An International Journal of Analytical Chemistry

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# electro*analytical* abstracts

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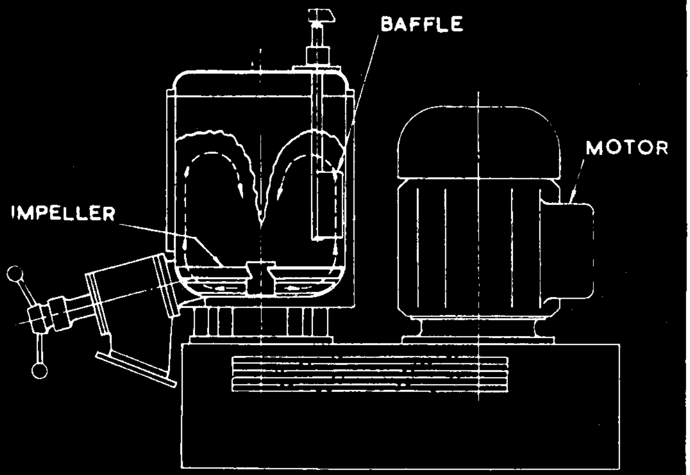

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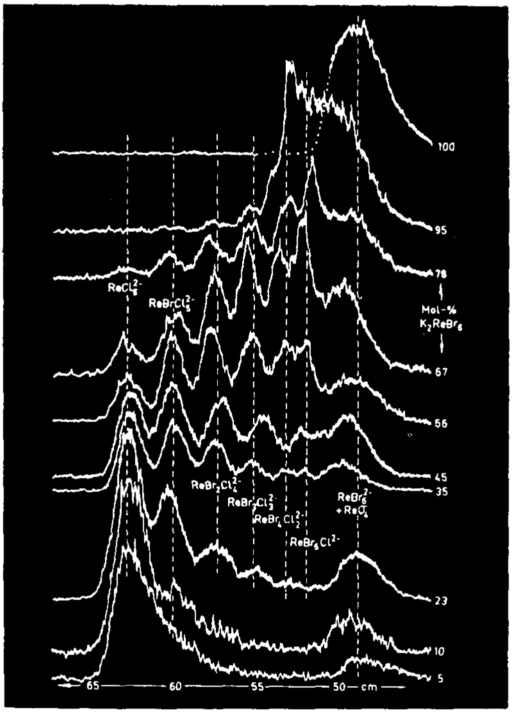
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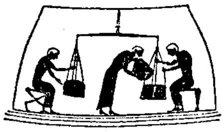

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# DETERMINATION OF TITANIUM IN HIGH-PURITY MOLYBDENUM AND TUNGSTEN METALS WITH DIANTIPYRYLMETHANE AFTER SEPARATION BY EXTRACTION OF ITS CUPFERRON COMPLEX

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**Summary**—A method for determining 0·0005–0·10% of titanium in high-purity molybdenum and tungsten metals is described. After sample dissolution, titanium is separated from the matrix materials by chloroform extraction of its cupferronate from an alkaline (pH 8) tartrate–EDTA medium, then determined spectrophotometrically with diantipyrylmethane at 390 nm. Interference from manganese during extraction is eliminated with sodium sulphite. Iron, zirconium, thorium, tin, aluminium and antimony are partially extracted under the proposed conditions, but moderate amounts of these elements may be present in the sample solution without causing error in the results. Interference from iron(III) during colour development is eliminated with ascorbic acid. Other impurities in the two high-purity metals described do not interfere in the proposed method.

PUBLISHED information pertaining to the determination of small amounts of titanium in molybdenum and tungsten metals by wet chemical methods is sparse. Several spectrophotometric procedures have been applied to the determination of titanium in tungsten metal,[1,2] and molybdenum-base alloys,[3–5] but none of these methods is directly applicable to both metals without some modification. The present investigation was therefore undertaken to develop a method that would be suitable for the determination of trace amounts of titanium in high-purity samples of both metals.

