containing the two metals and to estimate it as sulphide, high results are obtained. This is probably due to zirconium ions being absorbed by the selenium sulphide precipitate. Even the character of the precipitate is changed; instead of an orange-red spongy mass a yellow substance is obtained, which is much more fragile. However, tartrate, used to keep zirconium in solution, does not interfere with the precipitation of pure selenium sulphide.

(B) *Tin and zirconium*: When tin is separated from a mixture containing zirconium and estimated as sulphide by decomposing its thiosalt, with acids (2N, 8N, 10N glacial acetic acid and 2N HCl) high results are obtained. This is due to the coprecipitation of zirconium with tin sulphide. Tartrate cannot be used to dissolve the zirconium, as it inhibits the precipitation of tin sulphide.

ACKNOWLEDGEMENTS

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SUMMARY

It has been shown that the methods for separating arsenic, antimony, tellurium, and mercury from zirconium, based on the decomposition of thiosalts, give fairly correct results in quantitative analysis. However, the method fails in the following combinations of metals: (1) selenium and zirconium, (2) tin and zirconium.

RÉSUMÉ

Les séparations de l'arsenic, de l'antimoine, du tellure et du mercure d'avec le zirconium, basées sur la décomposition des thio-sels, donnent de bons résultats en analyse quantitative. Cependant cette méthode ne peut pas être utilisée pour les séparations suivantes: (1) sélénium et zirconium, (2) étain et zirconium.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass die Trennungen von Arsen, Antimon, Tellur und Quecksilber vom Zirkonium, welche sich auf die Zerstörung der Thiosalze gründen, bei der quantitativen Analyse recht gute Resultate geben. Die Methode versagt aber bei den folgenden Kombinationen: 1. Selen und Zirkonium, 2. Zinn und Zirkonium.

REFERENCES

- ¹ I. K. TAIMNI AND M. N. SRIVASTAVA, *Anal. Chim. Acta*, 15 (1956) 517.
² M. N. SRIVASTAVA, *Anal. Chim. Acta*, 21 (1959) ACA 1656.

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THE DETERMINATION OF MOLECULAR WEIGHT USING THERMISTORS

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It has been demonstrated by HILL¹ that a solution when exposed to vapor of the same solvent assumes some temperature higher than that of solvent alone exposed to the same vapor. This temperature difference is due to vapor condensation on the solution whereas the solvent being subject to equal rates of evaporation and condensation remains at the temperature of the vapor.

This principle has been applied by MÜLLER AND STOLTEN² to the determination of molecular weight by using thermistors as the temperature sensing elements and stainless steel cups to hold the solvent and solution. They found that approximately 30 min is required for the stainless steel cup and solution therein to reach a maximum temperature.

The principal modifications of the apparatus used here permit the solution to

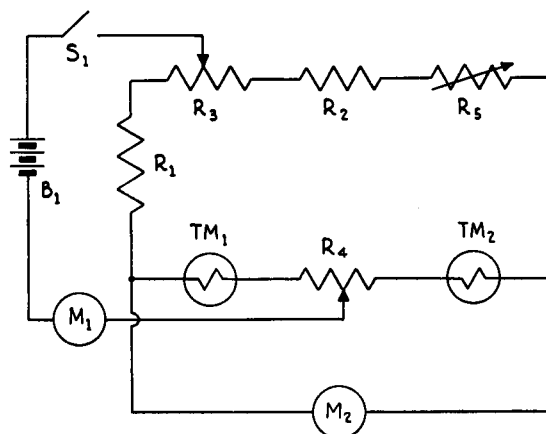


Fig. 1. Wheatstone bridge circuit.

reach its maximum temperature in about 3 min, make possible a substantial temperature rise of the solution for a given solute concentration and allow convenient and rapid determination of the molecular weight of successive samples.

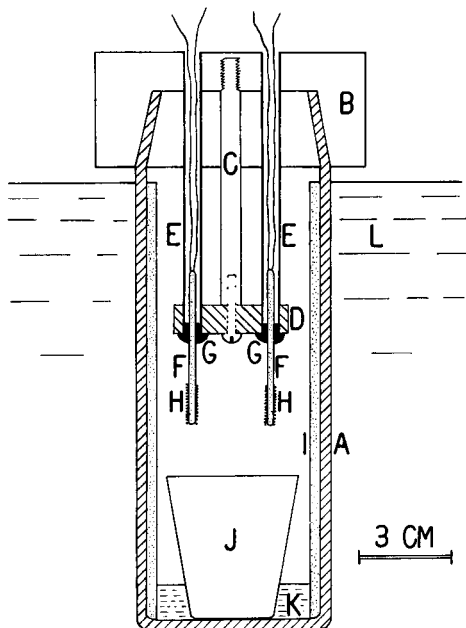


Fig. 2. Solvent-vapor chamber vs. thermistor assembly.

APPARATUS

The Wheatstone bridge circuit used in these experiments is shown in Fig. 1. The various components of the circuit are as follows:

B₁: 4.5 Volt battery; S₁: Single-pole, single-throw switch; R₁ and R₂: 100,000 ohm wire-wound fixed resistors; R₃: 1,000 ohm wire-wound variable resistor; R₄: 20 ohm wire-wound variable resistor; R₅: 1,000 ohm ten-turn, wire-wound micropotentiometer; TM₁ and TM₂: Type GA51P8 thermistors made by Fenwal Electronics, Inc., Framingham, Massachusetts; M₁: 0 to 50 microammeter; M₂: Null Detector Model No. 104WIG made by the Minneapolis-Honeywell Regulator Co., Minneapolis, Minnesota.

The solvent-vapor chamber and thermistor assembly are shown in Fig. 2. The various parts are as follows:

A: Glass solvent-vapor chamber; B: "Bakelite" cap machined to fit $\frac{71}{25}$ glass joint; C: 6 mm stainless steel rod support for thermistor assembly; D: "Teflon" thermistor support; E: 5-mm glass tubing; F: Fenwal Type GA51P8 thermistors; G: Cupric oxide-phosphoric acid cement; H: 40-turn platinum wire coils made with 0.3-mm diameter wire; I: 3 mm thick absorbent paper lining the total depth and about $\frac{3}{4}$ of the circumference of the inner chamber wall and covered on both sides with 1.5-mm mesh aluminum screen; J: Stainless steel crucible; K: Solvent; L: Constant temperature water bath.

PROCEDURE

Immerse the apparatus of Fig. 2 in a water bath thermostated at about $30^{\circ} + 0.01^{\circ}$. Pour solvent into the vapor chamber so that there is about 1 cm of excess solvent in the bottom of the chamber over that required to saturate the absorbent paper

lining the inside wall of the chamber. Rinse off both platinum wire coils covering the thermistors with about 0.1 to 0.2 ml of solvent. The solvent can be readily placed on the coils by means of an elongated medicine dropper inserted into the vapor chamber through a hole in the "Bakelite" cap. The medicine dropper is stored, when not in use, in copper tubing which is sealed on the bottom and immersed in the water bath. Set the micropotentiometer R_5 of Fig. 1 at zero resistance and turn on switch S_1 of Fig. 1. When temperature equilibrium has been established within the vapor chamber, balance the bridge using resistors R_3 and R_4 of Fig. 1. Replace the solvent in contact with the sensing thermistor TM_1 of Fig. 1 by rinsing with 0.1 to 0.2 ml of solution which has been previously brought to 30° by immersion of its container in the water bath. Balance the bridge using the 1,000 ohm micropotentiometer.

Approximately 3 min are required for the sensing thermistor to reach its maximum temperature. Record the maximum resistance of the micropotentiometer and use this value to calculate the molecular weight of the solute (see below). Rinse off the sensing thermistor with solvent and return the micropotentiometer to zero resistance. Temperature equilibrium will again be established in about 3 min at which time the molecular weight of the next sample may be determined. If desired, the sample may be recovered from the stainless steel crucible within the solvent-vapor chamber.

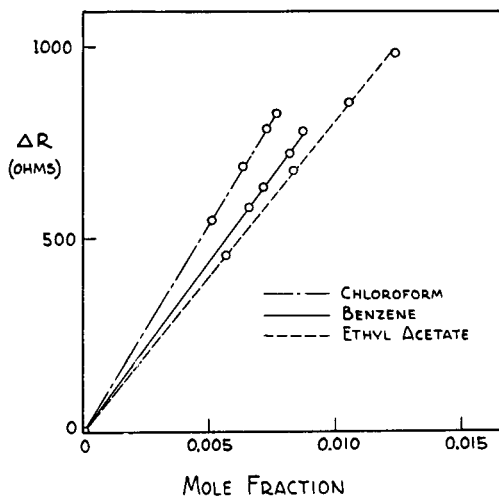


Fig. 3. Relationship of ΔR vs. mole fraction of solute.

Calculation

Thermistor resistance varies logarithmically with temperature but only a maximum of approximately 1% of the total resistance of one of the thermistors is utilized in these experiments so ΔT is essentially proportional to ΔR . It is also true that $\Delta R = K \cdot MF$ (see Fig. 3), where ΔT and ΔR are the changes in temperature and resistance, respectively, of the sensing thermistors, K is a proportionality constant

and MF is the mole fraction of solution. Substituting the appropriate terms for MF and rearranging yields the equation:

$$MW_{\text{solute}} = \frac{g_{\text{solute}} \cdot MW_{\text{solvent}} (K - \Delta R)}{\Delta R \cdot g_{\text{solvent}}}$$

where MW is molecular weight and g is weight in grams.

RESULTS

The molecular weights of 4 different compounds in three different solvents, as found by using the above procedure, are given in Table I.

The values of K listed in Table I are obtained from the slopes of the lines of plots of ΔR versus mole fraction of solute (Fig. 3).

The average deviation of a single determination of ΔR is between 3 and 4 ohms. This value was obtained by 30 consecutive determinations of the ΔR value of the same solution.

TABLE I
MOLECULAR WEIGHT DETERMINATIONS

<i>Solvent: Benzene, K = 88,700</i>				
<i>Compound</i>	<i>ΔR</i>	<i>Mole fraction</i>	<i>Molecular (found)</i>	<i>Weight (theor)</i>
Naphthalene	777	0.00866	127	128
1,2,4,5-Tetrachlorobenzene	633	0.00712	215	216
Dibenzyl	581	0.00659	183	182
Coumarin	723	0.00823	148	146
<i>Solvent: Ethyl Acetate, K = 80,400</i>				
<i>Compound</i>	<i>ΔR</i>	<i>Mole fraction</i>	<i>Molecular (found)</i>	<i>Weight (theor)</i>
Naphthalene	981	0.01230	129	128
1,2,4,5-Tetrachlorobenzene	453	0.00568	218	216
Dibenzyl	681	0.00835	179	182
Coumarin	855	0.01063	146	146
<i>Solvent: Chloroform, K = 107,900</i>				
<i>Compound</i>	<i>ΔR</i>	<i>Mole fraction</i>	<i>Molecular (found)</i>	<i>Weight (theor)</i>
Naphthalene	779	0.00728	129	128
1,2,4,5-Tetrachlorobenzene	545	0.00505	216	216
Dibenzyl	684	0.00632	182	182
Coumarin	825	0.00761	145	146

DISCUSSION

The thermistors shown in Figs. 1 and 2 are nominally rated at 100,000 ohms at 25° and have a negative temperature coefficient of about 4.6%.

The bridge null detector is conservatively rated as having a sensitivity of 0.001 $\mu\text{A}/\text{mm}$ so a 1 to 2 ohm unbalance in one arm of the bridge corresponding to about 10^{-10} A bridge unbalance can be detected.

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The water bath temperature need not be controlled closer than 0.01° . Assuming the reference and sensing thermistors are matched within 2000 ohms, a change in temperature of 0.01° within the vapor chamber will result in a bridge unbalance of approximately one ohm (calculated). Furthermore, water bath temperature fluctuations are damped before reaching the inside of the vapor chamber by the glass wall of the vapor chamber.

The purpose of the aluminum screen covering the surface of the absorbent paper within the vapor chamber is to help equalize temperature within the chamber.

It appears likely that solvents other than the three listed in the previous experiments could be used for the determination of molecular weight. Thus far, one or more of the three solvents has been suitable for determination of the molecular weight of samples dealt with by this laboratory.

Molecular weights as high as 2000 have been determined by this method. If 10% is set as the maximum useable concentration of solution and 350 ohms is chosen as the smallest value of ΔR which can be determined with a relative error of less than 2%, the method is sufficiently sensitive using chloroform as solvent to determine molecular weights up to about 3500.

The temperature rise of solutions of the solutes listed in Table I is only about 90% of the maximum theoretical temperature rise, but because the geometry of the thermistors in the solvent-vapor chamber is fixed, reproducible results are obtained.

SUMMARY

A method of less than 2% relative error, requiring less than 5 mg of sample and utilizing thermistors is described for the rapid determination of molecular weight.

RÉSUMÉ

Une méthode rapide est proposée pour la détermination de poids moléculaires permettant des mesures sur des quantités de substances inférieures à 5 mg.

ZUSAMMENFASSUNG

Es wird eine rasche Methode zur Molekulargewichtsbestimmung von Milligrammengen unter Anwendung von Thermistoren beschrieben.

REFERENCES

- ¹ A. V. HILL, *Proc. Roy. Soc. London*, A127 (1930) 9.
- ² R. H. MÜLLER AND H. J. STOLTEN, *Anal. Chem.*, 25 (1953) 1103.

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INDIRECT EDTA-TITRATION OF ALUMINIUM WITH LEAD(II) SOLUTIONS AND 4-(2-PYRIDYLAZO)-RESORCINOL (PAR) AS INDICATOR

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A problem of considerable importance in the field of inorganic analytical chemistry is to find improved methods for the determination of aluminium. The introduction of EDTA offers the possibility of titrating aluminium. A number of papers on this subject have been published, but it has proved difficult to find satisfactory methods for the direct EDTA-titration of aluminium, and only a few such methods have been suggested. On the other hand, a series of publications describe indirect methods of determination using different indicators and standard solutions for back titration of excess EDTA.

An excellent survey of the literature on EDTA-titration of aluminium (and other metals) has been published by FLASCHKA, BARNARD AND BROAD¹.

In a paper recently published by HONDA, KÖRBL, BAŽANT AND PŘIBIL², aluminium is indirectly determined with standard solutions of lead(II) and xylenol orange as indicator.

In another paper, WEHBER³ mentions that 4-(2-pyridylazo)-resorcinol (PAR) is an excellent indicator for metals and that a sharp end-point from red to yellow is obtained when lead(II)-solutions are titrated with EDTA. WEHBER does not, however, give any details about the procedure used or the results obtained.

In the present publication, the EDTA-titration of lead(II) with PAR as indicator is investigated, and the application of lead(II) standard solutions and PAR is introduced for indirect determination of macro and micro amounts of aluminium.

EXPERIMENTAL

Preparation of PAR

4-(2-pyridylazo)-resorcinol is synthesized according to a procedure described by CHICHIBABIN⁴. The indicator can now also be purchased from chemical firms.

PAR solution

A 0.1% solution in distilled water of the sodium salt is applied. This solution can be stored for months.

Standard solutions

EDTA standard solution. 0.05M EDTA solution is prepared by dissolving 18.61 g of ethylenediaminetetraacetic acid, disodium salt, in distilled water and diluting to 1000 ml. This solution is standardized against the lead standard solution mentioned below. The molarity was 0.05004. A 0.001M EDTA solution is prepared by dilution.

Aluminium standard solution. 10.000 g of aluminium (super pure —99.997% Al) are dissolved in 1:1 hydrochloric acid and diluted to 1000 ml. The pH of this solution is about 2.

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Lead standard solution. A 0.05M lead(II) solution is prepared by dissolving 10.360 g of high purity (spectrographically standardized) in nitric acid and diluting to 1000 ml.

All other chemicals used are of analyzed reagent quality.

For the determination and regulation of pH, indicator papers are normally employed. For some pH determinations, a Beckman pH-meter model H2 is employed.

Titration of lead(II) with EDTA and PAR

Known amounts of lead are titrated with 0.001M EDTA at pH 5-7.

When a neutral, unbuffered solution of lead is titrated with EDTA, the pH will decrease owing to the release of hydrogen ions. Below pH 5, the end-point of the titration is obscure and appears before the equivalence point is reached.

In order to adjust the pH to 6.5-7 before the equivalence point is reached, a few drops of ammonia solution are added. The correct pH is controlled with indicator paper. If ammonia is added before the addition of EDTA, precipitation takes place. The precipitate is slowly redissolved in EDTA.

In Table I the results of a series of titrations of known amounts of lead(II) are given.

TABLE I
TITRATION OF LEAD(II) WITH 0.001M EDTA SOLUTION AND PAR
Volume of solution before titration about 100 ml

<i>Pb taken mg</i>	<i>EDTA used ml</i>	<i>Pb found mg</i>	<i>Error relative %</i>
5.180	24.98	5.176	-0.1
5.180	25.03	5.186	+0.1
5.180	24.97	5.174	-0.1
5.180	25.02	5.183	+0.06
5.180	25.01	5.182	+0.04

The end-point is reached when the colour changes from red to yellow-orange. The end-point is sharp and permits the use of highly diluted EDTA solutions.

Indirect determination of aluminium with EDTA, lead(II) and PAR

Known amounts of aluminium are taken, an excess of EDTA is added and back titration is carried out with lead(II) and PAR.

The reaction between aluminium and EDTA is quantitative (under these circumstances) at room temperature and at the pH of the aluminium standard solution (*viz.*, about pH 2). After the addition of 0.05M EDTA, the solution is diluted to about 100 ml, the pH is adjusted to 6.5-7 with ammonia solution and 0.05M lead(II) solution and PAR is employed for back titration. Before the end-point is reached, the pH is again adjusted. The final end-point is seen by a sharp colour change from yellow to yellow-orange.

In Table II, the results of a series of indirect determinations of aluminium are given.

Table III shows that micro amounts of aluminium also can be determined with a relatively high degree of accuracy. In this case, 0.001M solutions of EDTA and lead(II) are utilized.

TABLE II

INDIRECT DETERMINATION OF ALUMINIUM WITH 0.05004*M* EDTA SOLUTION, 0.05*M* LEAD(II) SOLUTION AND PAR

Volume of solution before back titration about 100 ml

<i>Al taken</i> <i>mg</i>	<i>EDTA</i> <i>added ml</i>	<i>Pb (II)</i> <i>used ml</i>	<i>Al found</i> <i>mg</i>	<i>Error</i> <i>relative %</i>
25.00	25.00	17.52	25.00	±0.0
25.00	25.00	17.50	25.00	±0.0
25.00	30.00	30.90	25.07	+0.3
25.00	20.00	3.95	25.02	+0.1
25.00	21.00	6.78	24.96	-0.2
25.00	22.00	9.29	25.06	+0.2

TABLE III

INDIRECT DETERMINATION OF MICRO AMOUNTS OF ALUMINIUM WITH 0.001*M* EDTA SOLUTION, 0.001*M* LEAD(II) SOLUTION AND PAR

<i>Al taken</i> <i>mg</i>	<i>EDTA</i> <i>added ml</i>	<i>Pb(II)</i> <i>used ml</i>	<i>Al found</i> <i>mg</i>	<i>Error</i> <i>relative %</i>
0.674	50.00	24.97	0.675	+0.1
0.674	50.00	25.08	0.672	-0.3
0.674	50.00	25.02	0.674	±0.0
0.674	35.00	9.88	0.677	+0.4
0.674	35.00	10.00	0.674	±0.0
0.674	35.00	10.01	0.674	±0.0

The end-point is again taken when the colour changes from yellow to yellow-orange.

Influence of pH

The stability constants of the aluminium- and lead(II)-EDTA complexes are $10^{16.13}$ and $10^{18.04}$ respectively. Owing to the difference of stability, the following substitution reaction may take place when a small excess of lead(II) solution is added at the end-point of the back titration:



This reaction is pronounced at pH values above 7 and does not permit ready observation of the end-point. As mentioned above, it is also found that at pH values below 5, lead(II) ions do not form a coloured complex with PAR.

Consequently, the back titration is carried out at a pH between 5 and 7.

In order to keep the pH constant during the back titration, some conventional buffers were tested. Buffers containing organic acids unfavourably influenced the end-point. The application of a phosphate buffer completely decoloured the indicator before back titration. The use of ammonia in combination with indicator papers for regulation and control of pH is preferred.

The formation of hydroxy compounds of aluminium is avoided by keeping the pH of the aluminium standard solution at or below 2, and by adding excess EDTA before pH is increased.

The influence of foreign ions on the complex formations between aluminium and EDTA

It is stated by HONDA and coworkers² that the rate of reaction between aluminium and EDTA is reduced appreciably in the presence of higher concentrations of foreign ions. In these cases, the rate of reaction can be increased by heating the aluminium solution after the addition of EDTA.

In Table IV a few titrations of small amounts of aluminium are carried out in the presence of higher concentrations of ammonium chloride and sodium nitrate. It is seen that in the presence of ammonium chloride the correct amount of aluminium can be found by heating the solution to boiling before back titration. On the other hand, when sodium nitrate is present, heating does not improve the accuracy.

TABLE IV

INDIRECT DETERMINATION OF ALUMINIUM WITH 0.001M EDTA, 0.001M LEAD(II) AND PAR IN THE PRESENCE OF FOREIGN IONS

0.674 mg Al taken. 30.00 ml EDTA added. Volume of solution about 100 ml pH 6-7.

<i>Ions present</i>	<i>Al found mg</i>	<i>Error relative %</i>	<i>Remarks</i>
10 g NH ₄ Cl	0.666	-1.2	No heating before back titration
10 g NH ₄ Cl	0.673	-0.1	Heated before back titration
10 g NaNO ₃	0.638	-5.3	No heating before back titration
10 g NaNO ₃	0.640	-5.0	Heated before back titration

SUMMARY

Indirect EDTA-titration of macro and micro amounts of aluminium is carried out with the utilization of standard solutions of lead(II) for back titration and 4-(2-pyridylazo)-resorcinol (PAR) als indicator.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'aluminium au moyen de l'acide éthylènediamino-tétracétique par titrage indirect avec une solution étalon de plomb.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Aluminium mit Hilfe von Aethylen-diaminotetraessigsäure durch indirekte Titration mit einer Bleisalzlösung.

REFERENCES

- ¹ H. FLASCHKA, A. J. BARNARD JR. AND W. C. BROAD, *Chemist Analyst*, 47 (1958) 22.
- ² M. HONDA, J. KÖRBL, V. BAŽANT AND R. PŘIBIL, *Chem. listy*, 51 (1957) 2259.
- ³ P. WEHBER, *Z. anal. Chem.*, 158 (1957) 10.
- ⁴ A. E. CHICHIBABIN, *Zhur. Russ. Fiz. Khim. Obshchestva*, 50 (1920) 512.

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A NEW RAPID TITRIMETRIC METHOD FOR COPPER

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INTRODUCTION

A wide variety of methods is available for the determination of copper^{1,2}, but they are too time-consuming in as much as they require elaborate procedures. The credit of first working out a rapid and simple method goes to RHEAD³. This method consists in reducing an acid solution of the cupric salt by direct titration with titanous chloride in the presence of a sufficient quantity of thiocyanate. A few drops of ferrous solution added to the copper solution give a red coloration due to oxidation of iron(II) to iron(III) by copper(II). The titration is continued until the colour is pure white. The method was further investigated by THORNTON⁴, MACH AND LEDERLE⁵ AND KOLTHOFF⁶. This method, though quite suitable for rapid routine estimation of copper has the drawback that it required titanous chloride which is expensive.

The present investigation is based on the reduction of a hydrochloric acid solution of cupric copper by stannous chloride in the presence of thiocyanate. A few drops of ammonium molybdate solution served as the indicator. Ammonium molybdate gives an intense red colour in the presence of thiocyanate when reduced by stannous chloride. This colour change is reversible, though slow, in the presence of cupric solution. In the presence of copper, the molybdate is reduced only after all the copper has reacted. In practice, however, the colour change at the end-point is from pale rose to red-brown, probably due to traces of iron in the hydrochloric acid used. Though the colour change is not sharp, it is discernible to a careful observer without difficulty.

Stannous chloride possesses a low oxidation potential ($\text{Sn}^{+2} \rightleftharpoons \text{Sn}^{+4} + 2e$, $E_0 = -0.14$ V) and hence is a strong reducing agent. Lack of suitable indicators was responsible for its limited practical application until MÜLLER AND GÖRNE⁷ made use of the potentiometric method for carrying out a series of titrations. They investigated the determination of iodine, ferric salts, dichromate, ferricyanide, gold(III), platinum(IV), mercuric salts and permanganate by means of stannous chloride. SZABO AND SUGAR⁸ developed indicator methods for the determination of ferric, ferrous, dichromate, vanadate, iodate, bromate and ferricyanide ions, and for iodine by direct titration with stannous chloride.

REAGENTS

(1) Ammonium molybdate, A.R., 2% aqueous solution. (2) Copper sulphate, A.R., 0.1N. (3) Stannous chloride, A.R., 0.1N: 12 g of crystalline stannous chloride and 80 ml of conc. hydrochloric acid are used per l. The solution is prepared according to the procedure outlined by SZABO AND SUGAR⁸. The solution is stored under CO₂ in an apparatus described by SCOTT AND FURMAN⁹. (4) Hydrochloric acid, A.R., 1:1. (5) Potassium thiocyanate, pure, Merck, 10% aqueous solution. (6) Potassium bromate, A.R., 0.1N solution. (7) Quinoline yellow, 0.2% aqueous solution.

RECOMMENDED PROCEDURE

Pipette 25 ml of the copper solution into a 300-ml Erlenmeyer flask, dilute with 75 ml of distilled water, add 10 to 15 ml of 1:1 hydrochloric acid followed by 5 drops of ammonium molybdate solution and 15 to 20 ml of thiocyanate solution. Add a pinch of sodium bicarbonate and immediately titrate with stannous chloride solution. Cuprous thiocyanate is precipitated and the colour of the contents of the flask turns to a pale rose when the end-point is being approached. Near the end-point add the stannous chloride solution slowly since the reaction does not appear to be instantaneous. At the end-point, the colour of the solution changes from pale rose or pink to red-brown. The volume of the solution being titrated should not be less than 130 ml or more than 200 ml. Standardize the stannous chloride with standard potassium bromate solution using 1 drop of quinoline yellow as the indicator. This titration should be carried out in an atmosphere of carbon dioxide.

EXPERIMENTAL

The stock solution of copper sulphate was standardized iodometrically according to the procedure described by VOGEL¹ (p. 411). The thiosulphate solution was standardized with standard potassium bromate solution. The same potassium bromate was also used for standardizing the stannous chloride solution. Various known volumes of the stock solution of copper sulphate were run from a burette into a conical flask and titrated with stannous chloride as described previously. These titrations were carried out under an atmosphere of carbon dioxide drawn from a cylinder. The copper content in each case was calculated from the titre of the stannous chloride and compared with that obtained iodometrically. The range and accuracy of the method are shown in Table I. Table II shows the precision of the method under the best conditions, determined according to the procedure outlined by MORAN¹⁰. Since the $X_1 \pm LU_{av}$ does not embrace the known value, the method is not very accurate. But since the error involved is within 0.5%, the method is recommended for routine technical analyses where an accuracy of the order of 1% is sufficient. The advantages of the method lie in its speed, simplicity and the fact that only ordinary and cheap chemicals are required. It can also be seen in Tables I and II that the method gives a constant positive error of the order of 0.5%.

TABLE I
THE DETERMINATION OF COPPER BY MEANS OF STANNOUS CHLORIDE

Each value is an average of 5 determinations

<i>mg Cu⁺²</i> <i>by means of</i> <i>Na₂S₂O₃</i>	<i>mg Cu⁺²</i> <i>by means of</i> <i>SnCl₂</i>	<i>Difference</i>	
		<i>mg</i>	<i>%</i>
61.64	61.89	+0.25	+0.40
92.47	92.81	+0.34	+0.36
123.29	123.73	+0.44	+0.35
154.11	154.70	+0.59	+0.38
184.93	185.89	+0.96	+0.51
215.75	217.30	+1.55	+0.71

TABLE II
PRECISION OF THE METHOD UNDER THE BEST CONDITIONS

Copper taken 156.97 mg

Expt. No.	Copper found mg	Deviation, <i>d</i> mg	$d^2 \times 10^4$
1	157.57	+0.061	37.21
2	157.57	+0.061	37.21
3	157.34	-0.169	285.61
4	157.42	-0.089	79.21
5	157.42	-0.089	79.21
6	157.42	-0.089	79.21
7	157.34	-0.169	285.61
8	157.57	+0.061	37.21
9	157.72	+0.211	445.21
10	157.72	+0.211	445.21

$$\text{Av.} = \bar{x}_1 = 157.509$$

$$\Sigma d^2 = 0.181$$

$$\text{Standard deviation group: } \sigma_{10} = \sqrt{\frac{0.181}{10}} = 0.1346$$

$$\text{Limit of uncertainty of the average } \text{LU}_{\text{av.}} = \bar{x}_1 \pm \frac{3\sigma_{10}}{\sqrt{10}} = 157.381 \text{ to } 157.637$$

Acidity and volume of the solution

The acidity and volume of the solution being titrated play an important part in this titration. Tables III and IV indicate the influence of these factors. An acidity of 0.17*N*–0.68*N* is recommended. Below this acidity, the value found is too low. At higher acidities the end-point is poor and is delayed. Also, near the end-point a premature red-brown colour is produced which disappears rather slowly. However, at higher acidities the reaction appears to be more rapid.

The volume of the solution being titrated has to be maintained between 130 and 200 ml. Unsatisfactory results are obtained if the volume is less than 130 ml, a premature colour change being obtained which takes some time to disappear.

TABLE III
EFFECT OF THE ACIDITY

Cu^{+2} taken: 154.11 mg; volume of the solution at the end of the titration: 150 ml; acid used: hydrochloric acid. Each value is an average of 5 readings.

Normality of acid	0.1 <i>N</i> SnCl ₂ ml	Cu^{+2} found mg	% Recovery
0.12	23.93	152.74	98.72
0.17	24.36	154.87	100.49
0.34	24.38	154.97	100.59
0.51	24.41	155.19	100.70
0.68	24.40	155.14	100.67
0.85	24.49	155.68	101.02

Titrations in sulphuric acid medium were not good. The end-point is poor, the reaction slow and the initial precipitation of cuprous thiocyanate delayed.

TABLE IV

EFFECT OF THE VOLUME OF SOLUTION BEING TITRATED

Acidity of the solution: 0.34*N* in hydrochloric acid; copper taken: 156.97 mg. Each value is an average of 5 determinations

<i>Volume of solution at end of titration ml</i>	<i>0.1 N SnCl₂ ml</i>	<i>Cu⁺² found mg</i>	<i>% Recovery</i>
195	24.81	157.72	100.47
170	24.77	157.46	100.31
165	24.75	157.34	100.23
135	24.76	157.40	100.27
120	Not satisfactory		

Titrations with and without passage of carbon dioxide

In technical analyses, it is necessary to simplify the procedure as much as possible. Hence the possibility of avoiding the passing of carbon dioxide through the solution during the titration was investigated. The results are tabulated in Table V. If no carbon dioxide is passed, a slightly higher value is obtained. However, if a pinch of sodium bicarbonate is added just before the titration and if the titration is finished quickly, the value is identical with that obtained when CO₂ is passed through the solution during the titration.

TABLE V

TITRATIONS WITH AND WITHOUT PASSAGE OF CARBON DIOXIDE

Volume of the solution: 150 ml; copper taken: 156.97 mg; acidity of the solution 0.34*N*

<i>Stream of CO₂ throughout the titration 0.1 N SnCl₂ ml</i>	<i>Titration in air 0.1 N SnCl₂ ml</i>	<i>Pinch of bicarbonate added just before titration 0.1 N SnCl₂ ml</i>
24.76	24.79	24.79
(Average of five titrations)	24.75	24.76
	24.81	24.76
	24.82	24.75
	24.81	24.75
	24.84	
	24.87	
	24.79	
	24.82	
	24.85	

SUMMARY

A rapid and simple titrimetric method for the estimation of copper is described. Hydrochloric acid solution of cupric copper is titrated directly with stannous chloride in the presence of thiocyanate using a few drops of 2% ammonium molybdate solution as indicator.

RÉSUMÉ

Une méthode titrimétrique, simple et rapide, est proposée pour le dosage du cuivre. On effectue ce titrage au moyen de chlorure d'étain(II), en présence de thiocyanate de potassium, en utilisant le molybdate d'ammonium comme indicateur.

ZUSAMMENFASSUNG

Es wird eine einfache, rasche Titrationsmethode zur Bestimmung von Kupfer beschrieben. Das Kupfer wird in Gegenwart von Thiocyanat und Ammonium-molybdat als Indikator mit einer Zinn(II)-chloridlösung titriert.

REFERENCES

- ¹ A. I. VOGEL, *A Text-Book of Quantitative Inorganic Analysis*, Longmans, Green and Co., London, 1947.
- ² R. BELCHER AND CECIL L. WILSON, *New Methods in Analytical Chemistry*, Chapman and Hall, London, 1955.
- ³ E. L. RHEAD, *J. Chem. Soc.*, 89 (1906) 1491.
- ⁴ W. M. THORNTON JR., *J. Am. Chem. Soc.*, 44 (1922) 998.
- ⁵ F. MACH AND P. LEDERLE, *Landwirtsch. Vers. Sta.*, 90 (1917) 191; *Z. anal. Chem.*, 56 (1917) 69; 58 (1919) 375.
- ⁶ I. M. KOLTHOFF, *Rec. trav. chim.*, 43 (1924) 816.
- ⁷ E. MÜLLER AND J. GÖRNE, *Z. anal. Chem.*, 73 (1928) 385.
- ⁸ Z. G. SZABO AND E. SUGAR, *Anal. Chim. Acta*, 6 (1952) 293.
- ⁹ W. W. SCOTT AND N. H. FURMAN, *Standard Methods of Chemical Analysis*, Vol. I, D. van Nostrand Co., New York, 1944, p. 480.
- ¹⁰ R. F. MORAN, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 361.

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SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

I. ANTHRANILIC ACID AS A REAGENT

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Anthranilic acid, in weakly acid or neutral solution, combines with copper, cadmium, nickel, cobalt, iron, mercury, lead, zinc, manganese, silver and palladium to form sparingly soluble precipitates, which can either be weighed directly or can be treated with bromate-bromide mixture and determined volumetrically¹.

In this paper the effectiveness of anthranilic acid as a spectrophotometric reagent for osmium is described. In the tetra-, hexa-, and octavalent states and at a pH between 5.5 and 6.5, this metal reacts with anthranilic acid to form a stable dark-violet coloured complex, which shows maximum absorption at 460 m μ . With osmium(IV) the colour develops on heating in less than 10 min, but with osmium(VI) and osmium(VIII) sufficiently stable colour development is attained in the cold after an hour. The colour system obeys Beer's law for osmium(IV) concentrations from 0.5 to 8 p.p.m., the optimum range, against a reagent blank, being 2 to 6 p.p.m., where the % relative error per 1% absolute photometric error is 2.8. The sensitivity of the colour reaction is 1 part of osmium in 125,000,000 parts of solution (SANDELL²).

The results obtained with the methods of continuous variation³, molar ratio⁴ and slope ratio⁵ suggest that with chloro-osmate the reagent forms a 1 : 1 complex, which may be assigned the formula $K[OsCl_4 \cdot C_6H_4NH_2COO^-]$, with an average dissociation constant of $4.6 \cdot 10^{-5}$. The molar ratio method further reveals that at pH 6.0 a portion

of the reagent, is oxidised by osmium tetroxide or by an osmate (OsO_4^{-2}), the reduced osmium(IV) then reacting with the rest of the reagent to form a 1 : 1 complex.

EXPERIMENTAL

Apparatus

All optical density measurements of solutions were made with a Unicam Sp 600 spectrophotometer, Correx glass cells of 1 cm thickness, being used. A Cambridge pH indicator was employed for all pH determinations.

Reagents

Standard osmium solutions. A standard solution of osmium(IV) was prepared by dissolving an accurately weighed quantity of potassium chloro-osmate (K_2OsCl_6), of Johnson and Matthey, in 1N hydrochloric acid.

A 250-ml solution of osmium(VIII) in 0.02N caustic soda solution was prepared from a 0.1 g ampoule of osmic acid (OsO_4), of Dr. Theodor Schuchardt, according to the method of AYRES⁶.

For the preparation of a standard solution of osmium(VI), an aliquot of the above stock solution of osmium tetroxide, after reduction by a minimum amount of 1 : 2 alcohol, was made up to a definite volume with distilled water. The solution thus prepared can only be kept for 7 days at an average room temperature of 22°.

Reagent solution. A 2% solution of anthranilic acid (Na salt) was prepared by dissolving 2 g of recrystallised reagent of m.p. 145° in 200 ml water and adding the required amount of sodium carbonate.

Buffer solution. Buffer solution of pH 5.9 was obtained by mixing 9.5 ml of 0.2N sodium acetate with 0.5 ml of 0.2N acetic acid.

Other reagents. Test solutions of palladium(II), ruthenium(III) and rhodium(III) were prepared by dissolving their pure chlorides in dilute hydrochloric acid. The solution of platinum(IV) was obtained by dissolving pure platinum wire in aqua regia and removing the nitric acid from the solution by repeated evaporation with hydrochloric acid. The solution of iridium(IV) was prepared by fusing iridium sponge with a mixture of sodium carbonate and sodium peroxide in a nickel crucible, extracting the product with hot water and acidifying with hydrochloric acid. This solution contained nickel as an impurity.

All other metal solutions were obtained by dissolving analytical grade chlorides, sulphates, nitrates or oxides in water or hydrochloric acid.

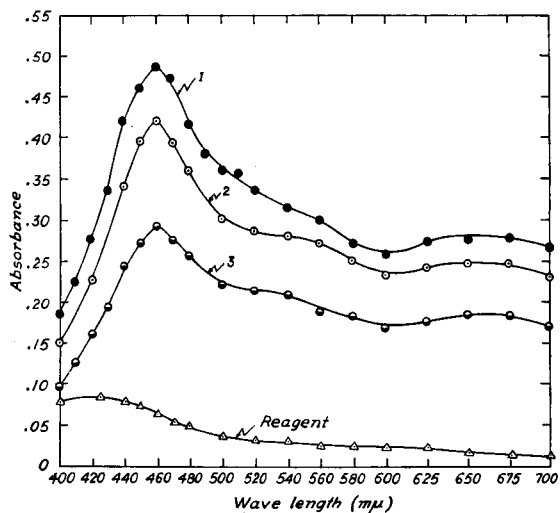


Fig. 1. Absorption curves of sodium anthranilate and its osmium complex at pH 6. Curve 1: 4 p.p.m. osmium(IV) + 5 ml of 2% reagent. Curve 2: 3.98 p.p.m. osmium(VI) + 5 ml of 2% reagent. Curve 3: 3.18 p.p.m. osmium(VIII) + 5 ml of 2% reagent.

Absorbance curves

For osmium(IV), an aliquot of potassium chloro-osmate solution was put into a 30-ml beaker and mixed with 5 ml of the reagent solution. After adjusting the pH to 6.0 with dilute sodium hydroxide, the solution was heated on the water bath for 10 min. Then it was allowed to cool to room temperature and afterwards transferred to a 25-ml flask, the solution being made up to volume with distilled water. In the case of osmium(VI) and osmium(VIII), the colour was developed by adding osmate or osmium tetroxide solution to 5 ml of the reagent solution in a 25-ml flask and making up to volume with the buffer solution. The reagent blanks for each valence state were prepared in exactly the same way as the coloured products, omitting the osmium.

The absorption curves of the coloured products obtained from osmium(IV), osmium(VI) and osmium(VIII), measured against reagent blanks, are represented in Fig. 1 together with that of the same amount of the reagent against water at the same pH. In all three cases the colour and its intensity are the same at a pH of about 6.0, and the absorbance curves obtained are superposable, the maxima always being at 460 $m\mu$. The only difference observed was that for full colour development osmium(VI) and osmium(VIII) required, respectively, three and five times as much reagent as osmium(IV).

Effect of pH, reagent and time

It was found that the absorbance of the colour system formed with an excess of reagent increased with increasing pH up to 5.5; from pH 5.5 to 6.5 the absorbance remained constant and then decreased on further increase of the pH. Therefore all subsequent measurements were carried out at pH 5.5 to 6.5

3 ml of the reagent solution was required for maximum development of the colour in the case of 1 to 8 p.p.m. of osmium. Addition of more reagent, up to 5 ml, had no adverse effect on the density of the colour as long as the measurements were made against a reagent blank.

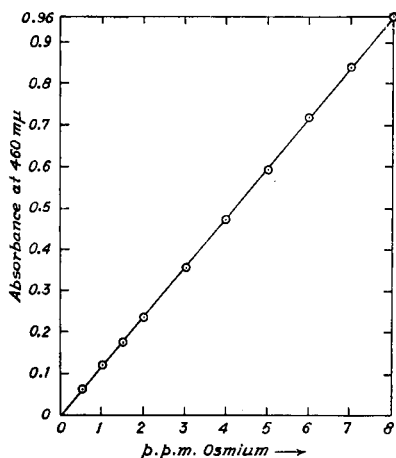


Fig. 2. Beer's law plot for the osmium(IV) complex at pH 6.

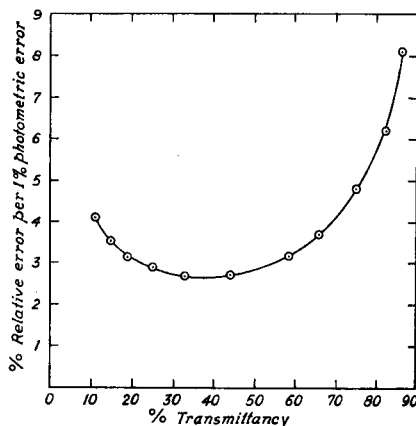


Fig. 3. Evaluation of % relative error ($dc/c \times 100$) relative to 1% absolute photometric error.

Osmium(IV) reacted very slowly with the reagent in the cold, but at the optimum pH and with optimum reagent concentration, the maximum colour was found to develop in less than 10 min when the solution was heated on the water bath. Once developed the colour intensity remained the same for a period of 24 h. The rate of colour development with osmium(VI) and osmium(VIII) was rapid even in the cold and a sufficiently stable colour developed in 1 hour. The colour thus formed was found to maintain its density for 4 hours. When the solution was kept overnight only a very slight increase in the absorbance reading was recorded.

Beer's law, optimum range and accuracy

That the organo-osmium complex obeys Beer's law in the range 0.5 to 8 p.p.m. of osmium(IV) is evident from the straight line obtained on plotting the absorbances against the concentrations (Fig. 2).

Using AYRES equation⁷ the % relative error $\left(\frac{dc}{c} \times 100\right)$ per 1% absolute photometric error was calculated and plotted against transmittancy to show how the analytical error varies with the transmittancy (Fig. 3).

To evaluate optimum range and analytical accuracy, RINGBOM'S⁸ curve was drawn by plotting % absorbancy at 460 m μ as the ordinate and log concentration as the abscissa. Since the accuracy is highest where the curve has the steepest slope, the optimum concentration range (Fig. 4) is between 2 and 6 p.p.m. of osmium. On evaluating the accuracy in this range according to AYRES method⁷, a relative analytical error of 2.8% per 1% absolute photometric error was obtained. This is very close to the theoretical value of maximum attainable accuracy (2.72% relative error per 1% absolute error) imposed by Beer's law.

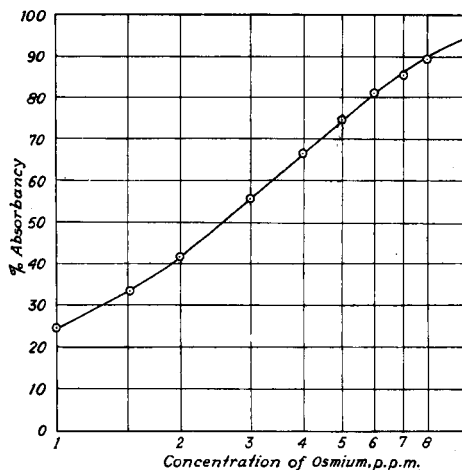


Fig. 4. Calibration curve for the osmium(IV) complex at 460 m μ ; pH 6.

Sensitivity

Employing SANDELL'S² expression for sensitivity, the spectrophotometric sensitivity, as calculated from the Beer's law curve, is given by 0.008 $\mu\text{g}/\text{cm}^2$. This corresponds to a sensitivity of 1 part of osmium per 125,000,000 parts of solution.

Effect of diverse ions

In order to study the effect of diverse ions solutions were prepared, following the same method as described above, with 3.336 p.p.m. of osmium(IV), varying concentrations of each ionic species to be examined and 0.5 ml of 1% ethylenediaminetetraacetic acid (EDTA) (disodium salt) solution, which was the maximum amount that could be tolerated by the amount of osmium(IV). A difference of more than 0.005 absorbance unit was arbitrarily taken as an interference (*cf.* Table I). In the absence of EDTA, however, most of the common ions and the platinum metals interfered, either by forming a precipitate or a coloured product with the reagent. EDTA (disodium salt) behaves in the same way towards the colour reaction of osmium tetroxide, as it does in the case of osmium(IV) but it considerably reduces

TABLE I

Ions	Maximum amount of ion tolerated p.p.m.	Ions	Maximum amount of ion tolerated p.p.m.
Ru ⁺³	2.252	Mg ⁺²	400
Rh ⁺³	8.18	Ca ⁺²	400
Pd ⁺²	18.6	Sr ⁺²	400
Ir ⁺⁴	13	Ba ⁺²	100
Mn ⁺²	20	Zn ⁺²	40
Cr ⁺³	15	As ⁺³	200
Fe ⁺³	10	VO ₃ ⁻	76
Co ⁺²	20	WO ₄ ⁻²	52
Ni ⁺²	20	UO ₂ ⁺²	34
Hg ⁺²	40		

the capacity of osmate to form complexes. The presence of tartrate and potassium cyanide should be avoided as they themselves considerably diminish the colour of the complex. Salts of copper, cadmium, aluminium, thorium, zirconium, antimony,

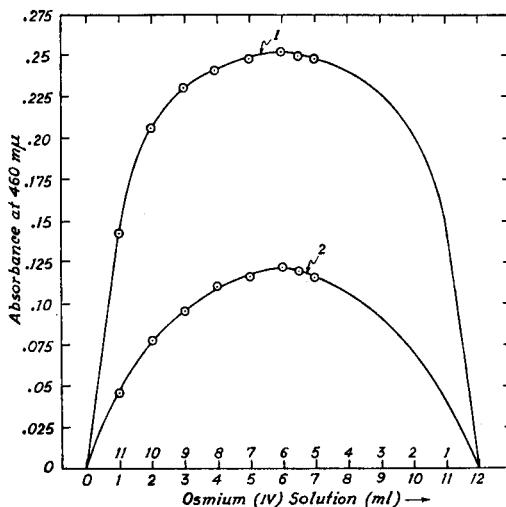


Fig. 5. Determination of the ratio of reagent to osmium(IV) by Job's method. Curve 1: Concn. of osmium(IV) = concn. of anthranilic acid = $25.14 \cdot 10^{-5}M$. Curve 2: Concn. of osmium(IV) = concn. of anthranilic acid = $13.14 \cdot 10^{-5}M$. Total volume in each case 12 ml.

bismuth and the rare earths must be absent. Gold and platinum interfere as the former precipitates in the metallic state and the latter produces a colour effect.

Composition of the complex in solution

(1) The curves in Fig. 5 were obtained by the application of Job's method³ of continuous variation. The peaks of the curves obtained on plotting optical density against increasing amounts of potassium chloro-osmate solution indicate a reagent to osmium(IV) ratio of 1 : 1.

(2) For the molar ratio method⁴, solutions were prepared, at pH 6, so that the osmium(IV) concentration remained constant but the ratio of the moles of reagent to the moles of osmium varied from 0.7 to 4. The absorbances of these solutions were measured at 460 m μ against a water blank. The curve in Fig. 6 shows a sharp break at the molar ratio of 1 : 1.

(3) In order to apply the slope ratio method⁵ two series of solutions were prepared. One series contained 10 p.p.m. of osmium(IV) as the constant component with varying amounts of the reagent and in the other series the quantities of the reagent and osmium were reversed. The absorbances of the solutions, diluted to 25 ml, were measured at 460 m μ , against a water blank for the first series and a reagent blank for the second. From the results shown in Fig. 7, the slopes of curve 1 (reagent excess) and curve 2 (osmium excess) were calculated to be 0.40 and 0.41, respectively, indicating an osmium to reagent ratio of 1 : 1.

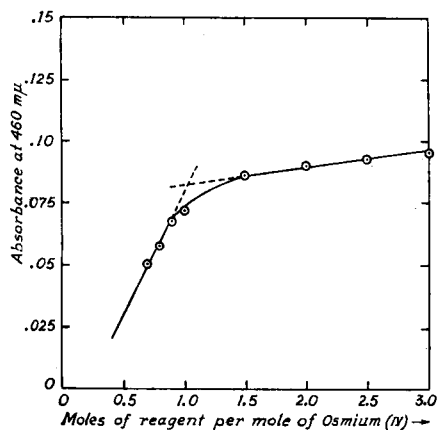


Fig. 6. Determination of the ratio of reagent to osmium(IV) by the molar ratio method.

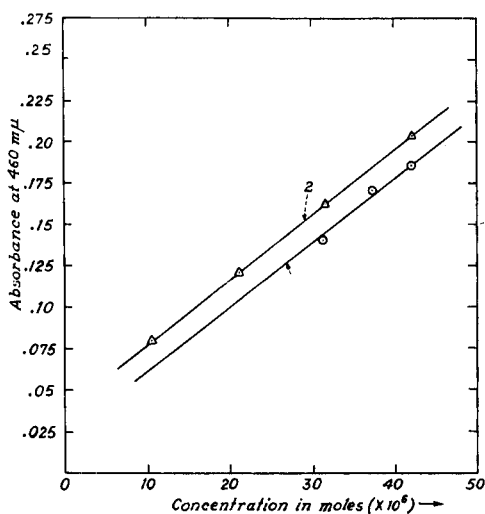


Fig. 7. Determination of the ratio of reagent to osmium(IV) by the slope ratio method.

The results obtained with these three methods prove conclusively that in solution osmium(IV) forms a 1 : 1 complex with the reagent. However, difficulties were encountered when excess of osmium and smaller amounts of reagent were present, because in those cases black osmium dioxide together with metallic osmium were

precipitated when the pH of the solution increased on the addition of buffer solution. Optical densities of such solutions were, therefore, not measured.

In order to investigate the reaction ratios between osmium tetroxide and the reagent on the one hand and osmate (OsO_4^{-2}) and the reagent on the other by the molar ratio method, solutions were prepared in a 25-ml flask so that the osmium concentration remained constant but the ratio of the moles of reagent to the moles of osmium varied from 0.8 to 6. After the development of the colour by the addition of a drop of 6M sulphuric acid, the volume of each solution was made up with the buffer solution. The solutions were allowed to stand for about 2 h before the density against a water blank was measured at 460 m μ (Fig. 8). Curve 1, for osmium tetroxide, and 2, for osmate, show that breaks occur at the points where the ratios between the metal and the reagent are 1 : 5 and 1 : 3, respectively. Since the colour, pH effect, and the wave length of maximum absorption (Fig. 1) of the complex obtained by mixing the reagent with osmium tetroxide or osmate, are the same as those of osmium(IV), it is inferred that most probably the amino groups of the reagent are first oxidised by osmium tetroxide or osmate and that then the reduced osmium(IV) in each case forms a 1 : 1 complex with the excess unoxidised reagent. Thus osmium tetroxide and osmate oxidise, respectively, four and two amino groups of four and two molecules of the reagent and at the same time lose two and one oxygen atoms, respectively.

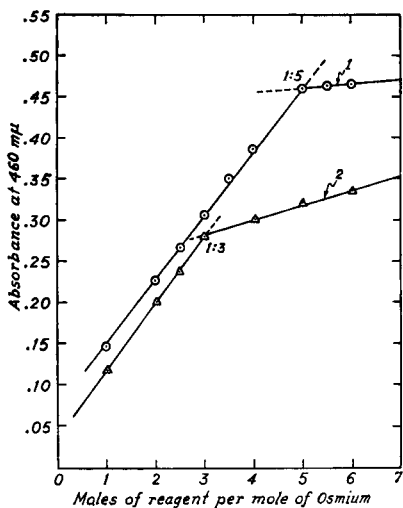


Fig. 8. Determination of the reaction ratios of reagent to (1) osmium(VIII) and (2) osmium(VI) by the molar ratio method.

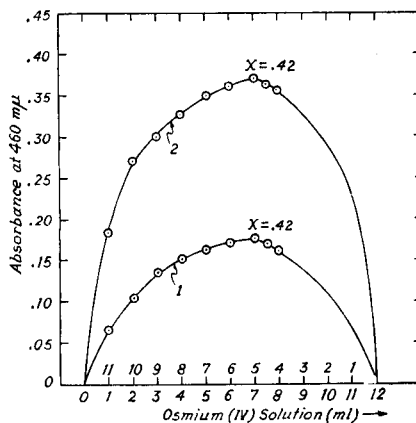


Fig. 9. Absorbance of mixtures of non-equimolecular solutions. Curve 1: $13.14 \cdot 10^{-5}M$ osmium(IV); $26.28 \cdot 10^{-5}M$ sodium anthranilate. Curve 2: $25.14 \cdot 10^{-5}M$ osmium(IV); $75.42 \cdot 10^{-5}M$ sodium anthranilate.

Dissociation constant

From the absorption data (Fig. 9) of the mixtures, at a pH of about 6.0, of non-equimolecular solutions of potassium chloro-osmate and the reagent, the dissociation

constant, K , has been evaluated according to the equation reported previously by one of us⁹.

Since the values of m and n are 1, the dissociation constant, K , is obtained by substituting in the equation the values of X , p and c given in Table II.

TABLE II

Fig.	Curve	Concn. of Os(IV) $M \cdot 10^5$	Concn. of anthranilic acid $M \cdot 10^5$	X	p	$K \cdot 10^5$
9	2	25.14	75.42	0.42	3	3.6
9	1	13.14	26.28	0.42	2	5.6

Mean: $K = 4.6 \cdot 10^{-5}$.

SUMMARY

Anthranilic acid has been found to be a highly sensitive reagent for the spectrophotometric determination of osmium(IV), osmium(VI) and osmium(VIII) at pH 6.0. In all three valence states the metal reacts with the reagent to form a dark-violet coloured compound, which shows maximum absorbance at 460 m μ . Osmium(IV) can be determined in the presence of diverse ions, if EDTA (disodium salt) is used as a masking agent. The optimum concentration range for the method is 2 to 6 p.p.m. of osmium(IV), where the % relative error per 1% absolute photometric error is only 2.8. By applying Job's method of continuous variation, the molar ratio method and the slope ratio method, it was established that a 1 : 1 complex is formed between osmium(IV) and the reagent. The reaction of the reagent with osmium tetroxide or osmate indicates that the reagent is first oxidised and that then the reduced osmium(IV) forms a 1 : 1 complex with unoxidised excess reagent. The complex is stable in water and alcohol and has an average dissociation constant of $4.6 \cdot 10^{-5}$.

RÉSUMÉ

L'acide anthranilique est proposé comme réactif sensible pour le dosage spectrophotométrique de l'osmium. Ce dernier peut être dosé en présence de nombreux autres ions, en utilisant l'acide éthylènediaminotétracétique comme réactif de masquage.

ZUSAMMENFASSUNG

Als empfindliches Reagenz zur spektrophotometrischen Bestimmung von Osmium wird Anthranilsäure vorgeschlagen. Die Gegenwart zahlreicher anderer Ionen stört nicht, sofern sich diese mit Aethylendiaminotetraessigsäure maskieren lassen.

REFERENCES

- J. F. FLAGG, *Organic Reagents Used in Gravimetric and Volumetric Analysis*, Vol. IV, Interscience Publ., Inc., New York.
- E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd ed., Interscience Publ. Inc., New York, 1950.
- P. JOB, *Ann. chim.*, [10] 9 (1928) 113; *Compt. rend.*, 180 (1925) 928;
- W. C. VOSBURGH AND G. R. COOPER, *J. Am. Chem. Soc.*, 63 (1941) 437.
- J. H. YOE AND A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 111.
- A. E. HARVEY AND D. L. MANNING, *J. Am. Chem. Soc.*, 72 (1950) 4488.
- G. H. AYRES AND W. N. WELLS, *Anal. Chem.*, 22 (1950) 317.
- G. H. AYRES, *Anal. Chem.*, 21 (1949) 652.
- A. RINGBOM, *Z. anal. Chem.*, 115 (1938) 332.
- A. K. MAJUMDAR AND M. M. CHAKRABARTY, *Anal. Chim. Acta*, 19 (1958) 372.