The usual methods for determining titanium spectrophotometrically were not considered in the present investigation either because of their low sensitivity or because the chromogenic reagents employed (hydrogen peroxide, chromotropic acid, thymol, tiron, *etc*) also form coloured complexes with molybdenum and/or tungsten.[6] Diantipyrylmethane was chosen as the chromogenic reagent because of its sensitivity and comparative specificity.[4,7–10] This reagent, introduced by Minin,[11] forms a yellow complex, $[\mathrm{Ti(diantipyrylmethane)_3}]^{4+}$, with titanium(IV) in hydrochloric acid media, with a molar absorptivity of $1 \cdot 5 \times 10^3$ $\mathrm{l.mole^{-1}.mm^{-1}}$ at 385 nm.[12] Polyak[4,5] used this reagent to determine titanium in aluminium and molybdenum-base alloys, without prior separation of the titanium, and reported that the usual components of these alloys, including tungsten, did not interfere. Titanium also forms mixed complexes with diantipyrylmethane and various other reagents (sodium thiocyanate,[13] pyrocatechol,[14] catechol[15]). However, because these reagents are known to react with molybdenum and/or tungsten and with many other metal ions,[16]

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it was considered that a method based on this type of complex would be more subject to interference than one based on the 1:3 diantipyrylmethane complex.

## EXPERIMENTAL

### *Reagents*

*Standard titanium solution.* Dissolve 0·1668 g of pure titanium dioxide (National Bureau of Standards Sample 154a is 99·6% pure titanium dioxide) by heating in a 125-ml Erlenmeyer flask with 8 g of ammonium sulphate and 25 ml of concentrated sulphuric acid. Cool, then, using 5% sulphuric acid solution to wash the flask, transfer the resulting solution to a 500-ml volumetric flask containing 350 ml of water. After further cooling, dilute to volume with the same acid solution. Dilute 5 ml of this stock solution to 100 ml with 5% sulphuric acid solution. Prepare fresh as needed (1 ml of this diluted solution contains 10 $\mu$g of titanium).

*Diantipyrylmethane, 3% solution in 1M hydrochloric acid.* Dissolve 6 g of 4,4′-methylenediantipyrine in 50 ml of water containing 17 ml of concentrated hydrochloric acid, add 10 ml of 10% ascorbic acid solution, filter and dilute to 200 ml with water. This solution is stable for at least two days.

*Ascorbic acid, 10% solution, w/v.* Prepared fresh every two days.

*EDTA, disodium salt, 10% solution, w/v.*

*Ammonium tartrate, 25% solution, w/v.*

*Hydrochloric acid, 9M solution.*

*Sulphuric acid, 5%* and *50% solutions, v/v.*

*Cupferron, 5% solution, w/v.* Prepared fresh as required.

*Sodium sulphite, 10% solution, w/v.* Prepared fresh as required.

*Chloroform.* Analytical reagent grade.

### *Calibration curve*

Add 5 ml of 50% sulphuric acid solution to each of five 100-ml beakers; then, by burette, add to the last four beakers 1, 2·5, 5 and 7·5 ml, respectively, of standard 10 $\mu$g/ml titanium solution. The first beaker contains the blank. Add to each beaker 2 ml of 25% ammonium tartrate solution and 5 ml of 10% ascorbic acid solution and neutralize the resulting solution with concentrated ammonia solution to pH 6·5 ± 0·5. (This pH adjustment is adequate even though the solution becomes hot at this point.) Then add 10 ml of 9*M* hydrochloric acid solution, transfer the solution to a 100-ml volumetric flask and cool to room temperature. Add 10 ml of 3% diantipyrylmethane solution, dilute to volume with water, mix and allow to stand for at least 30 min to complete the colour development. Determine the absorbance of each solution against the blank as the reference solution, using 40-mm cells, at a wavelength of 390 nm and plot weight of titanium against absorbance.

### *Procedure for molybdenum and tungsten metals*

In the following procedure a reagent blank is carried along with the samples.

Transfer a 0·5-g sample of the powdered metal to a 250-ml Teflon beaker, add 5 ml of water, 5 ml of 50% sulphuric acid solution, 2 ml of hydrofluoric acid and 2 ml of concentrated hydrochloric acid and cover the beaker with a Teflon cover. Add 2 ml of concentrated nitric acid, heat gently until all of the metal is in solution, then remove the cover and evaporate the solution to fumes of sulphur trioxide. After cooling, wash down the sides of the beaker with a small amount of 5% sulphuric acid solution, and again evaporate to fumes to ensure complete removal of hydrofluoric acid. (At this stage tungsten is in the insoluble hydrated trioxide form.) Cool, then add, in succession, approximately 5 ml of 5% sulphuric acid solution, 10 ml of 25% ammonium tartrate solution, 5 ml of 10% EDTA solution, 10 ml of 10% sodium sulphite solution, a small piece of red litmus indicator paper and neutralize the resulting solution with 50% sodium hydroxide solution. (If the tungsten solution is slightly cloudy at this point, heat gently until it clears.) Allow the solution to cool to room temperature, then adjust the pH to 8·0 ± 0·1 with either 25% sodium hydroxide solution or hydrochloric acid (1 + 3). Transfer the resulting solution to a 125-ml separatory funnel, add 10 ml of 5% cupferron solution, mix, add 5 ml of chloroform and shake for 2 min. Allow several min for the layers to separate, then drain the chloroform extract into a 100-ml beaker. Re-extract the sample solution three more times, using 5 ml of chloroform and shaking for 2 min each time. Combine these extracts with the first one and evaporate to dryness in a water-bath. Add 5 ml each of 50% sulphuric acid solution, water, concentrated hydrochloric acid and concentrated nitric acid to the residue in the beaker, cover with a watch glass and boil to destroy organic material. Then remove the cover and evaporate the solution to fumes of sulphur trioxide. Cool, wash down the sides of the beaker with a small amount of 5% sulphuric acid solution and again evaporate to fumes.

For samples containing 75 μg of titanium or less proceed as follows. Dilute both sample and blank solutions by adding approximately 5 ml of 5% sulphuric acid solution, then add 2 ml of 25% ammonium tartrate solution and 5 ml of 10% ascorbic acid solution and neutralize to pH 6·5 ± 0·5 with concentrated ammonia solution. Add 10 ml of 9*M* hydrochloric acid, filter (if necessary), and proceed with the colour development as described for the calibration curve.

For samples containing 75–500 μg of titanium proceed as follows. Dilute both sample and blank solutions by adding approximately 10 ml of 5% sulphuric acid solution, filter (if necessary) into 50-ml volumetric flasks, using the same acid solution to wash the beakers and filter papers and to dilute to volume. Transfer either a 5- or 10-ml aliquot of both solutions, depending on the titanium content of the sample, to 100-ml beakers, add sufficient 50% sulphuric acid solution (4 or 3 ml, respectively) so that approximately 2·5 ml of concentrated acid are present and proceed with the colour development as described above.

Measure the absorbance of the sample against the reagent blank and determine the titanium content of the whole sample or aliquot of the sample by reference to the calibration curve.

## RESULTS

### *Factors influencing formation of the 1:3 titanium–diantipyrylmethane complex*

*Effect of ammonium tartrate.* Lazareva and Lazarev[17] have shown that in solutions 0·25*M* in hydrochloric acid, 0·3–0·5*M* in tartaric acid and 0·05*M* in diantipyrylmethane, titanium forms a mixed titanium–diantipyrylmethane–tartrate complex with a molar absorptivity (700 $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 326–330 nm) approximately half that of the 1:3 complex. However, in the present work, tests showed that 0·5 g of ammonium tartrate (or a concentration of about 0·027*M*) does not interfere in the formation of the 1:3 complex. The molar absorptivity of the complex formed under these conditions ($1{\cdot}48 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 390 nm) agrees with that reported by Minin and Erofeeva ($1{\cdot}5 \times 10^3$ at 385 nm)[12] and the absorption spectrum shows only the maximum (384–396 nm) for the 1:3 complex.