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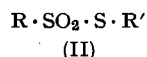
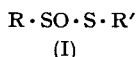
THE DETECTION AND ESTIMATION OF THIOLSULPHINATES AND THIOLSULPHONATES

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Only recently, in the course of work on the autoxidation of mixtures of olefins and disulphides, has the importance of thiolsulphinates (I) as retarders of free radical chain reactions been recognised^{1,2}. It became necessary during this investigation to detect, often in complex mixtures, trace amounts of the latter together with thiolsulphonates (II) as products of their decomposition and further oxidation.

Methods of analysis of these compounds appear to have been only scantily investigated and this paper concerns the development, firstly, of a semi-quantitative paper-chromatographic technique for their detection and, secondly, of methods of functional group analysis by which the purity of larger samples may be accurately measured.



I. CHROMATOGRAPHIC SEPARATION AND DETECTION

Attempts to use untreated paper and conventional solvent systems were unsuccessful giving R_F values of approximately unity both for disulphides and derivatives (I) and (II). Treatment of the paper with phenoxyethanol followed by development with *n*-heptane^{3,4} gave well defined spots of useful R_F values and enabled not only thiolsulphinates to be separated from similarly substituted thiolsulphonates but different members of either series to be resolved. Other components of oxidation mixtures did not interfere, olefins and disulphides having high, and olefin hydroperoxide low, R_F values respectively.

Experimental

The chromatographic procedure was exactly as described by LYNN, STEELE AND STAPLE⁴ except that Whatman No. 1 filter paper was used and the materials were applied in chloroform solution (loadings up to 60 μg). After development (6–16 h) well defined, almost round spots of 1–2 cm diameter were obtained. Because of unavoidable variations in the amount of phenoxyethanol absorbed on the paper, absolute R_F values were not reliable and either I or II, ($\text{R} = \text{R}' = \text{Ph}$), as appropriate, was used as an internal standard. In Table I R_Φ is defined as: distance travelled by sample/distance travelled by standard. These relative values were reproducible to ± 0.03 for thiolsulphinates and ± 0.01 for thiolsulphonates, even when different

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batches of paper or widely different times of development were used, provided care was taken to get a uniform distribution of phenoxyethanol on the paper. In this respect vertical draining of the paper after soaking in the acetone–phenoxyethanol solution was found more satisfactory than blotting off the excess as originally recommended.

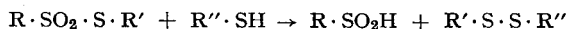
Location of the spots on the air-dried paper

A. Thiolsulphinates. Two methods have been found equally satisfactory and the choice would depend on the other materials present.

(1) Exposure to hydrochloric acid fumes, with a contact time of 10 sec, is followed immediately by a starch–iodide spray to give a blue-violet spot on a white background with a sensitivity of better than $5 \mu\text{g}/\text{cm}^2$. Thiolsulphonates and certain sulphoxides give similar spots more slowly and with greatly decreased sensitivity. Acyl peroxides and hydroperoxides also give positive results but are not detected by procedure (2).

(2) The paper is exposed to bromine vapour for 10 sec and sprayed with starch–iodide solution after removal of excess bromine in a rapid stream of air (*ca.* 1–2 min). Blue-violet spots are given by all sulphur compounds which are converted under these conditions to products containing “active” halogen. Aryl and alkyl thiol-sulphinates, mono- and di-sulphides can be detected with a sensitivity of $2 \mu\text{g}/\text{cm}^2$, sulphoxides with a sensitivity of *ca.* $10 \mu\text{g}/\text{cm}^2$, thiolsulphonates and thiols with a sensitivity of $40 \mu\text{g}/\text{cm}^2$ and sulphones not at all. The method is similar in principle to the chlorination technique of RYDON AND SMITH⁵ for the detection of amino acids and peptides. These, however, do not respond to the milder conditions employed here and negative results were given even by such examples as methionine or cystine which contain mono- and disulphide groups respectively. RYDON AND SMITH similarly found that sulphur-containing amino acids were not detected by their method implying that some interaction between the amino group and halogenated sulphur group is responsible for the failure in both cases. This is confirmed by the work of SCHWARTZ AND PALLANSCH⁶ who found, using *tert.*-butyl hypochlorite as the chlorinating agent, that although methionine and other sulphur-containing amino acids again gave negative results, methionine sulphoxide and sulphone, in which S-halogenation is made difficult or impossible, were detected with high sensitivity.

B. Thiolsulphonates. The paper is dipped in a solution of thiophenol in low-boiling petrol (2% v/v), and lightly sprayed, after drying, with bromophenol blue indicator (0.1% solution of sodium salt in water, pH 7). Thiolsulphonates show as distinct yellow spots on a blue background with a sensitivity of better than $5 \mu\text{g}/\text{cm}^2$. This response is due to the specific reaction of these compounds with thiols to yield sulphinic acids,



Thiolsulphinates also react readily with thiols⁷ but give no acidic product and do not interfere even when present in relatively large amounts.

Thiophenol is unpleasant to use and this procedure may be replaced, if desired, by spraying the paper directly with a freshly prepared, aqueous solution of cysteine hydrochloride (5%) and bromophenol blue (0.1%) adjusted to pH 7. The loss in sensitivity under these conditions is slight.

In all the methods of location the size and intensity of the spots are well graduated with respect to the amount of material, which may be estimated semi-quantitatively by visual comparison with a series of standard spots, run on the same sheet of paper, at 5 μg intervals at the lower levels, and containing up to 50 μg of material. Accuracy rapidly diminishes above 40 μg . Spots obtained by a starch-iodide spray are stable for a few minutes only while those due to thiolsulphonates remain unchanged for several hours.

TABLE I
 R_F VALUES OBTAINED FOR THIOISULPHINATES AND THIOISULPHONATES

<i>Thiolsulphinat</i> (I)	R_F	<i>Thiolsulphonat</i> (II)	R_F
R = R' = phenyl	1.0 ^a	R = R' = phenyl	1.0 ^b
R = R' = <i>p</i> -tolyl	1.4	R = R' = <i>p</i> -tolyl	1.3
R = R' = <i>p</i> -chlorophenyl	1.3		
R = R' = <i>p</i> -methoxyphenyl	0.25	R = R' = <i>p</i> -methoxyphenyl	0.22
R = phenyl, R' = <i>p</i> -methoxyphenyl	0.60	R = R' = benzyl	0.60
R = <i>p</i> -methoxyphenyl, R' = phenyl	0.50	R = R' = ethyl	0.84
R = R' = ethyl	0.80	R = R' = <i>n</i> -propyl	1.48
R = R' = <i>n</i> -butyl	1.72	R = R' = <i>n</i> -butyl	1.97
Ph · SO · S · C ₆ H ₄ · O · C ₆ H ₄ · S · SO · Ph	0.06		

^a R_F = ca. 0.4

^b R_F = ca. 0.3

II. ANALYSIS OF THIOISULPHINATES AND THIOISULPHONATES

A. Thiolsulphinates

Unlike sulphoxides, thiolsulphinates could not be quantitatively reduced with titanous chloride. Thus, under the conditions used for saturated sulphoxides⁸, results of 60-70% of theory were obtained while reductions in the presence of thiocyanate ion gave improved but variable figures ranging from 85-110% of theory.

The liberation of iodine from iodide ion by thiolsulphinates in the presence of acid has been reported to be quantitative by BRETSCHNEIDER AND KLOTZER⁹, and by SCHÖBERL AND GRÄFJE¹⁰. We have found that, in the presence of mineral acid, decomposition as well as reduction of thiolsulphinates occurs to give results lower than theoretical, while in acetic acid solution the reaction with iodide ion is stoichiometric only under anaerobic conditions.

Experimental

Materials. Aryl and alkyl thiolsulphinates were prepared by a slight modification of the method of BACKER AND KLOOSTERZIEL¹¹ and purified by repeated crystallisation or fractional distillation as appropriate. Their physical properties and analytical data are described elsewhere¹².

Recommended procedure. The sample (20-80 mg) is dissolved in acetic acid (15 ml, AnalaR grade) in a small Erlenmeyer flask equipped with a side arm and magnetic stirrer. The solution is outgassed with a stream of carbon dioxide introduced *via* a coarse capillary through the side arm. The capillary is then withdrawn from the solution and washed down with a little oxygen-free acetic acid. A similarly outgassed, saturated, aqueous solution of potassium iodide (2 ml) is added and the mixture

stirred for 2 min in the stoppered flask. The liberated iodine is then titrated slowly, and with stirring, under an atmosphere of carbon dioxide, to a starch end-point using standard thiosulphate.

$$\% \text{ purity} = \frac{\text{Mol. wt. of thiosulphinate} \times \text{thiosulphate normality} \times \text{titre} \times 100}{2000 \times \text{sample wt.}}$$

Results

The results are summed up in Tables II and III.

TABLE II
ANALYSIS OF PHENYL BENZENETHIOLSULPHINATE

Sample wt. (g)	Thiosulphate required (ml 0.0200N)	Found (% of theory)	Mean	Standard deviation
0.0516	21.75	98.7		
0.0522	22.15	99.3		
0.0500	21.30	99.7	99.3	0.45
0.0504	21.40	99.4		
0.0486	20.50	98.8		
0.0501	21.35	99.8		

TABLE III
ANALYSIS OF OTHER THIOSULPHINATES (1)

(1)	Found (% of theory)	Standard deviation
R = R' = <i>p</i> -methoxyphenyl	98.4	0.30
R = R' = ethyl	96.6	0.52
R = R' = <i>n</i> -butyl	95.7	0.33
Ph · SO · S · C ₆ H ₄ · O · C ₆ H ₄ · S · SO · Ph	94.7	0.34

Discussion

Oxygen-free conditions were found necessary to prevent an induced oxidation of iodide which otherwise led to results higher than the theoretical by 2-3% and a lower precision. Thus 5 replicate analyses in air of the sample of phenyl benzenethiolsulphinate used for the results in Table II gave a mean value of 102.7% of theory with a standard deviation of 1.35.

The sample size could be varied between wide limits provided a concentration of 80 mg/15 ml solvent was not exceeded. As shown in Table IV higher concentrations led to correspondingly lower results for reasons which are not completely understood.

As thiosulphonates are the most likely impurity associated with thiosulphinates it was of importance to examine any interference they might cause. Alone they liberated iodine, under the recommended conditions, equivalent to *ca.* 25% of theory (based on complete reduction of the >SO₂ group) while in the presence of thiol-sulphinate their reduction was further suppressed to less than half of this figure. Thus, as shown in Table V, for a mixture of thiol-sulphinate and thiosulphonate the found values for the former were higher than the calculated values by only a fraction of the thiosulphonate content.

The chromatographic procedure detailed earlier may be conveniently used to confirm the presence or absence of thiolsulphonate in thiolsulphinic acid.

(B) Thiolsulphonates

The reaction of thiolsulphonates with thiols has been investigated by several workers¹³⁻¹⁶ mainly in respect of the identity of the products. It has now been shown that, under the proper conditions, the yield of sulphinic acid is stoichiometric and may be used to estimate, as well as to detect, thiolsulphonates.

Experimental

Materials. Aryl thiolsulphonates were obtained by the spontaneous decomposition of the appropriate sulphinic acids¹⁷. Chlorination of disulphides in acetic acid solution containing water (4 mole/mole disulphide) gave alkyl thiolsulphonates as the major product in contrast to the results of LEE AND DOUGHERTY¹⁸. Benzyl disulphide was oxidised directly to the corresponding thiolsulphonate as described by HINSBERG¹⁹. Solid products were crystallised to constant melting point from petrol-chloroform; liquids were repeatedly distilled in high vacuum. Fractional elution from silica gel with carbon tetrachloride-chloroform was used in certain cases for final purification.

Recommended method

A. The sample (1 mmole) is dissolved in acid free ethanol (5 ml) and a solution of thiophenol in ethanol (2 ml, 20% v/v) added with swirling. The resulting sulphinic acid is titrated with 0.1N sodium hydroxide to the first blue colour of bromophenol blue as indicator. The end-point is sharp and the indicator blank less than one drop of titrant.

Smaller samples (0.1-0.2 mmole) may be similarly analysed by reducing the volume of thiophenol solution to 1 ml and the strength of the sodium hydroxide to 0.02N. The indicator blank is proportionately larger and it is advisable to perform such a blank first and to match the end-point of subsequent titrations to the end-point colour of the blank. The accuracy and precision of analyses of aryl thiolsulphonates on this smaller scale is unaltered but in the case of alkyl derivatives the results tend to be slightly lower (ca. 1%) than on the full scale, with a lower precision also (standard deviation ca. 2).

$$\% \text{ purity} = \frac{\text{titre} \times \text{normality of alkali} \times \text{mol.wt. of thiolsulphonate} \times 100}{1000 \times \text{sample weight}}$$

B. Where the sample is dissolved in a water-immiscible solvent the unfavourable partition properties of the sulphinic acid make direct titration with aqueous alkali difficult. An aliquot of the sample containing 0.5-1 mmole is dissolved in acid-free chloroform (2 ml) and a solution of thiophenol in chloroform (2 ml, 20% v/v) added with swirling followed by an excess (15-20 ml) of 0.1N sodium hydroxide solution. After a vigorous shaking the alkali remaining is then titrated with 0.1N hydrochloric acid using bromophenol blue as indicator. The end-point is taken as the blue-grey transition colour of the indicator and, with care, may be judged to within one drop of titrant. A blank analysis is performed omitting only the thiolsulphonate.

$$\% \text{ purity} = \frac{(\text{Blank-titre}) \times \text{normality of acid} \times \text{mol.wt. of thiolsulphonate} \times 100}{1000 \times \text{sample weight}}$$

TABLE V
INTERFERENCE BY THIOSULPHONATE IN ANALYSIS OF THIOSULPHINATE

	Composition of mixture			Thiol sulphinate found (% w/w)
	Phenyl benzene-thiol-sulphininate (% w/w)	Phenyl benzene-thio-sulphonate (% w/w)		
	87.6	12.4		88.8
	81.0	19.0		84.9
	49.0	51.0		59.4
	0.0	100.0		44.0

TABLE IV
INFLUENCE OF SAMPLE SIZE ON ACCURACY OF ESTIMATION OF PHENYL BENZENETHIOSULPHINATE

Sample wt. (g) in 15 ml solvent	Found (% of theory)
0.0504	99.4
0.0666	98.8
0.0790	98.5
0.1116	97.0
0.1358	96.4
0.2005	91.2
0.2015 ^a	98.7

^a Dissolved in 30 ml acetic acid

TABLE VI
PHYSICAL CONSTANTS OF THIOSULPHONATES

Structure	M.p.	B.p.	n_D^{20}	Found	Required
R = R' = phenyl	37.5—38.5°	—	—	C, 57.5; H, 4.0; S, 25.6	C, 57.6; H, 4.0; S, 25.6
R = R' = ethyl	—	70°/0.02 mm	1.4988	C, 31.4; H, 6.5; S, 41.4	C, 31.2; H, 6.5; S, 41.6
R = R' = benzyl	103—105°	—	—	C, 60.6; H, 5.1; S, 23.3	C, 60.4; H, 5.0; S, 23.0
R = R' = <i>n</i> -propyl	—	79°/0.03 mm	1.4924	C, 39.7; H, 7.9; S, 34.9	C, 39.5; H, 7.7; S, 35.2
R = R' = <i>n</i> -butyl	—	103°/0.05 mm	1.4873	C, 45.9; H, 8.6; S, 30.5	C, 45.7; H, 8.6; S, 30.5
R = R' = <i>p</i> -methoxyphenyl	87—8°	—	—	C, 54.5; H, 4.5; S, 20.5	C, 54.2; H, 4.5; S, 20.6

Results

See Tables VII and VIII.

TABLE VII
ANALYSIS OF PHENYL BENZENETHIOLSULPHONATE

Method	Sample wt (g)	Found (% of theory)	Mean	Standard deviation
A	0.0500	99.7		
A	0.0506	100.7		
A	0.0505	99.4		
A	0.0513	99.9	99.8	0.46
A	0.0505	99.3		
A	0.1452	99.9		
A	0.2149	99.6		
B	0.0484	100.9		
B	0.0750	100.0		
B	0.1259	98.4		
B	0.1481	99.6	99.4	1.02
B	0.1842	98.4		
B	0.2241	98.9		
B	0.2490	100.4		
B	0.2954	98.2		

TABLE VIII
ANALYSIS OF OTHER THIOLSULPHONATES

Structure (II)	Method	Found (% of theory)	Standard deviation
R = R' = ethyl	A	99.1	0.11
R = R' = ethyl	B	100.4	1.08
R = R' = <i>n</i> -propyl	A	99.0	0.18
R = R' = <i>n</i> -butyl	B	96.5	0.51
R = R' = benzyl	B	98.5	0.15
R = R' = <i>p</i> -methoxyphenyl	B	96.7	0.68

Discussion

The reaction between thiolsulphonates and thiols is practically instantaneous at room temperature. There appears to be no restriction on sample size from 0.1 mmole upwards provided that excess thiol is present and that suitable adjustments are made in the strengths of alkali and acid used.

In the direct titration of a sulphinic acid in the presence of thiophenol it can be calculated by standard methods that the equivalence point under the given experimental conditions will be reached at pH 4.2–4.4 taking the pK_A values for thiophenol²⁰ and a sulphinic acid²¹ as 7.8 and *ca.* 1.5 respectively. Of the indicators whose transition period includes this pH range bromophenol blue was found to be the most useful. No screened indicator tried was suitable.

No interference by impurities, other than those which are acidic to the indicator, has been encountered. Thus thiolsulphinates, even when present in large amounts, do not affect the estimation although they react equally readily with thiols⁷.

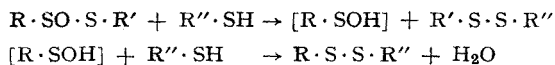


TABLE IX
ESTIMATION OF PHENYL BENZENETHIOLSULPHONATE IN THE PRESENCE
OF PHENYL BENZENETHIOLSULPHINATE

<i>Thiolsulphonate</i>	<i>Thiolsulphinat</i> e	<i>Thiolsulphonate found</i> (% of theory)
0.0494	0.2265	98.7
0.3165	0.1778	98.7

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SUMMARY

Procedures are described for the separation and detection of thiolsulphinates and thiolsulphonates on paper chromatograms, together with methods for the estimation of these substances.

RÉSUMÉ

Des méthodes chromatographiques sont proposées pour la détection et la séparation des thio sulfinate et des thiosulfonates, ainsi que des méthodes pour le dosage de ces substances.

ZUSAMMENFASSUNG

Es wird ein papier-chromatisches Verfahren beschrieben zur Trennung und zum Nachweis von Thiosulfinate und Thiosulfonaten, sowie Methoden zur deren Bestimmung angegeben.

REFERENCES

- 1 D. BARNARD, L. C. BATEMAN, E. R. COLE AND J. I. CUNNEEN, *Chem. & Ind., London*, (1958) 918.
- 2 *Brit. Pat. Appln.* 16546/57.
- 3 R. NEHER AND A. WETTSTEIN, *Helv. Chim. Acta*, 35 (1952) 276.
- 4 W. G. LYNN, L. A. STEELE AND E. STAPLE, *Anal. Chem.*, 28 (1956) 132.
- 5 H. N. RYDON AND P. W. G. SMITH, *Nature*, 169 (1952) 922.
- 6 D. P. SCHWARTZ AND M. J. PALLANSCH, *Anal. Chem.*, 30 (1958) 219
- 7 L. D. SMALL, J. H. BAILEY AND C. S. CAVALLITO, *J. Am. Chem. Soc.*, 69 (1947) 1710.
- 8 D. BARNARD AND K. R. HARGRAVE, *Anal. Chim. Acta*, 5 (1951) 536.
- 9 H. BRETSCHNEIDER AND W. KLOTZER, *Monatsh.*, 81 (1950) 589.
- 10 A. SCHÖBERL AND H. GRÄFJE, *Proc. Intern. Wool Textile Research Conference, Australia* 1955, Vol. C, Part 1, p. 157.
- 11 H. J. BACKER AND H. KLOOSTERZIEL, *Rec. trav. chim.*, 73 (1954) 129.
- 12 D. BARNARD AND E. R. COLE, to be published.
- 13 C. PAULY AND R. OTTO, *Ber.*, 11 (1878) 2070.
- 14 R. OTTO AND A. ROSSING, *Ber.*, 19 (1886) 3132.
- 15 S. SMILES AND D. T. GIBSON, *J. Chem. Soc.*, 125 (1924) 176.
- 16 H. G. GILMAN, L. E. SMITH AND H. A. PARKER, *J. Am. Chem. Soc.*, 47 (1925) 851.
- 17 R. OTTO, *Ann.*, 145 (1868) 13, 137.
- 18 S. W. LEE AND G. DOUGHERTY, *J. Org. Chem.*, 5 (1940) 81.
- 19 O. HINSBERG, *Ber.*, 41 (1908) 2838.
- 20 G. SCHWARZENBACH AND H. EGLI, *Helv. Chim. Acta*, 17 (1934) 1176.
- 21 HOUBEN-WEYL, *Methoden der organischen Chemie*, Vol. IX, Georg Thieme Verlag, Stuttgart, 1955.

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A SEMIMICRO METHOD FOR THE DETERMINATION OF FLUORINE AND PHOSPHORUS IN ORGANIC COMPOUNDS CONTAINING BOTH THESE ELEMENTS

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In the course of the development of an analytical method for the determination of fluorine in organic compounds¹, we were confronted with the need for extending this method to organic fluoro compounds containing also phosphorus. Our original method was based on the oxidative combustion of the sample with sodium peroxide in an electrical ignition bomb of the Parr type, and determination of the fluoride ion formed by titration with thorium nitrate solution and alizarinsulfonate as indicator. The method is affected by even very small quantities of phosphate ion, which destroys the colored lake. It is therefore necessary to remove the phosphate prior to the determination of the fluoride. Various methods have been proposed, such as distillation of the hydrogen fluoride²⁻⁵, or precipitation of the phosphate ion⁶⁻⁹. Some experiments have been carried out to adapt FENNELL'S⁸ method (separation of the phosphate from the fluoride as silver phosphate) to organic compounds and to a semimicro scale. The melt obtained by combustion was dissolved and percolated through a cation-exchange resin. The effluent was acidified with nitric acid (pH 2), and the solution gently boiled to remove carbon dioxide, and neutralized with 0.1*N* sodium hydroxide. At pH 8.2-8.4 the phosphate was precipitated by vigorously stirring with an excess of 0.1*N* silver nitrate solution. By addition of 0.05*N* sodium hydroxide, the pH was brought to 10.6-10.8 and the yellow-brown precipitate of silver phosphate and silver hydroxide filtered and washed with alkaline water. The combined filtrate and washings were made up to 500 ml and the fluoride was determined in an aliquot of 10 ml as described¹, but using 0.1*N* nitric acid instead of hydrochloric acid. This method gave reasonably good results, when the analysis was carried out without interruptions. Too high values resulted, when the final solution was left standing for several hours.

It seemed worthwhile to separate the two anions by an exchange-resin and thus to make possible their simultaneous determination. While this work was in progress, two similar attempts have been reported^{10,11}.

EXPERIMENTAL

Reagents

Standard sodium fluoride solution, containing 0.1 mg F/ml; thorium nitrate solution, approximately 0.015*N*; sodium alizarin-sulfonate reagent; buffer solution, pH 3.55; sodium peroxide; hydrochloric acid, appr. 0.1*N*; ethyl alcohol; sucrose.

* Part of a thesis submitted by JOSEF LIPKE to the Technion-Israel Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

All the above mentioned reagents and solutions were prepared as specified before¹.

Potassium dihydrogen phosphate standard solution; sulfuric acid, appr. 1*N*; acetone; molybdate reagent.

These reagents and solutions were prepared according to BERNHARDT AND WREATH¹².

Sodium hydroxide solution 0.25*N* and 1*N*. The sodium hydroxide used should be of analytical grade and should contain not more than 1% carbonate.

Ion-exchange resins. The cation exchanger Amberlite IR-112 (Rohm and Haas, Philadelphia, Pa., U.S.A.), which is no longer supplied, has been replaced by Dowex-50 X 4, 20-50 mesh (Dow Chemical Co., Midland, Mich., U.S.A.); Amberlite IRA-400 (Rohm and Haas), an anion-exchange resin, 20-50 mesh.

Apparatus

In addition to the 8-ml semimicro electric ignition bomb described previously¹, three types of columns were prepared (Figs. 1, 2, 3). Their interior and tips were covered with paraffin, after a thorough cleaning with chromic acid-sulfuric acid mixture. They contained a perforated plastic disc at the bottom, supporting the resin column, and a small cotton plug in their constricted part, to prevent the resin from being washed out. The columns are provided with interchangeable ground joints and column II with an additional plastic diaphragm burette tap, containing no glass parts (Fig. 4). This valve permits control of the flow in the columns. Columns I and III contain the cation-exchange resin (acidic form), while column II contains the anion-exchange resin (basic form).

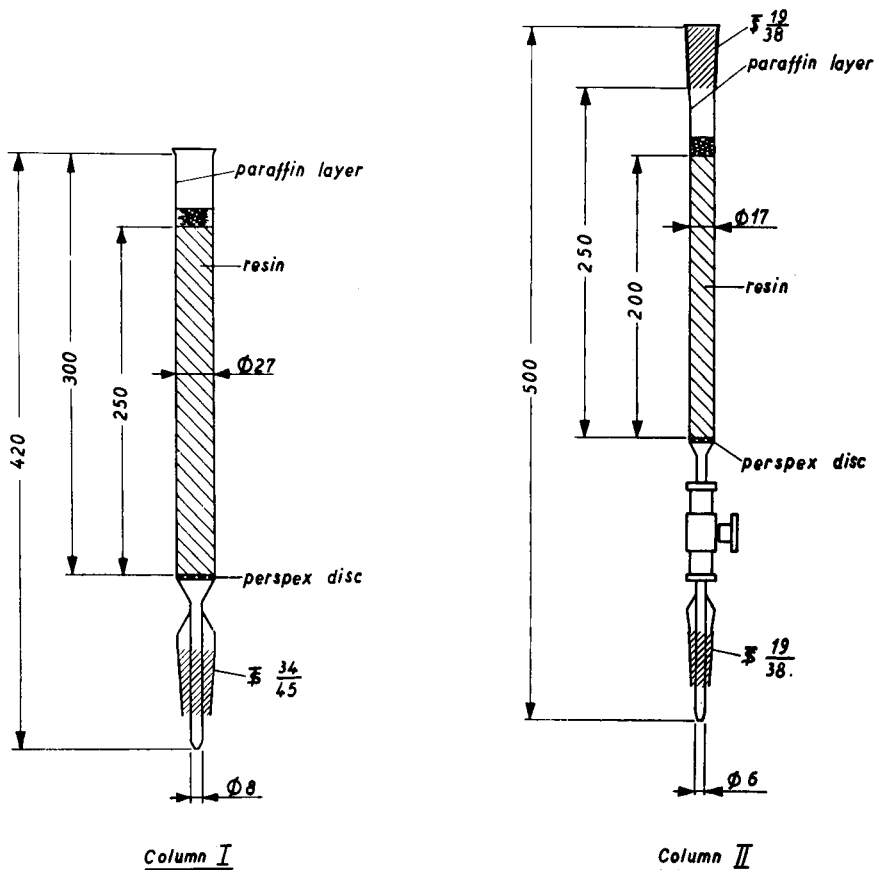
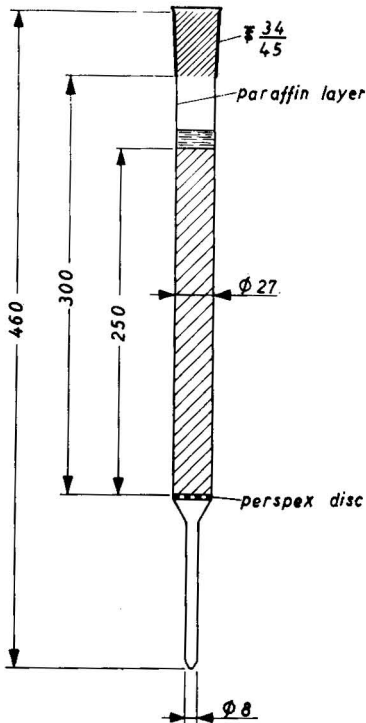


Fig. 1. Column I, containing the cation-exchange resin.

Fig. 2. Column II, containing the anion-exchange resin.

Procedure

The phosphate was determined according to BERNHARDT AND WREATH¹². We used a Hilger-Spekker absorptiometer H 760, fitted with No. 1 Kodak filters (transmittance 405 to 455 $m\mu$) and 2-cm Corex absorption cells. Calibration (see Table I) is carried out using a potassium dihydrogen phosphate solution in the range of 20 to 120 μg of phosphorus per 3 ml solution. This method gives good results, provided the glassware is scrupulously cleaned and the distilled water used contains no heavy metal ions. Working in a shaded place is recommended, as the molybdate deteriorates in direct sunlight.



Column III

Fig. 3. Column III, containing the cation-exchange resin.

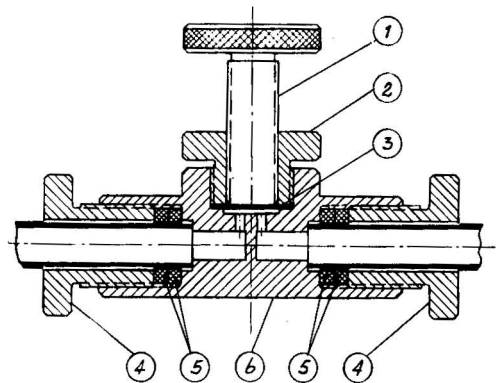


Fig. 4. Plastic diaphragm burette tap: 1. flow adjustment screw (P.V.C.); 2. diaphragm screw (P.V.C.); 3. diaphragm (polyethylene); 4. tube connectors (P.V.C.); 5. rubber seals; 6. body (Perspex).

TABLE I
CALIBRATION OF THE COLORIMETRIC PHOSPHATE DETERMINATION

$\mu\text{g P/3 ml}$	Absorbance $\times 10^3$						Mean value	Error %
	1	2	3	4	5	6		
20	045	047	048	051	045	042	0.046 ± 0.0013	2.8
40	086	083	085	084	087	086	0.085 ± 0.0006	0.7
60	124	123	126	125	126	119	0.124 ± 0.0011	0.9
80	158	159	161	160	161	156	0.159 ± 0.0008	0.5
100	197	196	195	198	191	191	0.195 ± 0.0012	0.6
120	231	230	235	230	228	229	0.231 ± 0.0010	0.4

The fluorine determination was carried out as described before¹.

Preparation of the ion-exchange columns

Pretreatment of the Dowex-50 X 4 resin. 500 g of the resin was washed several times with distilled water, 1*N* sulfuric acid, and 1*N* sodium hydroxide solution, each operation being continued until the supernatant appeared colorless.

Finally, the resin in the acid form was washed thoroughly with distilled water until no more sulfate ions could be detected in the washings.

Preparation of columns I and III. The columns were filled with the pretreated cation exchange resin, as uniformly as possible to prevent channeling, leaving a free space of about 5 cm height at the top of the columns.

Regeneration of columns I and III. After each analysis, columns I and III were connected, and 1 l of 1*N* sulfuric acid solution was passed through them. Each column was washed separately with distilled water until the percolate was free of sulfate ions.

Pretreatment of the Amberlite IRA-400 resin. A quantity of 100 g of the resin was washed several times with distilled water, 1*N* sodium hydroxide solution, and 1*N* hydrochloric acid solution. This sequence is repeated twice and each operation continued until the supernatant appears colorless.

Preparation of column II. The basic form of the pretreated resin is filled as uniformly as possible into the column, leaving again a free space of about 5-cm height at the top. One cycle of treatment was performed in the column and the latter washed with distilled water until the effluent had \pm pH 8.

Regeneration of column II. After each analysis, about 800 ml of 1*N* sodium hydroxide solution was passed through the column and the latter washed with distilled water until the effluent showed again pH 8. (In case the phosphate has been eluted from the column in the course of the phosphate determination, only half the volume of the regenerative solution is required.)

Amberlite IRA-400 changes its characteristics while in use, and its capacity diminishes in spite of the regeneration. Its activity should be checked from time to time and when not satisfactory, the filling of column II should be replaced. This check is carried out as follows: a mixture of 0.3 g of sodium monohydrogen phosphate dodecahydrate, 4 g of sodium hydroxide and 1 g of sodium carbonate is dissolved in 80–100 ml of distilled water and steps 1 and 2 are carried out as described below. An aliquot of 10 ml is then titrated with 0.015*N* thorium nitrate solution as usual, and should require only 0.03–0.04 ml. When this value is exceeded, the filling must be discarded.

ANALYTICAL METHOD

Up to 100 mg of the dried and powdered sample is ignited in the Parr sodium peroxide bomb, as described¹, the weight of the sample being chosen so that the final concentration of fluorine be 0.1–0.3 mg/10 ml. The phosphate concentration should be adjusted to the range quoted above by proper dilution. The melt is dissolved in distilled water, transferred to a 100-ml volumetric flask and filled up to the mark. Halogens other than fluoride and sulfur (as sulfate) can be determined independently in aliquots of this solution by standard methods. In contrast to fluorine, which must

be separated from the phosphate prior to its determination, the phosphorus (as phosphate) can be determined in aliquots by the described^{1,2} colorimetric method, as fluoride and other halogens, carbonate and sulfate ions do not interfere. Of course it can also be determined in an aliquot of the solution collected after separation of the fluoride ion by continuous elution of the column (step 3).

This last procedure is necessary in case the quantity of the sample available is limited and its fluorine and phosphorus content low.

Separation of fluoride and phosphate

The recommended rate of percolation is 4–5 ml/min. It should be controlled from

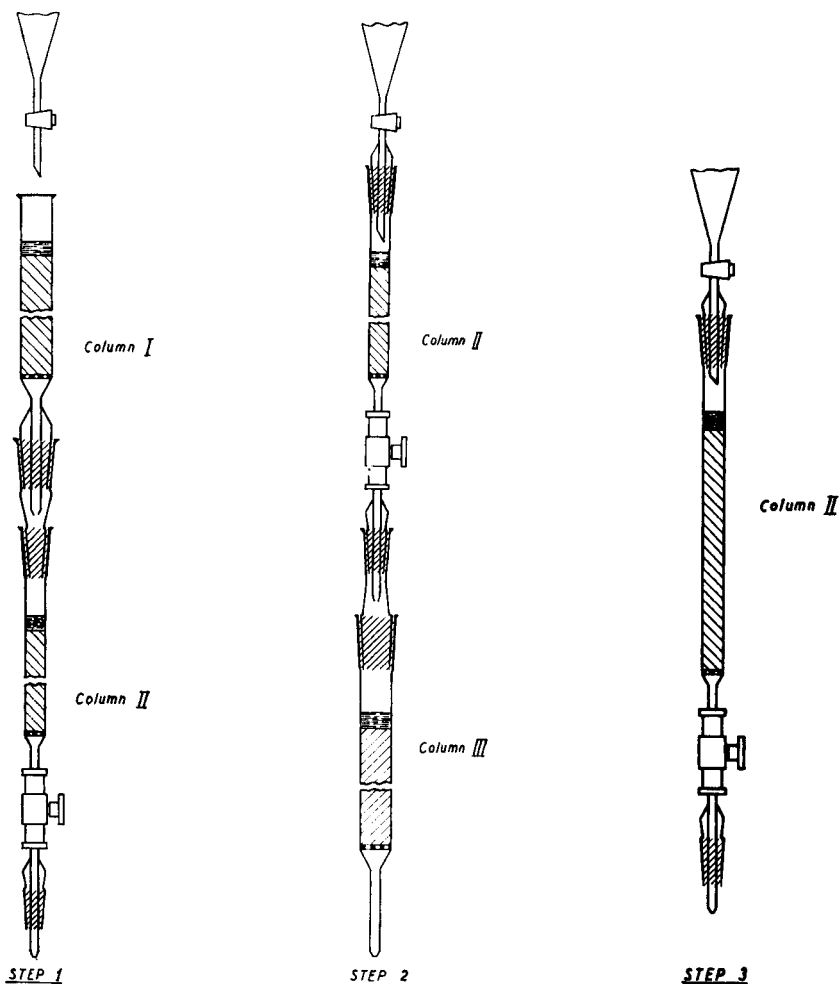


Fig. 5. First step of the analysis: adsorption of cations in column I and anions in column II.

Fig. 6. Second step of the analysis: elution of the fluoride ion and adsorption of the cations of the eluent in column III.

Fig. 7. Third step of the analysis: elution of the phosphate ion.

time to time, as it is dependent on, and proportional to, the liquid height. To ensure good adsorption and avoid channeling, the resins should always be covered with liquid.

First step. The solution is transferred into a separating funnel, attached to the top of both columns I and II (Fig. 5). The solution is percolated and washed down with 300 ml of distilled water; the effluent is discarded. Column I adsorbs the cations, while the anions in the resulting acid solution pass into column II and are adsorbed there.

Second step. Column I is disconnected and replaced by a separating funnel of 500 ml capacity. This and column II are placed on top of column III (Fig. 6), and about 600 ml of 0.25*N* sodium hydroxide is percolated. The first 100 ml of the effluent are discarded and the remaining 500 ml are collected in a 500-ml volumetric flask (alkaline reaction to phenolphthalein is maintained in the flask by addition of 0.25*N* sodium hydroxide solution) and made up to the mark with distilled water. The fluoride content is determined in 10 ml aliquots by the method described¹.

Third step. Column III is disconnected (Fig. 7), 450 ml of 1*N* sodium hydroxide solution passed through column II and the effluent collected in a 500-ml volumetric flask, acidified with approximately 26 ml of conc. sulfuric acid, giving an overall acid concentration of 1*N*, and brought up to the mark with 1*N* sulfuric acid solution. The phosphate content is determined in an aliquot by the colorimetric method¹².

RESULTS AND DISCUSSION

The method described here is based on differential elution of the anion-exchange resin. As the final solution analysed contains in addition to phosphate and fluoride

TABLE II
SEPARATION OF FLUORIDE AND PHOSPHATE IONS IN MIXTURES OF PURE SALTS

	Composition of salt mixture g	Found in step 2 g	Found in step 3 g
PO ₄ ⁻³	0.075	none	—
NaOH	4.0	—	—
Na ₂ CO ₃	1.0	—	—
PO ₄ ⁻³	0.075	none	—
NaOH	4.0	—	—
Na ₂ CO ₃	1.0	—	—
Cl ⁻	0.032	—	—
PO ₄ ⁻³	0.075	none	—
NaOH	4.0	—	—
Na ₂ CO ₃	1.0	—	—
SO ₄ ⁻²	0.066	—	—
F ⁻	0.0127	0.01266	—
PO ₄ ⁻³	0.075	—	0.074
NaOH	4.0	—	—
F ⁻	0.0127	0.01268	—
PO ₄ ⁻³	0.075	—	0.076
NaOH	4.0	—	—
Na ₂ CO ₃	1.0	—	—

ions, carbonate from the combustion of the organic matter, sodium hydroxide and in case of the presence of other elements in the sample, their respective ions, the accuracy of the method was proven by the analysis of artificial salt mixtures of approximately the same composition. It was found that the fluoride and the phosphate could be separated and quantitatively recovered and determined with good results. The results are summarized in Table II.

A number of organic phosphorus compounds containing fluorine has been analyzed by this method. The results are summarized in Table III. The mean error in these determinations is about -0.7% for fluorine and -1.2% for phosphate.

TABLE III

EXAMPLES OF FLUORINE AND PHOSPHORUS DETERMINATIONS IN ORGANIC COMPOUNDS

Compound	Formula	Calculated		Found		Error	
		% F	% P	% F	% P	% F	% P
Diisopropyl fluorophosphate	$C_6H_{14}FO_3P$	10.32	16.82	10.35	16.77	+0.29	-0.3
Diethyl 2-fluoroethyl-phosphate	$C_6H_{14}FO_4P$	9.49	15.48	9.39	15.33	-1.05	-0.97
Methanephosphonic acid difluoride	CH_3F_2OP	37.97	30.98	37.77	30.64	-0.53	-1.1
Diisopropyl 2-fluoroethyl-phosphate	$C_8H_{18}FO_4P$	8.33	13.57	8.27	13.37	-0.7	-1.5
Di-(2-fluoroethyl) benzenephosphonate	$C_{10}H_{18}F_2O_3P$	15.19	12.38	15.05	12.21	-0.9	-1.4
1,1-Di-(<i>p</i> -fluorophenyl)-ethylene-2-phosphonic acid	$C_{14}H_{11}F_2O_3P$	12.83	10.46	12.75	10.26	-0.6	-1.9

ACKNOWLEDGEMENT

The authors are indebted to Dr. ERNST D. BERGMANN and Dr. DAVID GINSBURG for their interest in this work and to Dr. ZVI PELCHOWICZ for the preparation of the samples.

SUMMARY

The fluorine and phosphorus in the organic compound are transformed into fluoride and phosphate ions. These ions are adsorbed after percolation of the whole solution through a cation-exchange resin, on a basic resin and eluted fractionally. Bromine, chlorine and sulfur can be determined simultaneously with the fluorine and the phosphorus.

RÉSUMÉ

Une méthode est proposée pour le semimicrodosage du fluor et du phosphore dans les composés organiques. Le fluorure et le phosphate obtenus par fusion au peroxyde de sodium sont traités par des échangeurs d'ions et séparés par élution fractionnée.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Halbmikro-Bestimmung von Fluor und Phosphor in organischen Verbindungen. Die nach dem Aufschluss mit Natrium-peroxyd erhaltenen Fluorid- und Phosphat-Ionen werden an einem Austauscherharz absorbiert und dann selektiv eluiert. Brom, Chlor und Schwefel können mitbestimmt werden.

REFERENCES

- ¹ CH. EGER AND A. YARDEN, *Anal. Chem.*, 28 (1956) 512.

- ² H. V. CHURCHILL, R. W. BRIDGES AND R. J. ROWLEY, *Ind. Eng. Chem., Anal. Ed.*, 9 (1937) 222.
³ S. GERICKE AND B. KURMIES, *Z. anal. Chem.*, 132 (1951) 334.
⁴ J. M. SALSURY, J. W. COLE JR., L. G. OVERHOLSER, A. R. ARMSTRONG AND J. H. YOE, *Anal. Chem.*, 23 (1951) 603.
⁵ H. H. WILLARD AND O. B. WINTER, *Ind. Eng. Chem., Anal. Ed.*, 5 (1933) 7.
⁶ R. BELCHER, E. F. CALDAS AND S. J. CLARK, *Analyst*, 77 (1952) 602.
⁷ R. BELCHER AND A. M. G. MACDONALD, *Mikrochim. Acta*, (1956) 899.
⁸ T. R. F. W. FENNEL, *Chem. & Ind. London*, (1955) 1404.
⁹ R. E. SHOUP, *Anal. Chem.*, 29 (1957) 1216.
¹⁰ W. FUNASAKA, M. KAWANE AND T. KOJIMA, *Mem. Fac. Eng., Kyoto Univ.*, 18 No 1 (1956); *Japan Analyst*, 4 (1955) 514.
¹¹ I. ZIPKIN, W. D. ARMSTRONG AND L. SINGER, *Anal. Chem.*, 29 (1957) 310.
¹² D. N. BERNHARDT AND A. R. WREATH, *Anal. Chem.*, 27 (1955) 440.

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PHOTOMETRIC DETERMINATION OF NICKEL IN COPPER-NICKEL ALLOYS

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Nickel may be determined in the presence of copper by the absorptiometric measurements of nickel nitrate solutions at a wavelength of 3900 Å. Precision photometric technique is used and the method has been used from about 1 to 32% nickel in copper-nickel alloys. A single determination can be completed within 5 min.

METHOD

Apparatus

A Beckman Model B spectrophotometer was used with 2 cm tube-cells.

Procedure

Dissolve 1.000 g of alloy in 10 ml of nitric acid (s.g. 1.4) in a 100-ml beaker and boil to remove nitrous fumes (nitrites interfere and boiling is necessary). Remove the beaker from the hot plate, allow to cool to about 80° then add 10 ml of phosphoric acid (1:10). (Manganese, as permanganate will interfere if phosphoric acid is added before boiling ceases). Cool and dilute to 25 ml in a volumetric flask. Examine the solution and if turbid, filter through a double No. 40 paper. (Tin as metastannic acid, silicon as silica, and carbon if present will interfere). Measure the transmittance at 3900 Å against a reference solution about 1% below the expected nickel content.

Preparation of calibration graphs

Weigh high purity copper and nickel to give a total of 1.000 g with nickel in the appropriate range. To each beaker containing the appropriate proportions of copper and nickel, add 10 ml of nitric acid (s.g. 1.4) and continue as under *Procedure*.

References p. 558

A convenient chart (Fig. 1) covering nickel up to 40% has been constructed using a Beckman Model B spectrophotometer, a blue photo tube, no filter, a wavelength of 3900 Å, 2-cm tube-cells and a solution temperature of 20°. For this chart, standard solutions of copper and nickel were prepared with nickel contents ranging from 0 to 40% in 2% increments, the total weight of copper and nickel being 1 g. From these solutions calibration graphs were plotted using reference solutions containing 0, 2, 4, 30% nickel. The graphs give straight-line curves within the range shown on the chart. Beyond this range (*i.e.* mainly those solutions with less than 20% transmission) the curves tend to become asymptotic and hence fail to continue to follow Beer's Law.

It is also evident that the graphs are not parallel, because $\tan \theta = y/x$ is decreasing with increasing nickel concentration. This effect is probably characteristic of the spectrophotometer, in so far that the more dense the colour, the greater the slit opening required to zero the instrument resulting in an increased band width.

By introducing "sensitivity" lines it is possible to dispense with a reference solution to zero the instrument for nickel determinations of unknown content up to 33%. These "sensitivity" lines were constructed by taking solutions up to 6% nickel and setting these known solutions at 100% transmittance at the maximum sensitivity, position 4. After removing the cell containing the solution, the sensitivity is retarded to position 3 and the transmittance read. A plot of these readings gives the line sens. 3, Fig. 1. Similarly, by taking solutions of known nickel content 3 to 13% and reading the transmittance at sensitivity 2, the line sens. 2 is plotted. The line sens. 1 is similarly plotted, by taking nickel solutions 10 to 20% and setting these solutions at 100% transmittance and sensitivity 4. After removing the cell containing the solution take the transmittance readings at a sensitivity of 1.

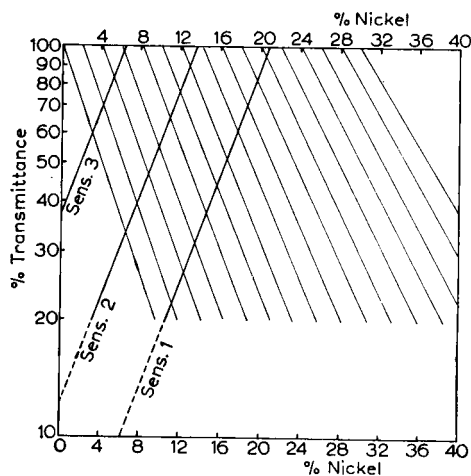


Fig. 1. Calibration graph (semi log.) for nickel nitrate in solutions of copper-nickel alloys.

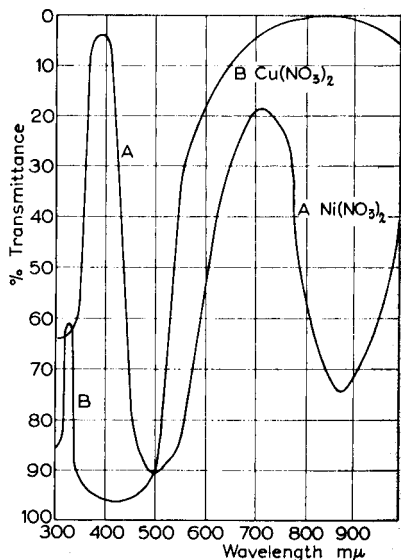


Fig. 2. Absorption spectra of nickel nitrate 2.65% solution, Curve A and of copper nitrate 2.5% solution, Curve B.

Now if the nickel content of an unknown copper-nickel alloy is to be determined, prepare the solution according to the *Procedure*. Then switch the spectrophotometer to sensitivity position 2. (This gives a range from 0 to 23.5% nickel).

An arbitrary standard, say between 0 and 13% nickel, is chosen. Take for example 10%. Then 10% nickel at sensitivity 2 on the chart is 58% transmittance. With no solution in the instrument adjust the transmittance scale to read 58. Insert the cell containing the solution and measure the transmittance at sensitivity 4. If this transmittance measurement is greater than 100%, then the nickel content of the unknown is less than 10% and a lower arbitrary standard is selected. If the transmittance is less than 20%, the nickel content is greater than 21% and a higher arbitrary standard is taken. Any transmittance measurement between 20 and 100% will give the nickel content of the unknown for this example.

If the percentage nickel of the unknown is between 10 and 15%, a satisfactory accurate measurement is obtained, otherwise it is advisable to take an arbitrary standard just below (not more than 2%) the estimated nickel content.

The finding of an appropriate arbitrary standard can be found in a matter of seconds.

This manner for determining nickel is in principle the reverse of that for the construction of the chart using "sensitivity" lines. It is, however, not applicable for accurate determinations of nickel greater than 25% using the Beckman Model B unless a photomultiplier is used.

Normally for routine analysis, the usual calibration graph is used with an appropriate reference solution of known nickel content.

Comparison of methods

A comparison of results from gravimetric dimethylglyoxime methods, polarographic methods and the described procedure is given in Table I.

RESULTS

Transmission curves

Transmission curves were plotted from a 2.65% nickel nitrate solution in water and a 2.5% copper nitrate solution in water (Fig. 2). Curve A shows that nickel nitrate has two absorbance peaks in the visible range, a maximum at 3900 Å and one at 7100 Å. Copper nitrate, curve B, has absorbance peaks at 3320 Å and a maximum at 8300 Å. Nitric acid does not disturb the curves. Copper chloride absorbs strongly at 3900 Å and the intensity is dependent on the chloride ion concentration¹, therefore chloride ions must be absent. Hence a wavelength of 3900 Å is suitable for measuring the absorbance of nickel nitrate solutions. The molecular extinction coefficient for nickel nitrate at this wavelength is 5.6.

Interfering elements

Of the elements which might be expected in copper-nickel alloys, tin, silicon and carbon are the only ones which will interfere with the method and these when present are filtered off. Interference from iron as ferric phosphate is negligible. When urea was used to remove nitrous oxides it was found that varying amounts of permanganate were formed. Ultimately, experimental work showed that by adopting the technique

described in the procedure, *i.e.* by cooling somewhat before adding phosphoric acid, any formation of permanganate was avoided. This indicates the probability that no perphosphoric acids were formed to cause oxidation.

Temperature

Nickel nitrate is somewhat temperature dependent. An error of $\pm 0.025\%$ nickel will occur for every 1° change in temperature, therefore the temperature of the sample should be within 1° of the temperature of the calibration. This is comparable to the temperature dependence of nickel perchlorate².

TABLE I
COMPARISON OF RESULTS BY DIFFERENT METHODS

% Mn	% Fe	% Ni found by:		
		Gravimetric (Dimethylglyoxime)	Polarographic method	Proposed method
—	—	1.01	1.06	1.00
—	—	1.82	1.72	1.79
0.63	1.17	5.06	5.16	5.10
0.70	1.20	5.82	6.00	5.90
0.99	1.42	10.10	10.30	10.03
0.86	1.30	11.16	11.40	11.10
1.14	0.62	29.94	30.10	30.00
1.50	0.94	31.82	31.70	31.85

SUMMARY

Nickel in copper-nickel alloys is determined as nitrate by precision photometry using a wavelength of 390 m μ . Nitrites, permanganate and insoluble particles such as metastannic acid and silica will interfere but these are readily removed. Chlorides, however, must be absent. A single determination can be completed within 5 min.

RÉSUMÉ

Une méthode photométrique rapide est proposée pour le dosage du nickel, sous forme de nitrate. Ce procédé peut s'appliquer en particulier aux alliages cuivre-nickel.

ZUSAMMENFASSUNG

Es wird eine photometrische Schnell-methode zur Bestimmung von Nickel in Form von Nickel-nitrat beschrieben. Das Verfahren eignet sich besonders für Kupfer-Nickel Legierungen.

REFERENCES

- ¹ G. R. SUTCLIFFE AND D. M. PEAKE, *Analyst*, 83 (1958) 122.
- ² R. BASTIAN, *Anal. Chem.*, 23 (1951) 580.

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POLAROGRAPHY OF LEAD IN HYDROXIDE AND CYANIDE MEDIA

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INTRODUCTION

Lead has long been known to give a polarographic wave in the presence of excess cyanide¹ and cyanide media have been recommended by a number of authors as suitable supporting electrolytes for the determination of lead in alloys²⁻⁴. It has usually been assumed that the lead is present in the form of a cyanide complex and a tentative estimate of the formation constant has been given⁵. Some preliminary experiments performed at the University of Kansas⁶ suggested that the characteristic behavior of lead in cyanide media was due to the presence of biplumbite ion rather than cyanide complexes, and the present investigation was undertaken to clarify this question.

The polarography of lead in sodium hydroxide medium was first studied in a classic investigation by LINGANE in 1941⁷. He showed the reduction to be reversible and the biplumbite ion to be the prevalent species in the range of about 0.01 to 1.0M hydroxide ion. For the purposes of the present investigation it was felt desirable to redetermine more exactly the halfwave potential of lead as a function of hydroxide ion concentration, particularly in the range of 0.01 to 0.05M, under conditions of constant ionic strength and negligible liquid junction potentials.

APPARATUS AND REAGENTS

Polarograms were determined using a Sargent Model XXI without damping. The potential at the beginning and at the end of each polarogram was measured to ± 0.1 mV with a Rubicon precision potentiometer, thus calibrating the scan voltage more accurately than would be possible using only the meters on the polarograph. Current measurements were made at the point of maximum drop size. The addition of a maximum suppressor was found to be unnecessary. Half-wave potentials were determined graphically and, where highest accuracy was desired, from plots of $\log [(i_a - i)/i]$ vs. E . The capillary was made from commercial marine barometer tubing ($m^{2/3} t^{1/3} = 1.59$ at -0.7 V vs. SCE in 1 N sodium hydroxide). Cell resistances were measured using an A. C. conductivity bridge. The reference cell potentials were determined with a Rubicon potentiometer.

All solutions were prepared with boiled, distilled water from reagent-grade chemicals. Sodium carbonate was excluded from the sodium hydroxide by dilution of supernatant liquid from a 10 N sodium hydroxide solution in which the sodium carbonate had been allowed to settle. Sufficient lead nitrate was added to make each solution $5.00 \cdot 10^{-4}M$ in lead. This amount of lead was found to give a precipitate in 2M sodium cyanide solution, and the supernatant liquid was used without disturbing the flocculent white precipitate. Samples were deaerated using prepurified tank nitrogen and held at 25.0° in a water thermostat.

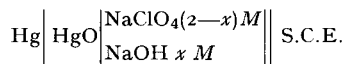
RESULTS AND DISCUSSION

The mercury-mercuric oxide reference electrode

The use of a convenient reference electrode without a liquid junction potential

References p. 565

was felt to be desirable and therefore the mercury/mercuric oxide electrode was selected. In order to check the potential of this electrode as a function of hydroxide ion concentration at constant ionic strength, measurements were made of the potential of the cell



The mercury/mercuric oxide half-cell was prepared by stirring mercury, yellow mercuric oxide, and the appropriate hydroxide-perchlorate mixture together and allowing to stand for at least 20 min for equilibration. The potential was usually found to be stable after this time but drifting occasionally occurred. It was observed that the potential would reach the equilibrium value and become stable more satisfactorily if a current of a few μA were passed anodically through the half-cell for a few moments. The results of the measurements of the stable half-cell potential against the saturated calomel electrode are given in Table I and a plot of E versus $\log(\text{OH}^-)$ is shown in Fig. 1. The variation of potential with pOH is seen to be linear over a

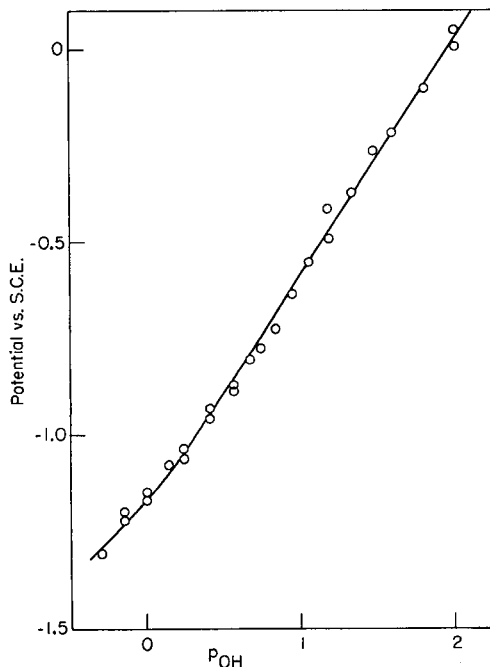


Fig. 1. Potential of the mercury-mercuric oxide electrode versus the S.C.E., as a function of pOH . Ionic strength made up to $2.00M$ with sodium perchlorate.

range of 0.25 to 2.0 pOH units and the slope, 0.0614 V/pOH , is close to the theoretical value of 0.0591 . Variation in the junction potential between the mercury oxide half-cell and the calomel electrode is evidently not serious over this range. The potential of the electrode at $0.0100N$ sodium hydroxide and $1.99M$ sodium perchlorate was

TABLE I
POTENTIAL OF THE MERCURY-MERCURIC OXIDE REFERENCE HALF-CELL

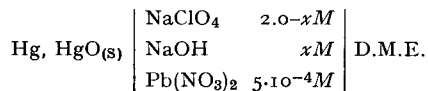
C_{OH^-} ^a	E (V vs. S.C.E.)	
	1st run	2nd run
2.00	-0.131	
1.43	-0.122	-0.120
1.00	-0.115	-0.117
0.718	-0.108	
0.572	-0.106	-0.104
0.387	-0.093	-0.096
0.276	-0.087	-0.088
0.214	-0.080	
0.182		-0.078
0.148	-0.072	
0.113		-0.062
0.087	-0.055	
0.066	-0.049	-0.041
0.047	-0.037	
0.033		-0.026
0.025	-0.022	
0.016		-0.011
0.010	+0.001	+0.005

^a Ionic strength made up to 2.00M with sodium perchlorate as required.

found to be +0.002 V *versus* the S.C.E. The standard potential given in the literature⁸ is not directly utilizable for polarography because values for the activity coefficients involved are not known. From the standpoint of convenience, stability and reproducibility, the electrode may be recommended for polarographic work.

Polarography in hydroxide media

Polarograms were determined using cells of the type



where x varied from 0.01 to 2.00M.

Small amounts of lead nitrate were found to have no effect upon the potential and therefore the same electrolyte was used throughout the cell, which was an H-type polarograph cell with a coarse fritted glass partition. The resistance of the solution in this apparatus varied between 100 and 140 ohms, depending on the hydroxide concentration. With such low resistances, the iR drop correction was less than 0.4 mV and was neglected.

The findings in sodium hydroxide media are summarized in Table II. Study of the polarography of lead confirms the general conclusions reached by LINGANE⁷

TABLE II
HALF-WAVE POTENTIAL OF BIPLUMBITE ION IN SODIUM HYDROXIDE

$C_{OH} \text{--}^a$	$E^{1/2}$	i_d^b
2.00	0.762	2.62
1.43	0.752	2.69
1.00	0.744	2.72
0.744	0.734	2.78
0.564	0.726	2.82
0.431	0.715	2.83
0.327	0.705	2.86
0.208	0.689	2.79
0.142	0.675	2.82
0.0710	0.646	2.76
0.0482	0.629	2.74
0.0330	0.615	2.63
0.0174	0.592	2.47
0.0100	0.577	2.43
0.0096	0.576	2.36
0.002	0.552	1.96 ^c

^a Ionic strength made up to 2.00M with sodium perchlorate as required.

^b Biplumbite concn. is $5 \cdot 10^{-4}M$.

^c Irreversible reduction wave.

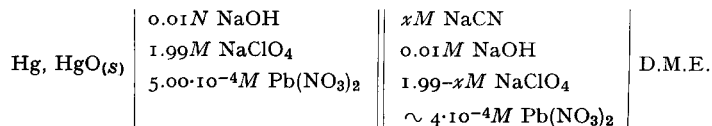
regarding the reversibility of the electrode reaction at hydroxide concentrations greater than 0.01M and the identity of the biplumbite ion as the species present. The results show, however, that by elimination of liquid junction potentials and use of a constant ionic-strength medium a slope for the plot of half-wave potential vs. pOH is obtained which is very close (87.5 mV/pOH) to the theoretical value of 89 mV/pOH. The half-wave potential of biplumbite ion in 1.00N sodium hydroxide at an ionic strength of 2.00 is -0.744 V vs. the S. C. E. From our data the value 12.62 for the logarithm of the overall formation constant of the biplumbite ion at an ionic strength of 2.00 can be calculated. Previous literature values are 12.15 (polarography at variable ionic strength)⁹, 13.34 (polarography in 1M nitrate medium)¹⁰, 13.94 (solubility with extrapolation to zero ionic strength)¹¹ and 13.95 (polarography with extrapolation to zero ionic strength)¹².

Polarography in cyanide media

In order to determine whether a lead cyanide complex was detectable polarographically or not, polarograms were taken of lead solutions containing various concentrations of cyanide from millimolar to 2.00M and added hydroxide from 0.0 to 0.1M. It was observed that 0.5 mM lead was incompletely soluble in 1.0 and 2.0M sodium cyanide and that the lead waves in such solutions coalesced with the anodic dissolution of the mercury drop so that no characteristic half-wave potential of the lead species could be determined. The characteristic wave of biplumbite ion in solutions containing sodium hydroxide did not appear to be affected by the addition of small amounts of cyanide. At hydroxide concentrations lower than 0.01M, with no cyanide present, the reduction waves were no longer reversible.

In order to look for evidence of a cyanide complex under the most favorable conditions possible, polarograms were run on solutions which were $0.01M$ in hydroxide and contained varying amounts of cyanide, using a cell which eliminated uncertainties due to liquid junction potentials. The hydroxide concentration was felt to be the lowest which would give a reversible reduction but yet might allow formation of a lead cyanide complex by competition of cyanide with hydroxide for the lead.

The following cell was used:



An H-type polarographic cell fitted with an exceedingly fine fritted glass partition served to keep the two solutions from mixing and thereby exclude cyanide from the reference half-cell. The resistance of this cell being approximately 200 ohms, the accompanying iR drop of 0.0005 V could be neglected in interpreting results. As will be seen from the results shown in Fig. 2 and tabulated in Table III, no indication of

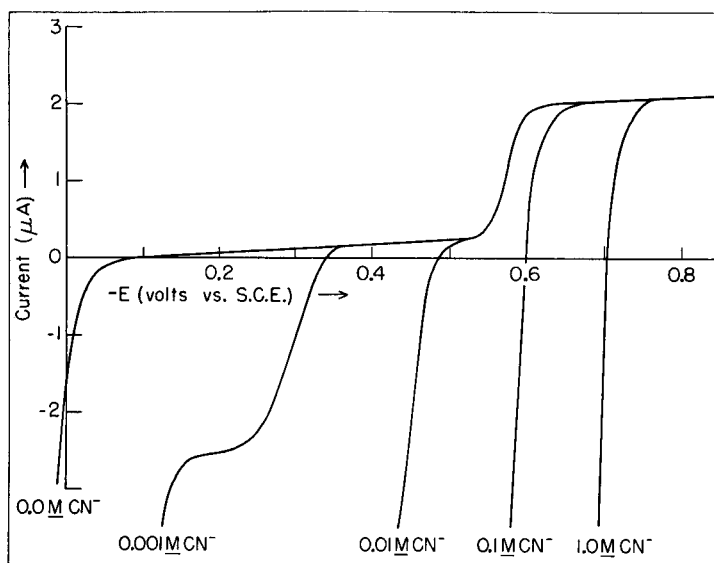


Fig. 2. Polarograms of lead in $0.01N$ sodium hydroxide with various amounts of added cyanide. Ionic strength made up to $2.00M$ with sodium perchlorate.

a cyanide complex was detectable. At sufficiently low concentrations, the anodic wave of cyanide gave a well-defined diffusion current, and showed the characteristics reported for it in the literature¹³. At cyanide concentrations greater than $0.03M$, the anodic dissolution potential of the mercury drop became more negative than the potential of the biphosphate ion and the lead wave is obscured by the anodic cyanide wave.

TABLE III
 HALF-WAVE POTENTIAL OF LEAD *vs.* S.C.E. AS A FUNCTION OF CYANIDE
 AND HYDROXIDE ION CONCENTRATION

C_{OH^-} ^a	C_{CN^-}	$E^{1/2}$
0.01	—	—0.573
0.01	0.010	—0.573
0.01	0.015	—0.574
0.01	0.020	—0.572
0.01	0.025	—0.573
0.01	0.030	—0.572
0.01	0.100	—0.61 ^b
0.01	1.00	—0.72 ^b
0.01	2.00	—0.74 ^b
0.1	1.00	—0.72 ^b
—	1.00	—0.72 ^b
—	2.00	—0.74 ^b
—	1.00	—0.72 ^c

^a Actual OH^- added.

^b Potential determined at $1/2$ cathodic current.

^c $\mu = 1$; all other solutions, $\mu = 2$.

Because 0.5 mM lead was incompletely soluble in 2M cyanide, the solubility of lead in this medium could be determined using the diffusion current data from Table II. Two separate determinations yielded values of $2.48 \cdot 10^{-4}$ and $2.55 \cdot 10^{-4}M$ lead for the solubility in 2M sodium cyanide. Although a basic lead cyanide is known to be formed under these conditions⁶, these values agree quite closely with the value $3.2 \cdot 10^{-4}M$ which can be calculated from the equilibrium data of GARRETT, VELLENGA AND FONTANA¹¹ assuming the lead to be dissolved by hydroxide ions from the hydrolysis of the cyanide.

In published procedures for the determination of lead using cyanide media, invariably a mixture containing excess hydroxide ion has been used²⁻⁴. It is evident from the present work that the lead wave obtained is actually that of biplumbite ion, a fact which only MILNER⁴ appears to have suspected. The presence of cyanide in these procedures is desirable, however, because it acts as a masking reagent to prevent the interference of other metals.

ACKNOWLEDGEMENT

This work has been supported in part by the United States Atomic Energy Commission, under Contract AT(30-1)-905.

SUMMARY

The polarographic reduction wave of lead in cyanide-supporting electrolytes has been shown to be due to the presence of the biplumbite ion. No evidence for a lead-cyanide complex in aqueous solution has been found. The polarographic characteristics of lead in alkaline solutions have been redetermined in media of constant ionic strength using cells without liquid junction potentials. The mercury/mercuric oxide electrode has been studied and its use as a reference electrode in polarography is recommended.

RÉSUMÉ

Les auteurs ont étudié la réduction polarographique du plomb, en présence de cyanure, comme électrolyte de base. Ils recommandent l'emploi de l'électrode mercure/oxyde mercurique, comme électrode de référence.

ZUSAMMENFASSUNG

Es wird die polarographische Reduktion von Blei in Gegenwart von Cyanid als Elektrolyt untersucht. Als Referenzelektrode wird eine Quecksilber/Quecksilberoxyd Elektrode empfohlen.

REFERENCES

- ¹ J. HEYROVSKÝ AND D. ILKOVIČ, *Collection Czechoslov. Chem. Commun.*, 7 (1935) 213.
- ² M. SPALENKA, *Z. anal. Chem.*, 126 (1943) 49.
- ³ G. W. C. MILNER, *Analyst*, 70 (1945) 250.
- ⁴ G. W. C. MILNER, *Metallurgia*, 36 (1947) 287.
- ⁵ I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Interscience Publ. Inc. New York, 1941.
- ⁶ J. E. BARNEY AND D. N. HUME, Unpublished experiments, University of Kansas (1946).
- ⁷ J. J. LINGANE, *Chem. Revs.*, 29 (1941) 1.
- ⁸ W. M. LATIMER, *Oxidation Potentials*, Prentice Hall, New York, 1952.
- ⁹ J. HEYROVSKÝ, *Trans. Faraday Soc.*, 19 (1923) 692.
- ¹⁰ G. W. GOWARD, *Thesis*, Princeton Univ., 1954, Univ. Microfilms 9414.
- ¹¹ A. B. GARRETT, S. VELLENGA AND C. M. FONTANA, *J. Am. Chem. Soc.*, 61 (1939) 367.
- ¹² A. A. VLČEK, *Collection Czechoslov. Chem. Commun.*, 20 (1955) 400.
- ¹³ L. NEWMAN, J. DE O. CABRAL AND D. N. HUME, *J. Am. Chem. Soc.*, 80 (1958) 1814.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

I. INTRODUCTION

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On a proposé depuis longtemps l'utilisation de cations organiques pour effectuer l'extraction à l'aide de solvants convenablement choisis, d'anions divers: organiques (RCO_2^- , ArSO_3^- , ArO^- etc.) et minéraux simples (I^-) ou complexes (ClO_4^- , SbCl_6^- , AuCl_4^- , etc.).

Les cations organiques utilisés sont les suivants: Ammonium (RNH_3^+ , R_2NH_2^+ . . . R_4N^+), Oxonium (ROH_2^+ , R_2OH^+ , R_2COH^+), Diazonium (RN_2^+), Arsonium (R_4As^+), Stibonium (R_4Sb^+), Phosphonium (R_4P^+), Sélénonium (R_3Se^+), Sulfonium (R_3S^+).

Le nombre des associations possibles anion + cation est donc très grand, ce qui explique le large développement que connaît actuellement cette méthode¹.

Mais ces cations sont en général incolores. Ils sont associés le plus souvent à des anions incolores ou peu colorés; la phase organique obtenue après extraction est donc elle-même incolore ou peu colorée. Il est donc impossible d'effectuer directement une spectrocromimétrie du corps extrait (en lumière visible). Si l'on désire réaliser simultanément la séparation et le dosage par spectrocromimétrie dans le visible, il faut

utiliser des cations organiques ou organo-métalliques colorés. De plus, la mise au point de dosages de traces, ou l'emploi des techniques microchimiques, entraîne l'utilisation de cations de coloration intense.

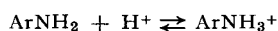
Deux groupes de cations sont alors utilisables :

(1) Les complexes que donnent certains cations métalliques (Fe^{+2} , Co^{+2} , Cu^{+2} . . .) avec des bases organiques comme l'*o*-phénanthroline² et ses dérivés: bathophénanthroline³, néocuproïne⁴⁻⁷, bathocuproïne^{8,8,9} la 2-2'-diquinoline¹⁰⁻¹³, ou l' α - α' -dipyridyle et ses dérivés¹⁴. On peut les utiliser pour séparer et doser, soit les éléments métalliques complexés, soit les anions associés.

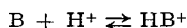
(2) Les cations correspondants aux colorants basiques.

Tout colorant renfermant une fonction basique (c'est le plus souvent une fonction amine) peut donner à partir d'un pH convenable un cation de couleur intense et généralement différente de celle de la molécule. Ces colorants sont parfois utilisés comme indicateur de pH (le rouge neutre par exemple).

Avec une fonction amine primaire, la réaction s'écrit :



En désignant par B la molécule de colorant basique, on peut schématiser cette réaction par :



C'est par cette formule que nous désignerons par la suite le cation coloré.

Quelques colorants¹⁵⁻¹⁷, et en particulier le bleu de méthylène¹⁸⁻²⁵ sont utilisés pour le dosage par extraction des détergents et agents tenso-actifs. Dans les autres domaines de l'analyse, à l'exception de la rhodamine B²⁶ qui a été proposée pour le dosage de l'antimoine²⁷⁻³⁵, de l'or³⁶, du gallium^{37,38} et du thallium^{39,40}, les colorants basiques sont actuellement peu utilisés: une benzylidènerhodanine pour l'extraction de l'or^{41,42}, la *p*-nitrosodiméthylaniline pour la séparation et le dosage du platine et du palladium^{43,44}, le violet de méthyle pour le dosage des traces d'antimoine^{45,46} et de thallium⁴⁷⁻⁵⁰, le vert brillant également pour le thallium⁴⁸. J'ai décrit précédemment⁵¹ une méthode utilisant le bleu de méthylène: l'anion fluoborique BF_4^- associé à ce colorant est extractible par le dichloro-1,2-éthane, ce qui permet sa séparation de nombreux anions et le dosage de traces de bore.

D'autres exemples sont décrits dans les mémoires suivants.

RÉSUMÉ

Deux sortes de cations colorés sont utilisables pour le dosage par extraction d'anions divers simples ou complexes: (a) les cations du type *o*-phénanthroline ferreuse $\text{Fe}(\text{o-ph})_3^{+2}$; ce sont surtout les dérivés de l'*o*-phénanthroline qui ont été utilisés; (b) les cations correspondants aux nombreux colorants basiques dont l'utilisation est jusqu'alors très limitée. Ils permettent des dosages d'une grande sensibilité.

SUMMARY

In the extraction method two kinds of coloured cations can be used for the determination of simple or complex anions: (a) *o*-Phenanthroline derivatives; (b) Cations of basic dyes. The method is especially suitable for the determination of trace elements.

ZUSAMMENFASSUNG

Für die spektrocolumetrische Bestimmung einfacher und komplexer Anionen nach dem Extraktionsverfahren sind 2 Gruppen von gefärbten Kationen verwendbar: (1) o-Phenanthrolin Derivate, (2) Kationen basischer Farbstoffe. Die diskutierte Methode ist besonders geeignet zur Bestimmung von Spurenelementen.

BIBLIOGRAPHIE

- 1 Consulter par exemple L. C. CRAIG, *Anal. Chem.*, 21 (1949) 85; 22 (1950) 61; 23 (1951) 41; 24 (1952) 66; 26 (1954) 110; 28 (1956) 723. G. H. MORRISON, *Anal. Chem.*, 30 (1958) 632.
- 2 D. W. MARGERUM ET C. V. BANKS, *Anal. Chem.*, 26 (1954) 200.
- 3 G. F. SMITH, W. H. MCCURDY ET H. DIEHL, *Analyst*, 77 (1952) 418.
- 4 G. F. SMITH ET W. H. MCCURDY, *Anal. Chem.*, 24 (1952) 371.
- 5 A. R. GAHLER, *Anal. Chem.*, 26 (1954) 577.
- 6 B. ZAK ET N. RESSLER, *Anal. Chem.*, 28 (1956) 1158.
- 7 A. J. FRANK, A. B. GOULSTON ET A. A. DEACUTIS, *Anal. Chem.*, 29 (1957) 750.
- 8 G. F. SMITH ET D. H. WILKINS, *Anal. Chem.*, 25 (1953) 510.
- 9 L. G. BORCHARDT ET J. P. BUTLER, *Anal. Chem.*, 29 (1957) 414.
- 10 J. G. BRECKENRIDGE, R. W. J. LEWIS, ET L. A. QUICK, *Can. J. Research*, 17 B (1939) 258.
- 11 J. HOSTE, *Anal. Chim. Acta*, 4 (1950) 23.
- 12 J. HOSTE, J. EECKHOUT ET J. GILLIS, *Anal. Chim. Acta*, 9 (1953) 263.
- 13 R. J. GUEST, *Anal. Chem.*, 25 (1953) 1484.
- 14 J. L. WALTER ET H. FREISER, *Anal. Chem.*, 26 (1954) 217.
- 15 F. KARUSCH ET M. SONENBERG, *Anal. Chem.*, 22 (1950) 175.
- 16 C. R. WALLIN, *Anal. Chem.*, 22 (1950) 616.
- 17 W. A. MOORE ET R. A. KOLBESON, *Anal. Chem.*, 28 (1956) 161.
- 18 J. H. JONES, *J. Assoc. Offic. Agr. Chemists*, 28 (1945) 398.
- 19 H. G. EVANS, *J. Soc. Chem. Ind. London*, 69 (1950) 76.
- 20 J. C. HARRIS ET F. R. SHORT, *Food Technol.*, 6 (1952) 275.
- 21 P. N. DEGENS, H. C. EVANS, J. D. KOMMER ET P. A. WINSOR, *J. Appl. Chem.*, 3 (1953) 54.
- 22 TAMOTSU KONDO, *J. Chem. Soc. Japan*, 76 (1955) 1374.
- 23 J. LONGWELL ET W. D. MANIECE, *Analyst*, 80 (1955) 167.
- 24 P. MUKERJEE, *Anal. Chem.*, 28 (1956) 870.
- 25 J. D. FAIRING ET F. R. SHORT, *Anal. Chem.*, 28 (1956) 1827.
- 26 R. W. RAMETTE ET E. B. SANDELL, *J. Am. Chem. Soc.*, 78 (1956) 4872.
- 27 T. H. MAREN, *Anal. Chem.*, 19 (1947) 487.
- 28 L. D. FREEDMAN, *Anal. Chem.*, 19 (1947) 502.
- 29 C. L. LUKE, *Anal. Chem.*, 25 (1953) 674.
- 30 F. N. WARD ET H. W. LAKIN, *Anal. Chem.*, 26 (1954) 1168.
- 31 HIROSHI ONISHI ET E. B. SANDELL, *Anal. Chim. Acta*, 11 (1954) 444.
- 32 W. NIELSCH ET G. BOLTZ, *Z. anal. Chem.*, 143 (1954) 264.
- 33 B. J. MACNULTY ET L. D. WOOLLARD, *Anal. Chim. Acta*, 13 (1955) 64.
- 34 R. W. RAMETTE ET E. B. SANDELL, *Anal. Chim. Acta*, 13 (1955) 455.
- 35 W. C. COPPINS ET J. W. PRICE, *Metallurgia*, 53 (1956) 183.
- 36 B. J. MACNULTY ET L. D. WOOLLARD, *Anal. Chim. Acta*, 13 (1955) 154.
- 37 HIROSHI ONISHI, *Anal. Chem.*, 27 (1955) 832.
- 38 HIROSHI ONISHI ET E. B. SANDELL, *Anal. Chim. Acta*, 13 (1955) 159.
- 39 F. FEIGL, V. GENTIL ET D. GOLDSTEIN, *Anal. Chim. Acta*, 9 (1953) 393.
- 40 HIROSHI ONISHI, *Bull. Chem. Soc. Japan*, 29 (1956) 945.
- 41 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Ed. Interscience Publishers Inc., New-York 1950, p. 349.
- 42 N. S. POLUEKTOV, *Trudy Vsesoyuz. Konf. Anal. Khim.*, 2 (1943) 393.
- 43 D. E. RYAN, *Analyst*, 76 (1951) 167.
- 44 J. H. YOE ET J. J. KIRKLAND, *Anal. Chem.*, 26 (1954) 1335.
- 45 M. JEAN, *Anal. Chim. Acta*, 11 (1954) 82.
- 46 HIDEHIRO GOTO ET YACHIYO KAKITA, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 73 (1952) 339; 77 (1956) 739.
- 47 S. D. GUR'EV, *Sbornik Nauch. Trudy, Gosudarsto. Nauch. Inst. Tsvet. Met.*, 10 (1955) 371.
- 48 N. T. VOSKRESENSKAYA, *Zhuv. Anal. Khim.*, 11 (1956) 585.
- 49 G. G. SHEMELEVA ET V. T. PETRASHEN, *Trudy Novoscherkas Politekh. Inst.*, 41 (55) (1956) 35.
- 50 M. KOVAŘIK ET M. MOUČKA, *Anal. Chim. Acta*, 16 (1957) 249.
- 51 L. DUCRET, *Anal. Chim. Acta*, 17 (1957) 213.

DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

II. UTILISATION DES COMPLEXES DE L'*o*-PHÉNANTHROLINE POUR LA SÉPARATION ET LE DOSAGE DE PETITES QUANTITÉS DE NICKEL EN PRÉSENCE DE FER ET DE COBALT

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RAPPEL DE FAITS CONNUS

On sait que l'*o*-phénanthroline donne avec certains cations des complexes très stables dans un large domaine de pH. Ceux des métaux ferreux en particulier ont fait l'objet d'études nombreuses et diverses: sur les vitesses de réaction, les constantes de stabilité, les mécanismes de dissociation et de racémisation, l'action des rayons X et γ , l'action biologique... etc. (fer¹⁻²², nickel²³⁻³⁴, cobalt³⁵⁻³⁸). Par contre l'extraction de ces divers complexes n'a été que peu utilisée en analyse³⁹, alors que des dérivés de l'*o*-phénanthroline comme la bathophénanthroline⁴⁰, la néocuproïne⁴¹⁻⁴⁴ ou la bathocuproïne^{43'45'46} ont fait l'objet dans ce domaines de plusieurs publications.

Nous rappelons que le fer(II) donne avec l'*o*-phénanthroline (*o*-ph) un complexe rouge très stable^{1,3,4'5,10,11,16} de formule $\text{Fe}(\text{o-ph})_3^{+2}$ que certains auteurs désignent sous le nom de „ferroïne”. Le fer(III) donne également un complexe très stable, jaune-brun: $\text{Fe}(\text{o-ph})_3^{+3}$.

Les oxydants de potentiel élevé comme le permanganate, le cérium(IV) oxydent la ferroïne en un complexe bleu^{2,20,21}; le système est couramment employé comme indicateur d'oxydo réduction.

Le cobalt(II)^{36,38} se comporte comme le fer(II); il donne un complexe jaune $\text{Co}(\text{o-ph})_3^{+2}$ dont la forme oxydée est brune.

Le nickel présente des propriétés différentes. On a décrit trois complexes de formule générale $\text{Ni}(\text{o-ph})_n^{+2}$ ^{31,32,34} ou n prend les valeurs 1³⁴ 2³², 3^{25,28,31} et dont les couleurs sont respectivement bleu, violet, lilas. Pour ces complexes, on ne connaît pas de forme oxydée.

EXTRACTION DES COMPLEXES DE L'*o*-PHÉNANTHROLINE AVEC LES CATIONS DES MÉTAUX FERREUX*

Les complexes de formule $\text{M}(\text{o-ph})_3^{+2}$ donnent avec certains anions comme I^- , SCN^- , $\text{CCl}_3\text{CO}_2^-$, des combinaisons extractibles quantitativement dans un large domaine de pH (0 à 7 environ) par les solvants suivants: alcool benzylique, dichloro-*r*, 2-éthane, *o*-nitrotoluène, *o*-bromotoluène. Le complexe du fer(III) se comporte de manière identique sauf avec l'iodure qui est oxydé en iode. D'autres anions comme

* L. PATEAU - Thèse d'ingénieur D.P.E. CNAM Paris (non publiée).

BF_4^- , ClO_4^- , IO_4^- donnent des composés peu solubles dans l'eau, extractibles par l'un des solvants indiqués ci-dessus; par exemple les complexes $\text{M}(o\text{-ph})_3^{+2}$ et $\text{Fe}(o\text{-ph})_3^{+3}$ associés à l'anion perchlorique ClO_4^- , sont extractibles par l'alcool benzylique, l'*o*-nitrotoluène et l'*o*-bromotoluène; associés à l'anion fluoborique BF_4^- , par l'alcool benzylique.

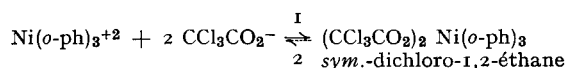
Par contre, les formes oxydées de la ferroïne et du complexe du cobalt (II) ne sont pas extractibles.

Nous avons utilisé ces diverses propriétés pour la séparation et le dosage du nickel.

DOSAGE DU NICKEL EN PRÉSENCE DE FER ET DE COBALT

Principe

Nous supposons que la solution acide renferme les cations Fe^{+3} , Co^{+2} , Ni^{+2} . Après réduction de Fe^{+3} par le métabisulfite, on ajoute un excès d'*o*-phénanthroline: les complexes de formule générale $\text{M}(o\text{-ph})_3^{+2}$ se forment. L'addition de cérium(IV) en excès fait passer les complexes du fer(II) et du cobalt(II) sous forme oxydée. Dans ces conditions, seul le nickel (II) reste extractible si l'on associe le complexe à l'un des anions cités précédemment. La présence d'un excès de sels cériques empêche l'utilisation des anions et solvants réducteurs: I^- , SCN^- , alcool benzylique, dérivés du toluène. Nous avons donc choisi l'anion trichloracétique et comme solvant, le dichloro-1,2-éthane. La réaction est quantitative:



L'expérience montre d'autre part que les résultats obtenus sont plus précis, si, après extraction du nickel, la phase organique est séparée et agitée pendant quelques minutes avec une solution diluée de cérium(IV) qui oxyde les dernières traces de fer qu'elle renferme. On ajoute à cette solution de l'acide trichloracétique et de l'*o*-

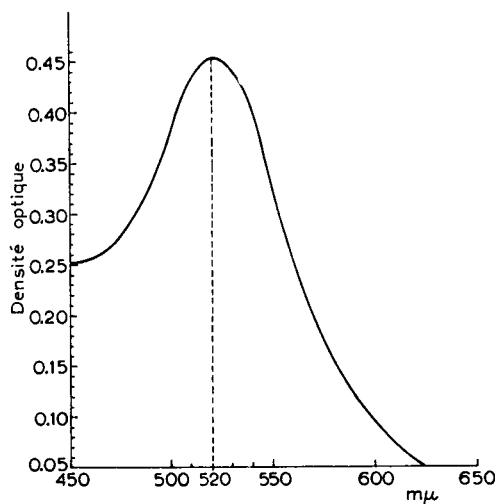


Fig. 1. Spectre d'absorption du trichloracétate d'*o*-phénanthroline de nickel(II) dans le dichloro-1,2-éthane.

phénanthroline pour éviter le déplacement de l'équilibre précédent dans le sens 2. L'expérience montre qu'au cours de cette opération, le nickel ne passe pas dans la couche aqueuse.

Le spectre d'absorption de la combinaison extraite par le dichloro-1,2-éthane (à 20°), est représenté sur la Fig. 1; le maximum est situé à 520 m μ . L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type „Algérie”.

Mode opératoire

Nous avons adopté le mode opératoire ci-dessous, applicable par exemple à 5 ml de solution sulfurique ou chlorhydrique amenée à un pH voisin de 1, et renfermant au plus 15 à 16 mg de métal ou d'alliage, dont 5 mg de fer au maximum. La présence d'ions nitrates est incompatible avec le principe du dosage qui suppose la réduction de Fe⁺³ en Fe⁺². Pour éviter la présence de ces ions, l'attaque du métal ou de l'alliage peut être effectuée à l'ébullition par l'acide sulfurique 9*N* auquel on ajoute peu à peu de l'eau oxygénée à 110 volumes. L'excès de ce réactif est ensuite détruit par ébullition prolongée. Après refroidissement, la solution est amenée à un pH voisin de 1.

Réactifs utilisés

Solution étalon de nickel. Le sel de nickel utilisé est le sulfate „Prolabo R.P.” NiSO₄, 7 H₂O amené à poids constant par chauffage au four électrique à 450°. Par pesée, on prépare une solution dans H₂SO₄ *N*/10 renfermant exactement 2 g de nickel par l, soit 2 mg/ml.

Solution de métabisulfite. Solution aqueuse à 5% du sel de potassium pur, préparée au moment de l'utilisation.

Solution d'o-phénanthroline. Solution aqueuse environ *M*/10, obtenue en dissolvant 5 g de base pure dans 25 ml d'acide sulfurique normal que l'on dilue ensuite à 250 ml avec de l'eau distillée. Elle est conservée à l'abri de la lumière.

Solution de cérium. a) Solution aqueuse de sulfate cérique environ *M*/10 dans l'acide sulfurique *N*.

b) Solution aqueuse de sulfate cérique environ *M*/100 dans l'acide sulfurique 2*N*/10.

Solution d'acide trichloracétique. Solution aqueuse *M*/2 du produit pur (8% environ).

Dichloro-1,2-éthane. Le produit commercial pur est redistillé; on recueille la fraction distillant à 83 ± 1°.

A 5 ml de la solution à analyser, ajouter 0.5 ml de solution de métabisulfite, et attendre environ 1 min. Ajouter ensuite 10 ml de solution d'o-phénanthroline et attendre 5 min. La solution cérique *M*/10 est ensuite ajoutée goutte à goutte, en agitant, jusqu'au virage de la ferroïne (apparition de la forme oxydée bleue). Si la solution ne renferme pas de fer, on peut ajouter 1 ml de la solution d'o-phénanthroline ferreuse utilisée habituellement comme indicateur d'oxydo-réduction. Ajouter encore 2 ml de la solution cérique, puis 3 ml de la solution d'acide trichloracétique. Placer ce mélange dans une ampoule à décanter de 125 ml avec 10 ml de dichloro-1,2-éthane, et agiter énergiquement pendant 3 min environ. Après décantation, la phase organique est séparée et placée dans une autre ampoule à décanter avec le mélange suivant qui constitue la solution de lavage: 10 ml de la solution cérique *M*/100, 1 ml de la solution d'o-phénanthroline et 1 ml de la solution d'acide trichloracétique. Agiter énergiquement pendant 2 min; après décantation, séparer la phase organique, la centrifuger, et effectuer la mesure de la densité optique pour $\lambda = 520 \text{ m}\mu$.

Essai à blanc

Il est effectué en remplaçant la solution à doser par 5 ml d'acide sulfurique *N*/10. Sa densité optique est en général très faible (0.015 à 0.020); elle n'est pas due aux

traces de nickel que renferment les réactifs, mais à une faible quantité de produits colorés jaunes qui sont vraisemblablement des impuretés de l'*o*-phénanthroline.

Étalonnage

On applique le mode opératoire précédent en remplaçant la solution à doser par des mélanges connus de la solution étalon de nickel et d'acide sulfurique *N*/10. La loi de Beer est suivie comme le montre la droite d'étalonnage de la Fig. 2, obtenue à 22°, en utilisant une cuve de 2 cm d'épaisseur.

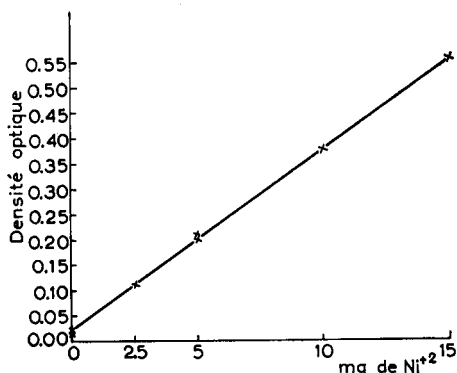


Fig. 2. Courbe d'étalonnage pour le dosage du nickel.

Précision

Pour une densité optique voisine de 0,50, les résultats sont reproductibles à 0,005 unité près, ce qui permet de doser 10 mg de nickel avec une erreur relative voisine de 1%. Les résultats du dosage du nickel en présence de quantités variables de fer et de cobalt sont rassemblés dans le Tableau I. Nous avons utilisé des volumes connus de solution d'alun de fer (Prolabo R.P.) et de sulfate de cobalt (Prolabo R.P.) renfermant 1 et 5 mg de métal par ml.

Cette méthode un peu moins précise que la gravimétrie classique, utilisant la diméthylglyoxime, présente sur celle-ci l'avantage d'une grande rapidité d'exécution.

TABLEAU I

Fe(mg)	Co (mg)	Ni (mg) ajouté	Ni (mg) dosé
0	0	15,00	15,10
1	1	5,00 10,00	5,10 10,08
1	5	5,00 10,00	4,97 10,07
5	1	5,00 10,00	5,04 9,97
5	5	5,00	5,07
1	10	5,00	5,05

RÉSUMÉ

Un exemple de séparation et de dosage par extraction à l'aide des complexes de l'*o*-phénanthroline est décrit : le complexe du nickel(II) associé à l'anion trichloroacétique est quantitativement extractible par le dichloro-1,2-éthane, alors que les formes oxydées des complexes du fer(II) et du cobalt(II) ne le sont pas. La méthode, un peu moins précise que la gravimétrie classique utilisant la diméthylglyoxime, présente l'avantage d'une grande rapidité d'exécution.

SUMMARY

A rapid extraction method is described for the separation of nickel from iron and cobalt and the determination of Ni, in which *o*-phenanthroline is used as complexing agent.

ZUSAMMENFASSUNG

Es wird eine rasche Methode zur Trennung des Nickels von Eisen und Kobalt mit Hilfe von *ortho*-Phenanthrolin und die Bestimmung des Nickels nach dem Extraktionsverfahren beschrieben.

BIBLIOGRAPHIE

- 1 F. P. DWYER ET R. S. NYHOLM, *J. Proc. Roy. Soc. N.S. Wales*, 80 (1946) 28.
- 2 F. P. DWYER ET H. A. MCKENZIE, *J. Proc. Roy. Soc. N.S. Wales*, 81 (1947) 93.
- 3 T. S. LEE, I. M. KOLTHOFF ET D. L. LEUSSING, *J. Am. Chem. Soc.*, 70 (1948) 2348.
- 4 I. M. KOLTHOFF, T. S. LEE ET D. L. LEUSSING, *Anal. Chem.*, 20 (1948) 985.
- 5 T. S. LEE, I. M. KOLTHOFF ET D. L. LEUSSING, *J. Am. Chem. Soc.*, 70 (1948) 3596.
- 6 I. M. KOLTHOFF, D. L. LEUSSING ET T. S. LEE, *J. Am. Chem. Soc.*, 72 (1950) 2173.
- 7 I. M. KOLTHOFF, D. L. LEUSSING ET T. S. LEE, *J. Am. Chem. Soc.*, 73 (1951) 390.
- 8 N. R. DAVIES ET F. P. DWYER, *Trans. Faraday Soc.*, 49 (1953) 180.
- 9 F. P. DWYER, E. C. GYARFAS, W. P. ROGERS ET J. H. KOCH, *Nature*, 170 (1952) 190.
- 10 H. M. IRVING, M. J. CABELL ET D. H. MELLOR, *J. Chem. Soc.*, (1953) 3417.
- 11 F. BASOLO, J. C. HAYES ET H. M. NEUMANN, *J. Am. Chem. Soc.*, 76 (1954) 3807.
- 12 P. GEORGE ET D. H. IRVINE, *J. Chem. Soc.*, (1954) 587.
- 13 J. HASTINGS, T. A. McCLARITY ET E. J. BRODERICK, *Anal. Chem.*, 26 (1954) 379.
- 14 F. R. DUKE ET F. R. PARCHEN, *J. Am. Chem. Soc.*, 77 (1955) 3198.
- 15 A. E. HARVEY, JR. JOHN, A. SMART ET E. S. AMIS, *Anal. Chem.*, 27 (1955) 26.
- 16 C. M. COOK, JR. ET F. A. LONG, *J. Am. Chem. Soc.*, 73 (1951) 4119.
- 17 C. B. AMPHLETT, *Discussions Faraday Soc.*, 12 (1952) 144.
- 18 M. LEFORT ET J. PUCHEAULT, *J. chim. phys.*, 50 (1953) 580.
- 19 J. PUCHEAULT ET M. LEFFORT, *J. chim. phys.*, 50 (1953) 196.
- 20 A. E. HARVEY ET D. L. MANNING, *J. Am. Chem. Soc.*, 74 (1952) 4744.
- 21 W. W. BRANDT ET W. B. HOWSMAN, *J. Am. Chem. Soc.*, 76 (1954) 6219.
- 22 G. FREDERICK SMITH, *Anal. Chem.*, 26 (1954) 1534.
- 23 F. H. FIELD ET W. C. VOSBURGH, *J. Am. Chem. Soc.*, 71 (1949) 2398.
- 24 P. PFEIFFER, V. DOMINIK, A. FRITZEN ET B. WERDELMANN, *Z. anorg. Chem.*, 260 (1949) 84.
- 25 F. P. DWYER ET E. C. GYARFAS, *J. Proc. Roy. Soc. N.S. Wales*, 83 (1949) 232.
- 26 N. R. DAVIES ET F. P. DWYER, *Trans. Faraday Soc.*, 48 (1952) 244.
- 27 F. P. DWYER, E. C. GYARFAS, W. P. ROGERS ET J. H. KOCH, *Nature*, 170 (1952) 190.
- 28 F. BASOLO, J. C. HAYES ET H. M. NEUMANN, *J. Am. Chem. Soc.*, 75 (1953) 5102.
- 29 N. R. DAVIES ET F. P. DWYER, *Trans. Faraday Soc.*, 49 (1953) 180.
- 30 N. R. DAVIES ET F. P. DWYER, *Trans. Faraday Soc.*, 50 (1954) 24.
- 31 R. G. WILKINS ET M. J. G. WILLIAMS, *J. Chem. Soc.*, (1957) 1763.
- 32 R. G. WILKINS ET M. J. G. WILLIAMS, *J. Chem. Soc.*, (1957) 4514.
- 33 H. M. IRVING ET D. H. MELLOR, *J. Chem. Soc.*, (1955) 3457.
- 34 D. W. MARGERUM, R. I. BYSTROFF ET C. V. BANKS, *J. Am. Chem. Soc.*, 78 (1956) 4211.
- 35 F. H. FIELD ET W. C. VOSBURGH, *J. Am. Chem. Soc.*, 71 (1949) 2398.
- 36 B. O. WEST, *J. Chem. Soc.*, (1954) 578.
- 37 W. HIEBER ET J. SEDLMEIER, *Chem. Ber.*, 87 (1954) 25.
- 38 P. ELLIS, R. G. WILKINS ET M. J. G. WILLIAMS, *J. Chem. Soc.*, (1957) 4456.
- 39 D. W. MARGERUM ET C. V. BANKS, *Anal. Chem.*, 26 (1954) 200.
- 40 G. F. SMITH, W. H. MCCURDY ET H. DIEHL, *Analyst*, 77 (1952) 418.
- 41 G. F. SMITH ET W. H. MCCURDY, *Anal. Chem.*, 24 (1952) 371.
- 42 A. R. GAHLER, *Anal. Chem.*, 26 (1954) 577.
- 43 B. ZAK ET N. RESSLER, *Anal. Chem.*, 28 (1956) 1158.
- 44 A. J. FRANK, A. B. GOULSTON ET A. A. DEACUTIS, *Anal. Chem.*, 29 (1957) 750.
- 45 G. F. SMITH ET D. H. WILKINS, *Anal. Chem.*, 25 (1953) 510.
- 46 L. G. BORCHARDT ET J. P. BUTLER, *Anal. Chem.*, 29 (1957) 414.

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THE RAPIDLY DROPPING MERCURY ELECTRODE IN DIRECT CURRENT AND ALTERNATING CURRENT POLAROGRAPHY

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INTRODUCTION

In direct current (D.C.) polarography, the dropping mercury electrode (DME), which has a drop time between about 3 and 6 sec under the applied pressure of 30 to 60 cm of mercury, is usually employed as an indicator electrode. When the drop time is less than 1.5 sec, polarographic currents are generally disturbed by the vortex motion of the mercury of the electrode, *i.e.*, "Spüleffekt"¹.

The same electrode as in D.C. polarography has also been used in alternating current (A.C.) polarography. However, when the A.C. polarogram is recorded automatically with such an electrode, the true peak current is often skipped because of the relatively long drop time in comparison with the scanning rate of the applied voltage. In order to record the true peak current, therefore, the scanning rate must be made very slow, or better, the current must be measured point by point by manual operation. It has been found that this deficiency can be overcome by using the rapidly dropping mercury electrode (RADME) whose drop time is shorter than 1 sec.²

For this reason, it seemed desirable and worthwhile to reinvestigate the characteristics of the RADME, which hitherto has been considered to be an unsuitable electrode for polarographic studies. In this paper, some results of the application of the RADME to D.C. and A.C. polarography are presented, and the potentialities of the RADME in polarographic analysis are discussed.

REAGENTS AND APPARATUS

The lead solution was prepared by dissolving lead nitrate; it was standardized gravimetrically as lead sulphate. The standard solution of cadmium was prepared by dissolving a known amount of pure cadmium metal in nitric acid. All other chemicals used were analytical reagent grade. Redistilled water was used for the preparation of the solutions.

All D.C. polarograms were obtained with a manual polarograph³ and the A.C. polarograms were recorded with a Yanagimoto Y-GR Model 2 Galvarecorder. The drop time and the rate of flow of mercury of the DME used were 5.41 sec and 1.824 mg/sec, respectively, which were measured in air-free 0.1M potassium nitrate solution under an applied pressure of 55 cm of mercury at -0.50 V vs. S.C.E. Two RADME's were used, which had drop times of 0.86 and 0.98 sec and rates of flow of mercury of 16.98 and 16.83 mg/sec, respectively, measured under an applied pressure of 40 cm of mercury in the same solution and at the same potential as in the case of the DME. A saturated calomel electrode with a large area was used as the anode, which was connected to the cell solution by a HUME AND HARRIS-type agar bridge⁴. All measurements were carried out in a thermostat of 25.00° ± 0.01°. The dissolved oxygen in the solution was expelled by passing pure nitrogen gas through the solution before measurement. In the A.C. polarographic measurements, a platinum electrode with a large area was inserted into the solution as the third electrode and this was connected to the anode through a condenser of 100 μF in order to keep the impedance of the electrolysis cell as low as possible⁵.

RESULTS AND DISCUSSION

D.C. polarography

In the absence, or at very low concentration, of a surface-active substance, such as polyoxyethylene lauryl ether (LEO) or gelatin, maxima of the second kind were generally observed on the current-voltage curves obtained at the RADME. For example, the limiting current of mercuric ion at the RADME showed a maximum value near the potential of the electrocapillary zero and decreased markedly both at the more positive and negative potentials (Fig. 1). This maximum was completely suppressed by the addition of $2 \cdot 10^{-4}M$ LEO, and the further addition of LEO had little effect on the value of the limiting current. Such phenomena were also observed in the reduction of lead and cadmium ions at the RADME in $0.1M$ potassium nitrate solution (Figs. 2 and 3).

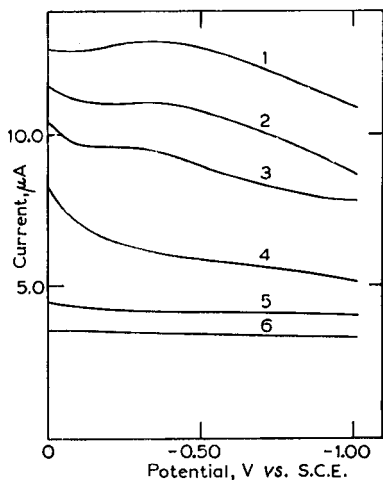


Fig. 1. Current-voltage curves of $2 \cdot 10^{-4}M$ Hg(II) in $0.1M$ HNO₃ solutions in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $1 \cdot 10^{-6}M$; (3) $2 \cdot 10^{-6}M$; (4) $2 \cdot 10^{-5}M$; (5) $1 \cdot 10^{-4}M$; (6) $4 \cdot 10^{-4}M$.

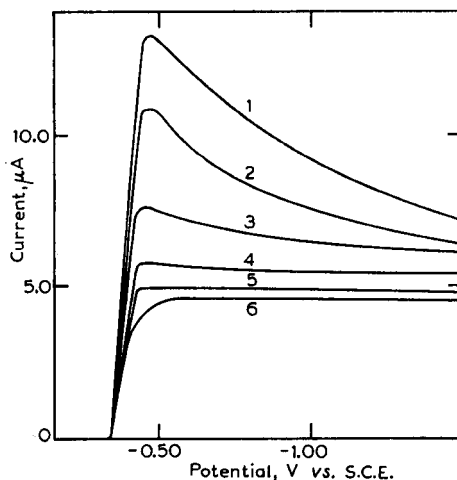


Fig. 2. Current-voltage curves of $2 \cdot 10^{-4}M$ Pb(II) in $0.1M$ KNO₃ solutions in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $2 \cdot 10^{-6}M$; (3) $1 \cdot 10^{-5}M$; (4) $2 \cdot 10^{-5}M$; (5) $5 \cdot 10^{-5}M$; (6) $5 \cdot 10^{-4}M$.

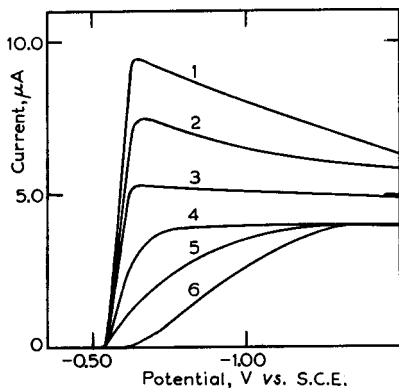


Fig. 3. Current-voltage curves of $2 \cdot 10^{-4}M$ Cd(II) in $0.1M$ KNO₃ solutions in the absence and in the presence of LEO. Concentration of LEO: (1) 0; (2) $5 \cdot 10^{-6}M$; (3) $2 \cdot 10^{-5}M$; (4) $7 \cdot 10^{-5}M$; (5) $2 \cdot 10^{-4}M$; (6) $4 \cdot 10^{-4}M$.

TABLE I

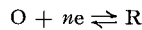
DIFFUSION COEFFICIENTS CALCULATED BY APPLYING THE MODIFIED ILKOVIC EQUATION TO THE LIMITING CURRENTS AT THE RADME

Maximum suppressor	Height of mercury column cm	Pb(II) ^a		Cd(II) ^a		Fe(C ₂ O ₄) ₃ ^{3b}	
		Drop time sec	D × 10 ⁶ cm ² /sec	Drop time sec	D × 10 ⁶ cm ² /sec	Drop time sec	D × 10 ⁶ cm ² /sec
0.1% gelatin	30	1.01	6.15	1.01	6.38	1.15	4.37
0.1% gelatin	50	0.61	6.07	0.61	6.25	0.68	4.25
5 · 10 ⁻⁴ M LEO	50	0.57	8.00	0.57	6.76		

^a In 0.1M KNO₃.^b In 0.5M K₂C₂O₄.

The apparent values of the diffusion coefficients of lead, cadmium and trioxalatoferate(III) ions in the solution containing 0.1% gelatin or 5 · 10⁻⁴M LEO were calculated by applying the modified ILKOVIC equation⁶ to the limiting currents of these ions obtained at the RADME (Table I). Table I shows that the apparent values of the diffusion coefficients are almost independent of the drop time, which proves that the maximum of the second kind at the RADME can be completely suppressed by the addition of a suitable amount of the surface-active substance, *e.g.*, 0.1% gelatin or 5 · 10⁻⁴M LEO. It can also be seen that the diffusion coefficients in the solution containing 0.1% gelatin are always smaller than those in the solution containing LEO. This result might be explained by assuming that the concentration of reducible ions decreases due to complex formation between reducible ions and gelatin molecules⁷.

When the oxidant O is reduced reversibly in the polarographic sense to the reductant R,



and when the reductant is soluble either in the solution or in the electrode, the current-voltage curve is expressed by the equations:

$$E = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_l - i} \quad \dots \dots \dots (1)$$

$$E_{1/2} = E_0 - \frac{0.059}{n} \log \frac{k_O}{k_R} \quad \dots \dots \dots (2)$$

In eqns. (1) and (2), E_0 is a constant, k_O and k_R are proportionality constants relating the polarographic current and the concentrations of the electroactive substances, and the other terms have their usual meanings. Since the values of k_O and k_R remain constant in the relatively narrow range of the electrode potential where the polarographic wave appears, it is to be expected from eqn. (1) that the relation between E and $\log i/(i_l - i)$ will be a straight line with a reciprocal slope of 0.059/ n V at 25°. This was experimentally verified with the D.C. current-voltage curve of cadmium ion obtained at the RADME in 0.1M potassium nitrate solution containing an insufficient amount of the surface-active substance to suppress the maximum of the second kind. A gradual increase of the reciprocal slope of the log-plot was generally observed when the concentration of gelatin was more than 0.05% (Table II). This might be attributed to the retardation of the electrode reaction at the RADME by the relatively high concentration of gelatin.

The actual value of k_0 in eqn. (2) can be experimentally estimated using the relation:

$$k_0 = \frac{i_l}{C_0} \dots \dots \dots (3)$$

where i_l is the limiting current, and C_0 is the bulk concentration of the oxidant. In the absence of the "Spüleffekt", the values of k_0 and k_R are determined by the drop time, the rate of flow of mercury of the electrode used, and the diffusion coefficients of oxidant and reductant, respectively. The "Spüleffekt" generally increases the values of k_0 and k_R . When the reductant dissolves in mercury as in the case of cadmium or lead, the influence of the "Spüleffekt" on k_R can be assumed to be much smaller than that on k_0 . In this case, according to eqn. (2), the change of half-wave potential is approximately equal to $0.059/n$ V at 25° when the value of k_0 is changed ten times. In our present experiments, the "Spüleffekt" at the RADME does not change the value of k_0 more than four times as shown in Tables II and III, and, consequently, it is to be expected that the corresponding change in half-wave potential will be less than $0.036/n$ V. If both the oxidant and reductant diffuse in the same medium as in the case of the trioxalatoferrate(III)–trioxalatoferrate(II) system, it is to be expected that the half-wave potential will not be affected by the "Spüleffekt", because, in such a case, it may be assumed that the influence of the "Spül-

TABLE II
HALF-WAVE POTENTIALS AND RECIPROCAL SLOPES OF LOG-PLOTS OF LEAD, CADMIUM AND TRIOXALATOFERRATE(III) IONS IN THE PRESENCE OF VARIOUS CONCENTRATIONS OF GELATIN

Concn. of gelatin %	Pb(II) ^a			Cd(II) ^a			Fe(C ₂ O ₄) ₃ ^{-3b}		
	k_0 $\mu A /$ mmoles	$E_{1/2}$ V vs. S.C.E.	Reciprocal slope mV	k_0 $\mu A /$ mmoles	$E_{1/2}$ V vs. S.C.E.	Reciprocal slope mV	k_0 $\mu A /$ mmoles	$E_{1/2}$ V vs. S.C.E.	Reciprocal slope mV
0	62.98	-0.388	31	52.61	-0.584	30	23.78	-0.240	60
0.005	42.62	-0.384	30	36.62	-0.582	31	16.63	-0.240	58
0.01	31.30	-0.382	31	28.93	-0.578	31	12.01	-0.240	58
0.05	23.67	-0.386	34	22.73	-0.578	33	8.18	-0.248	72
0.1	21.18	-0.390	36	22.70	-0.581	34	6.98	-0.250	72
0.2	18.25	-0.393	36	21.88	-0.582	36	6.83	-0.252	90

^a In 0.1M KNO₃.

^b In 0.5M K₂C₂O₄.

TABLE III
EFFECT OF THE HEIGHT OF THE MERCURY COLUMN ON THE HALF-WAVE POTENTIAL OF LEAD AND CADMIUM IONS AT THE RADME IN 0.1M KNO₃ SOLUTION CONTAINING NO SURFACE-ACTIVE SUBSTANCES

Height of mercury column cm	$E_{1/2}$ V vs. S.C.E.	
	Pb(II)	Cd(II)
30	-0.385	-0.582
50	-0.388	-0.584

effekt" on k_0 and k_R will be almost the same. The experimental results agreed with this expectation. The half-wave potentials of cadmium, lead and trioxalatoferrate (III) ions at the RADME were found to be practically constant in the concentration range of gelatin, less than 0.01%, where the maximum of the second kind appears on the current-voltage curve (Table II). Table III shows that the half-wave potentials of lead and cadmium ions at the RADME in the solution containing no surface-active substances are almost independent of the height of the mercury column, which also confirms the conclusion that the change of the half-wave potential due to the presence of the "Spüleffekt" is usually negligible in the case of the RADME.

When the concentration of LEO was higher than $2 \cdot 10^{-5}M$, the reduction of lead ion gave typical current-voltage curves similar to those obtained at the conventional DME, but the current-voltage curve of cadmium ion was very much drawn out at the relatively high concentrations of LEO. The limiting currents of lead and cadmium ions at the RADME in 0.1M potassium nitrate solution containing $2 \cdot 10^{-5}M$ LEO were found to be proportional to the concentrations over a wide concentration range (Table IV).

TABLE IV
RELATION BETWEEN THE LIMITING CURRENT, i_l , AT THE RADME
AND THE CONCENTRATION OF LEAD OR CADMIUM ION IN 0.1M KNO_3
SOLUTION CONTAINING $2 \cdot 10^{-5}M$ LEO

Concn. of ions (C) M	Pb(II)		Cd(II)	
	i_l^a μA	i_l/C $\mu A/mmoles$	i_l^b μA	i_l/C $\mu A/mmoles$
$1.00 \cdot 10^{-3}$	28.58	28.6	26.56	26.6
$5.00 \cdot 10^{-4}$	14.29	28.6	13.24	26.5
$2.00 \cdot 10^{-4}$	5.72	28.6	5.35	26.7
$1.00 \cdot 10^{-4}$	2.85	28.5	2.63	26.3
$5.00 \cdot 10^{-5}$	1.42	28.4	1.34	26.8
$2.50 \cdot 10^{-5}$	0.73	292	0.71	285
$1.00 \cdot 10^{-5}$	0.29	290	0.28	280

^a Measured at -0.47 V vs. S.C.E.

^b Measured at -0.70 V vs. S.C.E.

It is concluded from the results mentioned above that the RADME can be used for analytical purposes in D.C. polarography if suitable conditions are selected. The main advantages of the RADME are the reduction of oscillation of the polarographic current during the life of a mercury drop, and the increase in the sensitivity for the limiting current. In D.C. polarography, however, these advantages are partly cancelled by the complicated nature due to the presence of the maximum of the second kind.

A.C. polarography

In A.C. polarography, true peak currents could easily be determined with the RADME at the usual scanning rate of the applied voltage (e.g., 3 mV/sec); this is an important advantage that the RADME has over the conventional DME in routine polarographic analysis.

The effect of the surface-active substance on the height of the peak current of the

A.C. polarogram must be mentioned. Fig. 4 shows the effect of LEO on the peak currents of lead and cadmium ions in $1.0M$ potassium nitrate solution. It was found that the height of the peak current remains practically constant up to a concentration of LEO of $2 \cdot 10^{-5}M$, but decreases with a further increase of the concentration of LEO.

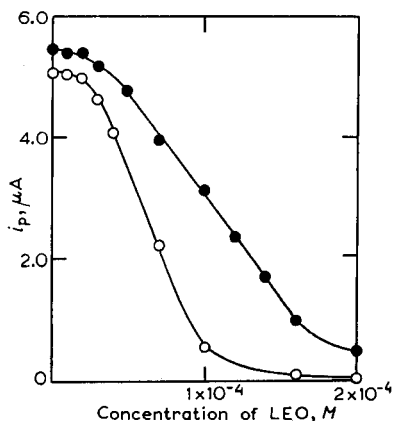


Fig. 4. Effect of the concentration of LEO on the peak currents of $1 \cdot 10^{-4}M$ Pb(II) and Cd(II) ions at the RADME in $1M$ KNO_3 solutions containing $1 \cdot 10^{-3}M$ HNO_3 . ●: Pb(II); ○: Cd(II).

Similar phenomena were also observed with the conventional DME, and can be explained by assuming that the electrode reaction is retarded. The experimental results concerning the effect of the surface-active substance indicate that the concentration of the surface-active substance is very critical in A.C. polarographic analysis. In A.C. polarography, it is undoubtedly desirable that the concentration of the surface-active substance should be as low as possible in order to obtain high sensitivity and a reproducible peak current.

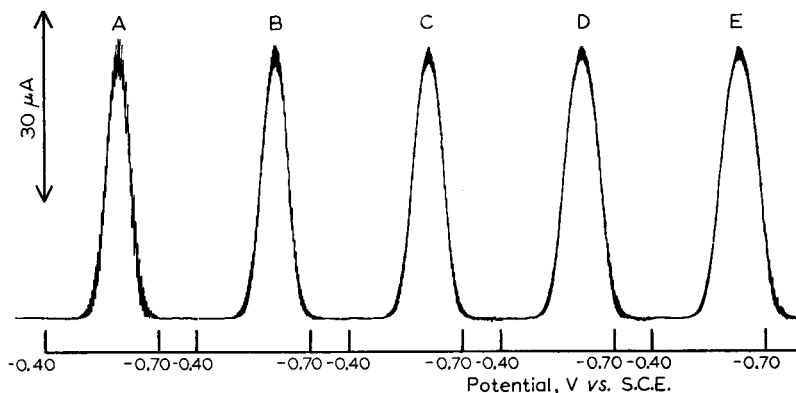


Fig. 5. A.C. polarograms of $8 \cdot 10^{-4}M$ Cd(II) ion obtained at the RADME in $1M$ KNO_3 solution containing $8 \cdot 10^{-6}M$ LEO, at various heights of the mercury column: (A) 20 cm; (B) 30 cm; (C) 40 cm; (D) 50 cm; (E) 60 cm.

With such a low concentration of the surface-active substance there exists a "Spüleffekt" at the RADME, as is clearly seen from the D.C. current-voltage curves (Figs. 1, 2 and 3). However, on the basis of theoretical considerations⁸ it is to be expected that the A.C. polarographic current will not be affected by the "Spüleffekt"; this was already verified with the rotated dropping mercury electrode applied to A.C. polarography⁹. The influence of the "Spüleffekt" on the A.C. polarographic current was examined by studying the effect of the height of the mercury column on the peak current of cadmium ion in 1.0M potassium nitrate solution containing $8 \cdot 10^{-6}M$ LEO (Fig. 5 and Table V). It can be seen that the height of the peak current is independent of the height of the mercury column for heights varying from 20 to 60 cm. This indicates that the influence of the "Spüleffekt" on the peak current is negligibly small as in the case of the rotated dropping mercury electrode.

TABLE V

RELATION BETWEEN THE PEAK CURRENT, i_p , AT THE RADME AND THE HEIGHT OF THE MERCURY COLUMN FOR 0.8 mM Cd(II) ION IN 1M KNO₃ SOLUTION CONTAINING $8 \cdot 10^{-6}M$ LEO

Height of mercury column cm	Drop time sec	Rate of flow of mercury mg/sec	Mean surface area of electrode (\bar{A}) cm ²	i_p μA	i_p/\bar{A} $\mu A/cm^2$
20	1.91	8.72	$3.33 \cdot 10^{-2}$	41.10	$12.35 \cdot 10^2$
30	1.38	11.97	$3.31 \cdot 10^{-2}$	40.92	$12.35 \cdot 10^2$
40	0.97	16.83	$3.29 \cdot 10^{-2}$	40.86	$12.41 \cdot 10^2$
50	0.82	20.3	$3.33 \cdot 10^{-2}$	41.10	$12.35 \cdot 10^2$
60	0.61	27.3	$3.33 \cdot 10^{-2}$	41.10	$12.35 \cdot 10^2$

The height of the peak current of cadmium ion in the medium mentioned above was found to be proportional to the concentration over the concentration range from $2 \cdot 10^{-5}$ to $1 \cdot 10^{-3}M$. Similar results were also obtained with lead ion in the presence of $2 \cdot 10^{-6}M$ LEO (Table VI). The summit potential, where the peak current was observed, was in agreement with the half-wave potential of the ordinary D.C. polarogram.

TABLE VI

RELATION BETWEEN THE PEAK CURRENT, i_p , AT THE RADME AND THE CONCENTRATIONS OF LEAD AND CADMIUM IONS IN 1M KNO₃ SOLUTION

Concn. of ions (C) M	Pb(II) ^a		Cd(II) ^b	
	i_p μA	i_p/C $\mu A/mmoles$	i_p μA	i_p/C $\mu A/mmoles$
$1.00 \cdot 10^{-3}$	54.60	54.60	51.60	51.60
$5.00 \cdot 10^{-4}$	27.36	54.72	25.80	51.60
$2.00 \cdot 10^{-4}$	11.10	54.60	10.32	51.60
$1.00 \cdot 10^{-4}$	5.46	54.6	5.16	51.6
$5.00 \cdot 10^{-5}$	2.73	54.7	2.58	51.6
$2.00 \cdot 10^{-5}$	1.08	54.0	1.02	51.0

^a In the presence of $2 \cdot 10^{-6}M$ LEO.

^b In the presence of $8 \cdot 10^{-6}M$ LEO.

From the experimental results mentioned above, it can be concluded that the RADME gives a reproducible peak current of high sensitivity for the reversible and quasi-reversible electrode reactions. Considering the fact that the A.C. polarographic current is not affected by the presence of the "Spüleeffekt", the RADME has a useful advantage over the conventional DME in A.C. polarography, *viz.*, the peak current can be easily and rapidly determined with the usual scanning rate of the applied voltage. Therefore, the use of the RADME is strongly recommended in routine A.C. polarographic analysis.

SUMMARY

The characteristics of the rapidly dropping mercury electrode (RADME) in direct current and alternating current polarography have been investigated. The RADME gives a maximum of the second kind on the D.C. current-voltage curve because of the "Spüleeffekt". This maximum is suppressed upon the addition of a large amount of surface-active substance, and typical current-voltage curves similar to those at the DME are obtained. The limiting current at the RADME is proportional to the concentration of the electroactive substance. In A.C. polarography the RADME gives the peak current more accurately than the conventional DME. The height of the peak current is not affected by the "Spüleeffekt", and is proportional to the concentration of the electroactive species.

RÉSUMÉ

Les auteurs ont étudié les caractéristiques de l'électrode à goutte de mercure rapide, en polarographie à courant continu et en polarographie à courant alternatif, en donnant des résultats obtenus avec cette électrode. Cette dernière, en polarographie à courant alternatif, présente des avantages sur l'électrode à goutte de mercure ordinaire.

ZUSAMMENFASSUNG

Es wird über Versuchsergebnisse mit der rasch-tropfenden Quecksilberelektrode bei der Gleichstrom- und Wechselstrom-Polarographie berichtet. Mit der rasch-tropfenden Quecksilberelektrode werden bei der Wechselstrom-Polarographie bessere Werte erhalten als mit der üblichen Quecksilbertropfelektrode.

REFERENCES

- ¹ M. VON STACKELBERG, *Fortschr. chem. Forsch.*, 2 (1951) 229.
- ² N. TANAKA AND M. KODAMA, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, 79 (1958) 410.
- ³ I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. I, Interscience Publishers, Inc., New York, 1952, p. 297.
- ⁴ D. N. HUME AND W. E. HARRIS, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 465.
- ⁵ B. BREYER, F. GUTMANN AND S. HACOBIAN, *Australian J. Sci. Research, Ser. A*, 4 (1951) 595.
- ⁶ I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Vol. I, Interscience Publishers, Inc., New York, 1952, p. 44.
- ⁷ T. TACHIBANA, K. TAMAMUSHI AND R. TAMAMUSHI, *J. Biochem. (Tokyo)*, 44 (1957) 33.
- ⁸ D. C. GRAHAME, *J. Electrochem. Soc.*, 99 (1952) 370C.
- ⁹ N. TANAKA, T. KOIZUMI, T. MURAYAMA, M. KODAMA AND Y. SAKUMA, *Anal. Chim. Acta*, 18 (1958) 97.

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COULOMETRIC TITRATION WITH ELECTROGENERATED +2 TIN TITRATION OF +3 GOLD AND +5 VANADIUM

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In a recent study¹ in this laboratory the conditions under which +2 tin can be electrogenerated with 100% current efficiency have been determined. Iodine and bromine can be titrated successfully by use of either a gold or platinum generator electrode provided a concentrated (3 to 4*M*) bromide solution of stannic chloride is used as supporting electrolyte. The titration of iodine serves for the determination of substances which oxidize iodide ion to iodine (coulometric iodometry) and the bromine titration can be employed for the determination of those organic compounds that undergo bromination or oxidation by bromine.

The present study extends the applications of coulometric titration with +2 tin to the determination of +3 gold and +5 vanadium. Although these elements can be titrated iodometrically, the direct titrations are more selective and subject to fewer interferences.

A coulometric titration of +3 gold to the elemental state in a hydrochloric acid medium with electrogenerated chlorocuprous ion, using potentiometric e.p. indication, has been described by LINGANE². The titration with +2 tin was performed using potentiometric, amperometric, and spectrophotometric end-points.

The titration of +5 vanadium has been performed previously with several coulometric reductants. With chlorocuprous ion³, or ferrous ion⁴, reduction of vanadium proceeds to the +4 state, while titanous ion⁵ causes reduction to +3 vanadium. With +2 tin the titration of +5 vanadium proceeds to the +4 state, and the e.p. can be recognized potentiometrically.

EXPERIMENTAL

The titration cell, apparatus, and conditions for 100% current efficiency have been described previously¹. Amperometric and potentiometric e.p. detection followed the usual practice⁶.

Absorption curves were recorded with a Cary Recording Spectrophotometer, Model 11 (Applied Physics Corp., Pasadena, Calif.). Spectrophotometric titrations were performed in a 180 ml tall form beaker held in a modified cell-holder of a Beckman DU Spectrophotometer. The generator electrode and the auxiliary electrode chamber were introduced into the cell through a stopper, from above, in such a manner as to be out of the light path. The solution was stirred by means of a magnetic stirrer beneath the cell compartment.

The optimum supporting electrolyte is 3 to 4*M* sodium bromide, 0.3*N* hydrochloric acid, and 0.2*M* stannic chloride. As discussed in a previous paper¹, with this electrolyte current efficiency for reduction of +4 tin remains at 99.5 to 99.9% with generating current densities of 10 to 84 mA/cm² at a gold generator cathode.

PERFORMANCE DATA

Titration of gold

The general characteristics of the potentiometric titration curve of +3 gold are

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shown by the automatically recorded curve in Fig. 1. The main inflection occurs after the equivalence point chiefly because the reaction is somewhat slow near the e.p. When the titration is performed manually, with 1 to 2 min waiting periods between each generation increment, the inflection coincides with the e.p.

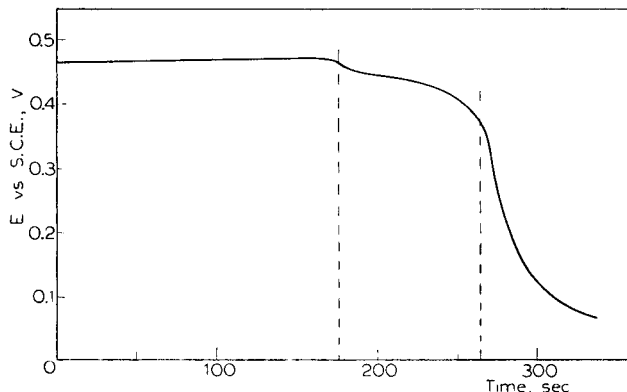
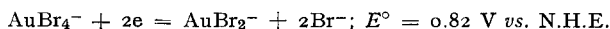
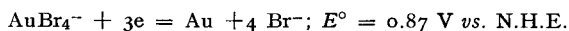
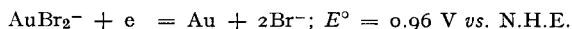


Fig. 1. Titration of 5.58 mg of +3 gold in 70 ml of 4*M* sodium bromide, 0.2*M* stannic chloride, and 0.3*N* hydrochloric acid, with a generating current of 31.1 mA. The potential of a gold indicator electrode during the titration was recorded automatically with a recording potentiometer.

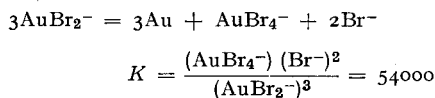
It is evident from the first small inflection that the reduction of AuBr_4^- proceeds stepwise, first to AuBr_2^- and finally to the metal. Just as in the titration of +3 gold with chloro cuprous ion in chloride medium², the potential of the gold indicator electrode increases slightly, but definitely, during the first two thirds of the titration. This anomaly, which persists even in manual titrations with several min waiting at each point, results from the fact that a gold electrode is very slow in acquiring its equilibrium potential in a solution containing a mixture of +3 and +1 gold. The increase in potential is considerably smaller than was previously observed² in chloride medium, which suggests that the $\text{AuBr}_4^-/\text{AuBr}_2^-$ couple behaves somewhat more reversibly than does the $\text{AuCl}_4^-/\text{AuCl}_2^-$ couple. This same anomalous increase in potential has also been observed by ERDEY AND RADY⁷ in their recent study of the titration of +3 gold with ascorbic acid in the ordinary volumetric manner.

During the last third of the titration the potential stabilizes rapidly and its value corresponds closely to the value expected from the standard potential of the $\text{AuBr}_2^-/\text{Au}$ couple.

Accurate measurements of the standard potentials of the three gold couples in bromide media do not appear to have been made at 25°. However, from the measurements of GRUBE *et al.*⁸ at 60°



From these values, we have for the disproportionation equilibrium at 60°



From the magnitude and form of this equilibrium constant it is clear, with a large total concentration of AuBr_2^- and AuBr_4^- , and a relatively small concentration of bromide ion, that +1 gold is unstable. However, under the diametrically opposite conditions of the present study (very small total concentration of gold and very large bromide ion concentration) the balance of the disproportionation equilibrium should be far to the left. The observed stepwise reduction of the +3 gold is consistent with this prediction.

The titration can also be followed amperometrically by observing the current between two identical, small gold electrodes (1 cm² each is suitable) across which a constant voltage of the order of 100 to 200 mV is impressed. Fig. 2 shows a typical amperometric titration curve. The anode is depolarized throughout the titration by the reaction $\text{Au} + 2\text{Br}^- = \text{AuBr}_2^- + e$, and the cathode, at which the reaction is initially $\text{AuBr}_4^- + 2e = \text{AuBr}_2^- + 2\text{Br}^-$ and finally $\text{AuBr}_2^- + e = \text{Au} + 2\text{Br}^-$, actually functions as the indicator electrode. The indicator current decreases continuously up to the e.p. in tune with the decreasing concentrations of AuBr_4^- and AuBr_2^- . The irreversible behaviour of the stannic-stannous couple causes the indicator current to remain very small beyond the e.p. There is some semblance of an increase in slope at the two-thirds point, which suggests that the overpotential required for

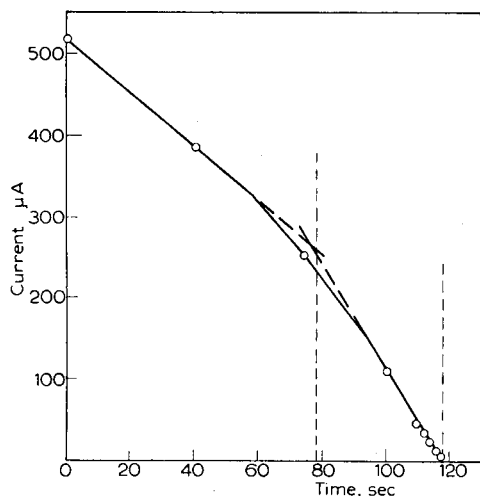


Fig. 2. Amperometric titration of 5.27 mg of +3 gold in 70 ml of 4M sodium bromide, 0.2M stannic chloride, and 0.3N hydrochloric acid, with a generating current of 64.9 mA. A constant voltage of 150 mV was impressed across the two identical gold indicator electrodes (area 1 cm² each).

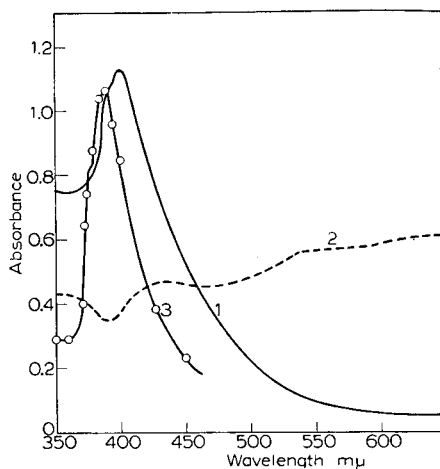


Fig. 3. Absorption spectra during the titration of 100 ml of 0.346 mM +3 gold in 4M sodium bromide, 0.2M stannic chloride, and 0.25M hydrochloric acid. (1) Original solution. (2) Solution titrated past the two-thirds point, containing AuBr_2^- and colloidal gold. (3) 0.402 mM +2 tin alone. Curves 1 and 2 were recorded with a 1-cm light path, but a 10-cm light path was used for curve 3.

the reduction of AuBr_2^- is smaller than that for the reduction of AuBr_4^- , but obviously this e.p. is too indistinct for practical use.

During the titration of AuBr_4^- with +2 tin, the solution, initially colored orange-yellow, changes to colorless when the titration is two-thirds complete, and then to various shades of purple as colloidal gold is formed. These color changes suggested the possibility of following the titration spectrophotometrically.

Fig. 3 shows spectrophotometric absorption curves taken during a titration of +3 gold with electrogenerated +2 tin. The absorption peak of AuBr_4^- at $400\text{ m}\mu$ has an extinction coefficient of $3,270\text{ l/mole cm}$. TURKEVICH *et al.*⁹ found that colloidal gold sols, in the presence of aurous gold, show a broad absorption band throughout the visible region, rising to a maximum at about $700\text{ m}\mu$. Curve 2 corresponds to this description. From curve 3 it is seen that SnBr_4^{-2} has an absorption peak at about $388\text{ m}\mu$ (depending slightly upon the tin concentration) with an extinction coefficient of only 268 l/mole cm . The stannic bromide complex absorbs only in the region of 300 to $360\text{ m}\mu$ with a maximum at about $320\text{ m}\mu$.

The spectrophotometric titration of +3 gold was performed by setting the Beckman DU spectrophotometer at a wave-length of $400\text{ m}\mu$, the slit width at 0.15 mm , and the absorbance at 0.00 with the cell removed from the holder. The use of air as reference (zero absorbance) is convenient, since only the change in absorbance rather than its absolute value is needed for titration purposes.

A typical spectrophotometric titration curve is shown in Fig. 4. The absorbance readings were independent of the stirring rate, and became stable within 1 min . After the e.p. (reduction of +3 to +1 gold) the readings took about 15 min to become fairly steady, because the gold sol was undergoing particle size (and absorption) fluctuations. In contradistinction to potentiometric and amperometric detection, spectrophotometric detection reveals only the first e.p. and the second is inaccessible.

Table I summarizes data obtained in 37 titrations using potentiometric, amperometric, and spectrophotometric e.p. detection. In each case the supporting electrolyte was pre-titrated to the e.p. before the gold sample was added. With either potentiometric or amperometric detection 0.5 to 23 mg of gold is titratable with an average error of *ca.* $\pm 0.3\%$. Spectrophotometric titration was both less precise and less accurate (average error *ca.* $+ 2\%$).

TABLE I
COULOMETRIC TITRATION OF +3 GOLD

Supporting electrolyte was $4M$ sodium bromide, $0.2M$ stannic chloride, and $0.3N$ hydrochloric acid, and the volume was 70 to 110 ml . The area of the gold generator cathode was 1 cm^2 , except with the 22.62 mg sample, in which case it was 4 cm^2 .

Gold taken mg	No. of trials	Current mA mg	Gold found (average) mg	Average deviation mg	End-point detection
5.271	5	63.90	5.259	± 0.015	} Potent.
5.271	4	32.14	5.276	± 0.018	
1.055	3	9.971	1.055	± 0.001	
22.62	4	100.75	22.76	± 0.04	} Amp.
5.271	7	65.00	5.266	± 0.012	
5.271	6	34.10	5.272	± 0.009	
5.271	3	9.961	5.271	± 0.007	
5.271	4	60.75	5.370	± 0.069	} Spectro.
5.271	1	33.36	5.267	—	

We have not investigated interference by other metals. However, of the elements commonly associated with gold, we would not expect interference from lead, silver or mercury. Quite possibly platinum may interfere as it does in the titration with chloro cuprous ion in chloride medium².

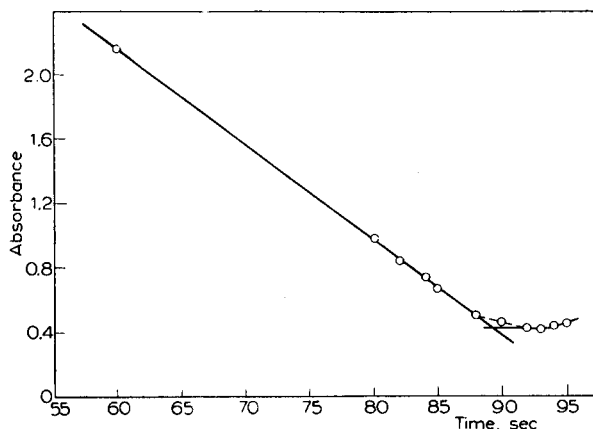


Fig. 4. Spectrophotometric titration of 5.27 mg of +3 gold in 100 ml of 4M sodium bromide, 0.2M stannic chloride, and 0.3N hydrochloric acid, with a generating current of 60.7 mA. Absorbance was measured against air at 400 $m\mu$. The end-point corresponds to reduction of the +3 gold to the +1 state.

Titration of +5 vanadium

The titration of +5 vanadium to the +4 state was performed with the same supporting electrolyte used for the titration of gold, using potentiometric e.p. detection. Amperometric e.p. detection is not suitable because in acidic bromide medium the $V^{+5}-V^{+4}$ couple behaves irreversibly, and since the stannic-stannous couple also functions irreversibly there is no clear definition of an end-point.

The titration can also be followed spectrophotometrically by measuring the change in absorbance at 390 $m\mu$. At this wave length +5 vanadium and +2 tin both absorb strongly, whereas +4 vanadium and +4 tin do not. Hence the titration curve is V-shaped with the e.p. at minimum absorbance.

In the acidic bromide medium used (4M sodium bromide, 0.25N hydrochloric acid, and 0.2M stannic chloride) the formal potential of the V^{+5}/V^{+4} couple is +0.63 V vs. S.C.E. (+0.87 V vs. N.H.E.). This is large enough, in the presence of a high concentration of bromide ion, so that some of the +5 vanadium is reduced by bromide ion when the sample is added to the supporting electrolyte. Because the bromine formed is partly lost by volatilization in the nitrogen stream used to remove dissolved air, this reaction causes a negative error.

For example, when eight 2.739-mg samples of +5 vanadium were titrated one after the other in the same batch of supporting electrolyte the errors in percent were *seriatim* -7.9, -5.1, -2.1, +0.3, 0.0, -0.4, -0.4, and -0.5. The negative error, initially quite large, disappeared after three samples were added and titrated. The reason for this effect is that +4 vanadium accumulates in the solution during the

successive titrations, and after about three samples have been titrated (*i.e.*, when the concentration ratio of +5 to +4 vanadium becomes 1/3 or smaller) the potential of the V^{+5}/V^{+4} couple is decreased sufficiently so that +5 vanadium no longer oxidizes bromide ion.

The obvious way to prevent this error in the first place is to add to the supporting electrolyte sufficient +4 vanadium (as vanadyl sulfate) so that the potential of the V^{+5}/V^{+4} couple is kept below the value at which bromide ion is oxidized. This was done in all subsequent titrations. In addition the supporting electrolyte (con-

TABLE II
COULOMETRIC TITRATION OF +5 VANADIUM

The supporting electrolyte was 4*M* sodium bromide, 0.2*M* stannic chloride, 0.25*N* hydrochloric acid, and 0.004*M* vanadyl sulfate, and the volume was *ca.* 70 ml. Dissolved air was removed with nitrogen. The area of the gold generator cathode was 1 cm². Potentiometric e.p. detection was employed.

Vanadium taken mg	No. of trials	Current mA	Vanadium found (average) mg	Average deviation mg
2.739	5	34.56	2.738	±0.002
2.739	5	34.46	2.738	±0.007
5.467	3	67.08	5.472	±0.010
5.467	4	68.50	5.461	±0.004
0.5462	7	10.48	0.5458 ^a	±0.0046

^a In these trials +2 tin was generated beyond the e.p. and the excess was back titrated with electrogenerated bromine using a 1-cm² platinum anode.

taining +4 vanadium) was pre-titrated to the e.p. before the sample of +5 vanadium was added.

Results obtained in 24 titrations of 0.5 to 5.5 mg quantities of +5 vanadium are summarized in Table II. The average deviation is seen to be *ca.* ±0.2% with the larger samples and ±0.8% with the 0.5 mg samples.

ACKNOWLEDGEMENT

Appreciation is expressed to the National Science Foundation for a fellowship held by one of us (A.J.B.).

SUMMARY

Methods are described for the titration of +3 gold and +5 vanadium with electrogenerated +2 tin in an acidic bromide medium. Quantities of gold from 1 to 23 mg are titratable with an average error of *ca.* +0.3%, using either potentiometric or amperometric e.p. detection. Spectrophotometric detection can also be used but is somewhat less precise. Using potentiometric detection 0.5 to mg of +5 vanadium is titratable to the +4 state with an average error of ±0.2%.

RÉSUMÉ

On décrit des méthodes pour le titrage coulométrique de l'or(III) et du vanadium (V) au moyen de l'étain(II), en solution acide, en présence de bromure, avec détection potentiométrique, ampérométrique ou photométrique du point final.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur coulometrischen Titration von Gold-(III) und Vanadium-

(V) mit Hilfe von Zinn-(II) in bromidhaltiger, saurer Lösung. Der Endpunkt kann potentiometrisch, amperometrisch oder photometrisch bestimmt werden.

REFERENCES

- ¹ A. J. BARD AND J. J. LINGANE, *Anal. Chim. Acta*, 20 (1959) 463.
- ² J. J. LINGANE, *Anal. Chim. Acta*, 19 (1958) 394.
- ³ D. J. MEIER, R. J. MEYERS AND E. H. SWIFT, *J. Am. Chem. Soc.*, 71 (1949) 2340.
- ⁴ W. OELSEN AND P. GÖBBELS, *Stahl u. Eisen*, 69 (1949) 33.
- ⁵ J. J. LINGANE AND J. H. KENNEDY, *Anal. Chim. Acta*, 15 (1956) 465.
- ⁶ J. J. LINGANE, *Electroanalytical Chemistry*, Interscience Publishers, 1958.
- ⁷ L. ERDEY AND G. RADY, *Talanta*, 1 (1958) 159.
- ⁸ G. GRUBE, T. MORITA, J. HELFER AND M. BÄRMANN, *Z. Elektrochem.*, 38 (1932) 117.
- ⁹ J. TURKEVICH, G. GARTON AND P. C. STEVENSON, *J. Colloid Sci.*, (1954) Sup. I, 26.

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THE DETERMINATION OF SILVER IN GALENA AND BLENDE BY RADIOACTIVATION ANALYSIS

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The abundance of silver in the igneous rocks of the crust of the earth is low, apparently *ca.* $10^{-6}\%$. The element is familiar however, due to its concentration in workable deposits and because it possesses desirable properties which have promoted production for many centuries. Much silver is extracted from ores of other metals, and the minerals galena and blende make a considerable contribution to silver production. The determination of silver in such minerals is therefore of economic importance. Moreover, from a geological standpoint accurate information on the distribution of a trace element such as silver may throw light on the origin of ore deposits.

In the present paper the determination of traces of silver in galena and blende by neutron-activation analysis is described. Neutron-activation analysis has the advantage of high sensitivity for many elements, and can generally be made specific for a given element. The possibility of using carriers in radiochemical separations avoids the difficulties of chemical operations with ultra-micro quantities, such as problems of coprecipitation, adsorption, and reagent blanks. The accuracy attainable by radioactivation analysis is also often better than that obtained by spectrochemical analysis.

A comprehensive bibliography on analyses of trace elements in galena and blende up to 1955 is provided in a review by FLEISCHER¹. A recent extensive study, utilizing the cathode-layer carbon arc spectrochemical method of analysis, has been made by EL SHAZLY, WEBB AND WILLIAMS².

The principles, applicability, and limitations of radioactivation analysis have been extensively reviewed elsewhere³⁻⁷, and will not be dealt with here.

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liquids or magnetic methods appeared to be unnecessary. Small apparently homogeneous crystals of the minerals were examined under high magnification and separated by hand-picking. These were ground to a fine powder in an agate mortar, with the usual precautions as to the avoidance of contamination. Samples consisting of *ca.* 0.3 g of powdered mineral were weighed out accurately into irradiation containers made from 4-mm internal diameter silica tubing, which were then sealed.

Neutron irradiation of samples and standards

In order to avoid self-shielding differences with samples and standards⁶, standards were prepared by adding known small quantities of silver to mineral specimens to be analyzed. This was done by adding aliquot portions of a dilute standard solution of silver, and a drop of wetting-agent, to 0.3 g samples of powdered mineral in 4 mm internal diameter silica irradiation tubes. The liquid in the tubes was allowed to soak into the mineral powder, and then was carefully evaporated to dryness, after which the tubes were sealed.

Standards containing the added silver and some samples of minerals of unknown silver content together with samples to which no silver had been added, were packed with glass wool into a standard 7.5 cm × 2.5 cm aluminium can for irradiation in BEPO. Irradiation was usually for 2–3 days. On delivery from Harwell after irradiation, the samples and standards were analyzed radiochemically for ^{110m}Ag–¹¹⁰Ag by the procedure described below.

Chemical separation

MEINKE AND ANDERSON¹¹ have studied the determination of silver by radioactivation analysis with a low-flux neutron source (25 mg Ra–Be) and measurement of the activity of ¹⁰⁸Ag. Samples were counted without chemical treatment. SMALES¹³ has determined silver in a sodium–potassium alloy using ^{110m}Ag also without chemical separation, but utilizing γ -scintillation spectrometry.

Various procedures involving carriers and “scavenging precipitations” have been described for the separation of silver activity, *e.g.* the separation from cyclotron targets¹⁴ and fission product mixtures^{15–17}, and in the radioactivation analysis of sodium–potassium alloy¹⁸. SUNDERMAN AND MEINKE¹⁹ have also investigated the radiochemical separation of silver on the basis of an evaluation of precipitation, electrodeposition, and isotopic exchange procedures. However, no radiochemical methods appear to have been published for isolating silver activity from irradiated minerals. In the present work, carrier chemistry and a series of scavenging precipitations have been used to secure the necessary separation of silver from a large number of other elements. The irradiated mineral samples and standards have been dissolved in nitric acid. Silver has been initially separated by precipitation of the chloride from the nitric acid solution. The silver then has been purified by ferric hydroxide scavenging and silver sulphide precipitation, both performed in ammoniacal solution. After repetition of the above cycle, the silver has been converted to the oxide and finally to the iodate AgIO₃, in which form it has been counted. Chemical yields of 50% or better have always been obtained.

Reagents

Ag carrier: 10 mg Ag/ml (added as AgNO₃ in very dilute HNO₃) standardized; Tl^I carrier: 10 mg Tl/ml (added as TlNO₃ in very dilute HNO₃); Fe^{III} carrier: 10 mg Fe/ml (added as FeCl₃).

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6H₂O in very dilute HCl); *N* HCl; 6*N* HCl; 6*N* HNO₃; conc. HNO₃; conc. H₂SO₄; KIO₃, saturated solution; 6*N* NaOH; conc. NH₄OH; (NH₄)₂S, saturated solution; Manoxol OT, 0.1% in water; 95% ethyl alcohol.

Preparation and standardization of carrier

Dissolve 15.75 g of AgNO₃ in a minimum amount of H₂O, add a few drops of HNO₃, and dilute the solution to 1 l.

Pipette exactly 5 ml of the carrier solution into a 50-ml centrifuge tube and dilute to 20 ml with H₂O. Add 1 ml of saturated KIO₃ solution and stir to coagulate the precipitate which forms. Add an additional drop of KIO₃ to test for completeness of precipitation. Filter the precipitate into a weighed sintered glass crucible of grade 3 or 4. Wash the precipitate with 5 ml of 95% ethyl alcohol and dry in an oven at 110° for 15 min. Cool and weigh as AgIO₃.

Radiochemical separation procedure

Step 1. Remove the silica tubes from the can, open them at the constriction, and transfer the solid samples to 50-ml centrifuge tubes. Wash out the tubes with a little warm dil. HNO₃ and transfer the washings quantitatively to the centrifuge tubes (a).

Step 2. To a sample in a 50-ml centrifuge tube add 2 ml of standard Ag carrier and 2 ml Tl⁺ carrier. Add 4 ml conc. HNO₃ and dissolve the sample by boiling the solution. Add a further 5 ml of conc. HNO₃ and boil for 10 min. Dilute to 40 ml, centrifuge, and discard any precipitate of sulphur.

Step 3. Add a few drops of Manoxol OT solution and heat to boiling (b). Add 6*N* HCl drop by drop until precipitation of AgCl is complete. Heat until the AgCl has coagulated. Centrifuge and discard the supernate.

Step 4. Wash the precipitate three times with 10 ml portions of boiling H₂O. Dissolve the AgCl in 2 ml conc. NH₄OH (c). Dilute to 20 ml with H₂O and add 1 ml of Fe^{III} carrier. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube, and discard the precipitate.

Step 5. To the solution add 1 ml of saturated (NH₄)₂S solution. Stir vigorously and centrifuge. Discard the supernate.

Step 6. Dissolve the Ag₂S precipitate by heating with 1 ml of conc. HNO₃. Dilute to 20 ml with H₂O and precipitate AgCl as in step 3.

Step 7. Repeat steps 4 and 5.

Step 8. Dissolve the Ag₂S precipitate by heating with 1 ml of conc. HNO₃. Make the solution alkaline with 6*N* NaOH, and add 3 drops in excess. Centrifuge the Ag₂O precipitate and discard the supernate. Dissolve the Ag₂O in 4 drops of conc. H₂SO₄ and evaporate completely to dryness (d). Cool.

Step 9. Dissolve the residue in 20 ml of distilled H₂O and add 1 ml of saturated KIO₃ solution. Centrifuge and discard the supernate.

Step 10. Dissolve the AgIO₃ precipitate in 4 drops of conc. NH₄OH. Centrifuge, transfer the supernate to a clean 50-ml centrifuge tube. Centrifuge and discard any S residue.

Step 11. Add 3 drops of conc. H₂SO₄ to the solution. Centrifuge the AgIO₃ precipitate and wash twice with water and once with 5 ml of 95% ethyl alcohol. The precipitate is then ready to be mounted for counting.

Notes

- (a) It is essential that steps 1 and 2 be carried out in an efficient fume-cupboard.
- (b) The addition of Manoxol OT helps to coagulate the AgCl and to prevent its adherence to the walls of the tube.
- (c) A little heating may be necessary.
- (d) It is not necessary to remove the last traces of H₂SO₄ on the walls of the tube.

Mounting and counting of the AgIO₃ precipitate

Slurry the washed AgIO₃ precipitate from step 11 of the radiochemical separation procedure with 95% ethyl alcohol onto a weighed aluminium counting tray (A.E.R.E. cat. no. 4-3/1068), by using a transfer pipette. Make sure the distribution of the precipitate on the tray is uniform. Dry at 110° for 15 min and weigh to establish the chemical yield (20 mg Ag \equiv 52.43 mg AgIO₃).

To avoid any self-absorption differences, the weights of AgIO₃ mounted from different samples should preferably be similar. It has been demonstrated, however, by measuring the activity of a given amount of ^{110m}Ag-¹¹⁰Ag with different weights of AgIO₃, that no correction for self-absorption needs to be made for the range of weights of AgIO₃ obtained by the radiochemical procedure.

In the present work the final precipitates of AgIO₃ were counted under a thin end-window Geiger-Müller counter (EHM 2/5), with conventional associated electronic equipment. A statistical accuracy of 0.5% was achieved by measuring a total of 40,000 counts where possible. When the activity was low, counting was carried out for a period of 40 min. All measured activities were corrected for paralysis, background, and chemical yield.

In order to check for radiochemical purity, standard aluminium absorption curves of samples were measured²⁰ and compared with curves from ^{110m}Ag-¹¹⁰Ag tracer supplied by the Radiochemical Centre, Amersham, which had been put through the radiochemical separation procedure described above. Typical results are shown Fig. 1.

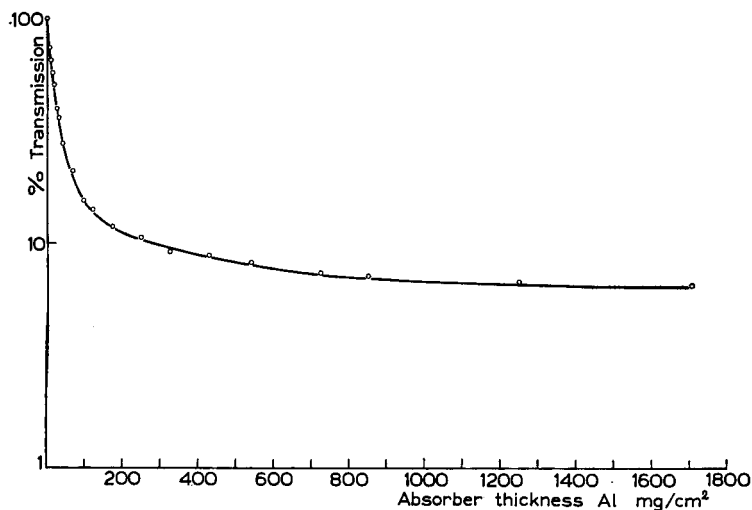


Fig. 1. Aluminium absorption curve of ^{110m}Ag-¹¹⁰Ag. The full curve is for purified silver tracer, while the recorded points are for a final precipitate from an analysis sample.

In addition, decay curves measured for a period of a few weeks corresponded satisfactorily with the published half-life of ^{110m}Ag .

To confirm that there was no trace of thallium contamination in the silver procedure, tracer tests were made using carrier-free 4.1 year ^{204}Tl (supplied by the Radiochemical Centre, Amersham). Aliquots of the tracer solution containing $> 300,000$ counts/min of ^{204}Tl were taken for the tests of the silver procedure. In two experiments the AgIO_3 precipitates at the end of the procedure contained no detectable activity above the background for the counter.

From the above work it is evident that the silver procedure provides satisfactory radiochemical purity.

RESULTS

If A_1 is the silver activity (corrected for paralysis, background, and chemical yield) for a standard containing w μg of added Ag, and A_2 is the corrected activity of a corresponding sample of the same weight but with no added Ag, it follows that an

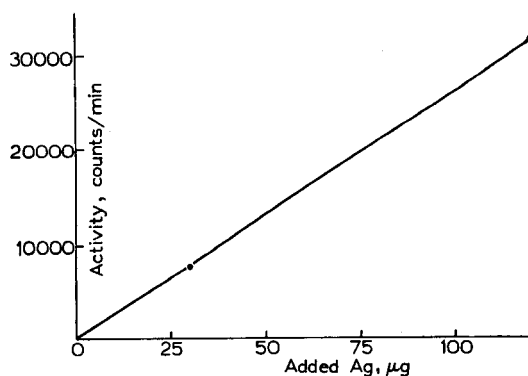


Fig. 2. Activity due to added silver in neutron irradiated standards plotted against weight of added silver. Each point is the mean of two measurements.

TABLE II

SILVER CONTENT OF GALENA AND BLENDE FROM MILLTOWN MINE, TULLA, CO. CLARE, EIRE,
DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

<i>Galena</i>		<i>Blende</i>	
Specimen 1G	0.105 %	Specimen 1B	0.00075 %
	0.104		0.00074
	0.104		0.00078
	0.105		0.00078
	0.102		0.00074
	0.102		0.00076
			0.00075
mean	0.104		0.00073
			0.00074
			0.00077
Specimen 2G	0.110	mean	0.00075
	0.109		
mean	0.110		

activity of A_1 — A_2 corresponds to w μg Ag. The silver content of samples may therefore be calculated from their corrected counting rates.

Fig. 2 shows a typical graph of corrected activity due to added silver in a series of standards plotted against the weight of added silver. The fact that graphs of this type are straight lines passing through the origin indicates that the standards are satisfactory, and that no "blank correction" needs to be made for silver in the conductivity water with which the standard solutions of silver were made.

Typical analysis results obtained by the radioactivation method are shown in Table II. These refer to samples of associated galena and blende from Milltown Mine, Tulla, Co. Clare, Eire. The results show that in this case there is a marked tendency for silver to concentrate in galena rather than in blende. This is in agreement with "size considerations" (ionic radii: Ag^+ 1.26 Å, Pb^{+2} 1.20 Å, Zn^{+2} 0.69 Å), which suggest that silver is more likely to undergo isomorphous substitution for lead than for zinc in minerals.

DISCUSSION

The method described in this paper may be applied to samples containing $< 0.0001\%$ silver, and the ultimate sensitivity of the method may easily be increased by lengthening the time of neutron irradiation. Conventional spectrochemical methods of analysis have a limiting sensitivity of *ca.* 0.0001% Ag^2 . Thus the radioactivation method of analysis has the advantage of better sensitivity, and also avoids various errors inherent in emission spectroscopy.

Precision (standard deviation) of the radioactivation analyses has always been better than $\pm 3\%$.

The method described in this paper should be applicable to various minerals other than galena and blende, although in some cases the need may arise for some modification of the radiochemical separation procedure.

In the neutron-activation analysis of silver in minerals, allowance must be made for the fact that elements other than silver undergo nuclear reactions leading to the formation of silver isotopes. Possible secondary reactions of this type are ^{110}Cd (n, p) $^{110\text{m}}\text{Ag}$ and ^{113}In (n, α) $^{110\text{m}}\text{Ag}$, whereby $^{110\text{m}}\text{Ag}$ — ^{110}Ag activity is produced from cadmium and indium. These nuclear reactions may occur with fast neutrons (of which there is a proportion in BEPO, possibly *ca.* 10% of the slow neutron flux in the case of irradiations used in the present work).

An estimate of possible interference has been made by irradiating samples of pure CdO and In_2O_3 , together with pure AgNO_3 standards, in the Pile for 1 week. The silver activity was separated and counted as before. The experimental results showed that if a mineral contained 1% of cadmium this might give rise to a maximum spurious silver content of 0.02 p.p.m. Similarly an indium content of 0.1% could give rise to a limiting spurious silver content of 0.002 p.p.m. Such interferences are sufficiently small to be ignored in the analysis of silver in galena and blende.

Any interference of importance due to the production of radioisotopes of silver other than $^{110\text{m}}\text{Ag}$ — ^{110}Ag would have been apparent from energy measurements made on the counted samples from mineral specimens.

ACKNOWLEDGEMENTS

Thanks are due to Mr. P. G. EMBREY and Dr. J. R. BUTLER for kindly providing mineral specimens.

SUMMARY

Neutron-activation analysis has been applied to the determination of traces of silver in specimens of galena and blende. Use has been made of the radionuclides ^{110m}Ag - ^{110}Ag . The radiochemical separation after the addition of carrier has been based mainly on precipitations of silver as chloride, sulphide, oxide, and iodate. Radiochemically pure silver was finally precipitated and counted as the iodate; the chemical yield was determined gravimetrically. In order to avoid errors due to self-shielding, standards were made by adding small known amounts of silver to analytical samples. Precision (standard deviation) of the radioactivation analyses has been better than $\pm 3\%$ in all cases.

RÉSUMÉ

On propose une méthode de dosage de l'argent, à l'état de trace, dans une galène ou dans une blende, par activation au moyen de neutrons. La séparation radiochimique après addition d'entraîneur est basée principalement sur les précipitations de l'argent comme chlorure, sulfure, oxyde et iodate. Un argent radiochimiquement pur est finalement précipité et compté, sous forme d'iodate.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren von Silber in Galena und Blende durch Aktivierung mit Neutronen. Die radiochemische Trennung wurde nach Zugabe eines Trägers hauptsächlich durch Fällung des Silbers als Chlorid, Sulfid, Oxyd und Jodat vorgenommen. Radiochemisch reines Silber wurde zum Schluss gefällt und als Jodat ausgezählt; die chemische Ausbeute wurde gravimetrisch ermittelt.

REFERENCES

- 1 M. FLEISCHER, *Econ. Geol.*, 50 (1955) 970.
- 2 E. M. EL SHAZLY, J. S. WEBB AND D. WILLIAMS, *Bull. Inst. Mining Metal.*, 604 (1957) 241.
- 3 G. E. BOYD, *Anal. Chem.*, 21 (1949) 335.
- 4 A. A. SMALES, *Atomics London*, 4 (1953) 55.
- 5 W. W. MEINKE, *Science*, 121 (1955) 177.
- 6 R. C. PLUMB AND J. E. LEWIS, *Nucleonics*, 13, No. 8 (1955) 42.
- 7 E. N. JENKINS AND A. A. SMALES, *Quart. Revs. (London)*, 10 (1956) 83.
- 8 *AEC Neutron Cross Section Advisory Group*, U.S. Atomic Energy Commission Document AECU-2040 and supplements.
- 9 D. STROMINGER, J. M. HOLLANDER AND G. T. SEABORG, *Revs. Modern Phys.*, 30 (1958) 585.
- 10 G. FRIEDLANDER AND J. W. KENNEDY, *Nuclear and Radiochemistry*, Wiley, New York, 1955.
- 11 W. W. MEINKE AND R. E. ANDERSON, *Anal. Chem.*, 25 (1953) 778.
- 12 H. IRVING, J. VAN R. SMIT AND L. SALMON, *Analyst*, 82 (1957) 549.
- 13 A. A. SMALES, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*. Vol. 15, United Nations, New York, 1956, p. 73.
- 14 W. W. MEINKE, *U.S. Atomic Energy Commission Report AECD 2738* (1949) p. 132.
- 15 J. KLEINBERG, *Los Alamos Scientific Laboratory Report LA-1721* (1954) p. 138.
- 16 T. B. NOVEY in C. D. CORYELL AND N. SUGARMAN (editors), *Radiochemical Studies: Fission Products*, McGraw-Hill Book Co, 1951, paper 266.
- 17 L. E. GLENDENIN, *ibid.*, paper 267.
- 18 A. A. SMALES, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, Vol. 9, United Nations, New York, 1956, p. 273.
- 19 D. N. SUNDERMAN AND W. W. MEINKE, *Anal. Chem.*, 29 (1957) 1578.
- 20 G. PHILLIPS AND E. N. JENKINS, *Atomic Energy Research Establishment, Harwell report AERE, C/R 1534* (1954).

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A SIMPLE METHOD FOR THE DETECTION OF SMALL AMOUNTS OF α -AMINO ACIDS

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INTRODUCTION

Copper salts react in alkaline media with α -amino acids to give water-soluble, blue diammino-diacid complexes¹. This capacity to form complexes has been employed by POPE AND STEVENS² in their method for the quantitative determination of α -amino acids in body fluids and by CRUMPLER AND DENT³ in distinguishing the α -amino acids from other amino acids.

In this paper, the dissolution of sediments of $\text{Cu}_3(\text{PO}_4)_2$ by α -amino acids is adapted to detect trace amounts of α -amino acids in a small volume of liquid in the range μl -ml by the impregnation method on blotting paper.

The principle of this method is based up on washing off the impregnating substance from the blotting paper and developing the background with rubeanic acid.

TECHNIQUE

Preparation of the impregnated blotting paper

Chromatographic or good blotting-paper strips (8 cm in width) can be impregnated with copper orthophosphate by dipping them into a copper chloride solution (0.3 g/l) and drying them after the excess of liquid is pressed out by a photographic roller. The strips are then dipped into sodium orthophosphate solution ($\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$, concn. 1.5 g/l); Na^+ and Cl^- ions are removed from the blotting paper by washing in a current of distilled water. Good impregnated blotting paper can also be obtained by methods described by KIEŁCZEWSKI⁴ or BUKATSCH AND WILDNER⁵.

The detection procedure

Small quantities of the liquids are placed on the blotting paper by a self-filling ultramicro pipette⁶, applying the glass apparatus for "ring" spot testing as constructed by BHUCHAR⁷, or the apparatus for spotting analysed substances on the chromatograms as devised by ANTOSZEWSKI⁸.

In order to put greater volumes of liquid on to the paper, (0.1 ml or more) the apparatus constructed by MAHR AND KLAMBERG^{9,10} can be applied. The detection of α -amino acids in the powdered samples can be carried out by the method described by TÖPPEL¹¹, after which the investigated sample is placed in the capillary through which the water or buffer solution runs. The preparation should be mixed with powdered cellulose (1 : 1 v/v). To detect the α -amino acids in biological samples, one can make use of the micro-extractor constructed by ANTOSZEWSKI¹².

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A drop of the investigated solution buffered by borax buffer (1 : 1 v/v) (57.21 g $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O} + 1000 \text{ ml H}_2\text{O} + 100 \text{ ml } 1N \text{ HCl}$ diluted to 2 l) is put on the impregnated paper, washed by a drop of distilled water, held over ammonia (2 min) and treated with, or dipped into a 0.1% ethanolic solution of rubeanic acid (dithio-oxamid)¹³. The white fleck on the dark green, nearly black background indicates the presence of α -amino acids.

RESULTS

By the described method, 0.02–0.05 μg of α -amino acids can be detected. When the volume of the sample exceeds 0.1 ml, any small amount of impregnating substance can be washed out from the paper even by pure water; therefore, a control test should be carried out. Soluble peptides can also cause white flecks on the impregnated paper. This method permits the detection of the α -amino acids in the presence of small amounts of ammonia and considerable quantities of urea and salts. It seems possible to regain the α -amino acids for further research after having carried out other micro-preparative operations.

At present, a quantitative modification of this method for chromatographical purposes as well as its adaptation for ultramicro-methods (using isotope ^{32}P) for cytophysiological purposes, is being investigated.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Professor Dr. W. MOYCHO, Department of Plant Physiology, University of Łódź, and Professor Dr. A. LEWANDOWSKI, Department of General Chemistry, University of Poznań, for their interest and helpful criticism of this work.

SUMMARY

A method for the detection of small amounts (0.02 μg or more) of α -amino acids on blotting paper impregnated by copper orthophosphate is described.

RÉSUMÉ

Une méthode est décrite pour déceler de faibles quantités d'acides aminés, en utilisant un papier imprégné de phosphate de cuivre.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zum Nachweis sehr kleiner Mengen α -Aminosäuren mit Hilfe von Filterpapier, das mit Kupferorthophosphat imprägniert ist.

REFERENCES

- ¹ A. A. GRINBERG, *Vvedeniye v khimiyu kompleksnykh soedineniy*; Leningrad, Moskva, 1951; Polish edition 1955, p. 197.
- ² C. G. POPE AND M. F. STEVENS, *Biochem. J.*, 33 (1939) 1070.
- ³ H. R. CRUMPLER AND C. E. DENT, *Nature*, 164 (1949) 441.
- ⁴ W. KIELCZEWSKI, *Chemia Analityczna*, 2 (1957) 336.
- ⁵ F. BUKATSCH AND G. WILDNER, *Fyton*, 7 (1956) 37.
- ⁶ J. OPIEŃSKA-BLAUTH *et al.*, *Chromatografia*, Warszawa 1957, P.W.N., p. 347.
- ⁷ V. M. BHUCHAR, *Microchim. Acta*, (1958) 557.
- ⁸ R. ANTOSZEWSKI, *Roczniki Chem.*, (in the press.).
- ⁹ C. MAHR AND H. KLAMBERG, *Angew. Chem.*, 66 (1954) 328.
- ¹⁰ C. MAHR AND H. KLAMBERG, *Arch. Eisenhüttenw.*, 28 (1957) 795.
- ¹¹ O. TÖPPEL, *Angew. Chem.*, 66 (1954) 555.
- ¹² R. ANTOSZEWSKI, *Naturwissenschaften*, 45 (1958) 42.
- ¹³ F. FEIGL, *Spot Tests*, Vol. I, Elsevier Publishing Company, Amsterdam, 1954, p. 83.

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ANNOUNCEMENT

GORDON RESEARCH CONFERENCES

The Gordon Research Conferences for 1959 will be held from 15 June to 4 September at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

Purpose. The conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and discussion groups. Sufficient time is available to stimulate informal discussions among the members of a conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for recreation, reading or participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas to an extent that could not be achieved through the usual channels of publication and presentation at scientific meetings. In addition, scientists in related fields become acquainted, and valuable associations are formed that often result in collaboration and cooperative efforts between different laboratories.

It is hoped that each conference will extend the frontiers of science by fostering a free and informal exchange of ideas among persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry and physics, but primarily to bring experts up to date on the latest developments, to analyze the significance of these developments, and to provoke suggestions concerning the underlying theories and profitable methods of approach for making new progress.

In order to protect individual rights and to promote discussion, it is an established requirement of each conference that no part of the information presented is to be used without specific authorization of the individual making the contribution, whether in formal presentation or in discussion. Scientific publications are not prepared as emanating from the conferences.

Attendance. Requests for attendance at the conferences, or for additional information should be addressed to W. GEORGE PARKS, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From 15 June to 4 September 1959 mail should be addressed to Colby Junior College, New London, New Hampshire.

GORDON RESEARCH CONFERENCES

ANALYTICAL CHEMISTRY SECTION

*17-21 August 1959**New Hampton School**New Hampton, New Hampshire*

JOHN MITCHELL, JR., Chairman

CHARLES N. REILLEY, Vice Chairman

17 August

- S. DAL NOGARE, Gas Chromatography.
 R. F. GODDU, Near Infrared Spectroscopy.
 L. C. JONES, JR., Far Ultraviolet Spectroscopy.

18 August

- R. BELCHER, Elemental Analysis.
 F. E. CRITCHFIELD, Functional Group Analysis.

19 August

- L. GIERST, Galvanostatic and Potentiostatic Methods.
 Open Discussion.

20 August

- D. L. WOOD, Infrared Spectroscopic Methods for Characterizing High Polymers.
 L. H. PHIFER, Decomposition of High Polymers.

21 August

- R. J. KEIRS, Fluorescence and Phosphorescence.

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ERRATUM

Analytica Chimica Acta, 20 (1959) 140.

Table I, on top of page 140: subheadings of columns: Instead of "2 ml of 1.0% solution" and "2 ml of 5.0% solution" read "2 ml of 0.1% solution" and "2 ml of 0.5% solution".

The subheadings of the lower part of Table I are correct.

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