*Effect of hydrochloric acid concentration.* Because the hydrochloric acid media employed by previous investigators[7–9,11,18] for formation of the 1:3 complex vary considerably in acid concentration (1–6*M*), tests were carried out to determine the optimum acidity required. The results of these tests, which were performed with solutions containing 75 μg of titanium and 300 mg of diantipyrylmethane, showed that, for the range of hydrochloric acid concentration tested (0·25–2·0*M*), complex formation is complete in the range 0·75–1·5*M*. Therefore, a concentration of approximately 1*M* was chosen for the present work.

*Effect of diantipyrylmethane concentration.* Tests performed with varying amounts of diantipyrylmethane solution showed that approximately 10 ml of a 3% solution are required to complex 75 μg of titanium under the conditions of the present investigation.

*Effect of time.* The rate of formation of the 1:3 titanium-diantipyrylmethane complex at room temperature is not instantaneous but depends on the hydrochloric acid concentration of the medium, the amount of titanium present and the excess of diantipyrylmethane employed.[19] Under the conditions of the present investigation approximately 30 min are required for complete complexation of 75 μg of titanium. The complex, once formed, is stable for at least 3 days.

### *Separation of titanium by extraction of its cupferronate*

Preliminary experiments to assess the applicability of diantipyrylmethane to the determination of small amounts of titanium in high-purity molybdenum and tungsten metals showed that a method involving this reagent was not feasible unless titanium was first separated from the matrix elements. Tungsten could not be maintained in solution under the conditions required for complex formation, and high background absorbance values were obtained in tests with molybdenum solutions.

Although several investigators[1,3] have employed ion-exchange techniques to separate small amounts of titanium from molybdenum and tungsten matrices, work by Starý and Smižanská,[20] Corbett,[21] and Cheng[22] suggested the possibility of separation by solvent extraction. Cheng found that titanium could be separated from small amounts of molybdenum and tungsten (0·01 mmole) by extraction of its cupferronate from an EDTA medium (presumably containing citrate) at pH 5·5. Corbett separated up to 5 mg of titanium from 25 mg of molybdenum by extraction in the presence of EDTA at pH 6. However, neither of these methods is suitable in the presence of large amounts of molybdenum (500 mg). Recently, Starý and Smižanská carried out a comprehensive investigation of the effect of pH on the solvent extraction of various metal cupferronates. Their extraction curves (pH *vs.* % extraction; based on data obtained by performing a single-stage extraction with chloroform) indicate that tungsten and molybdenum are not extracted above pH 4 and pH 7, respectively, while titanium is completely extracted up to approximately pH 5, then partially extracted up to pH 10. They attributed the decrease in the extractability of titanium at higher pH values to hydrolysis. From their data, it was considered that a multiple-stage extraction of titanium cupferronate from a slightly alkaline tartrate or citrate–EDTA medium (to prevent hydrolysis of titanium and possible interference from other ions) might provide an effective means of separating titanium from large amounts of molybdenum and tungsten. Although Corbett did not investigate the extraction of titanium cupferronate from alkaline media, Cheng states that above pH 7 the formation of the complex is almost completely inhibited. Preliminary tests showed that this is true in the case of extraction from alkaline citrate media but not from tartrate media; consequently, separation of titanium by extraction of its cupferronate from alkaline tartrate media was investigated in the present work.

Experiments were carried out over the pH range 6·8–8·3 with molybdenum and tungsten solutions containing 500 $\mu$g of titanium and prepared by decomposing 0·5 g of the metals as described under *Procedure*. In these tests, titanium cupferronate was extracted in four successive stages with 5 ml of chloroform each time, and the titanium was determined according to the described procedure. Although the formation of the distinctive yellow titanium–cupferron complex (which precipitates in acid media) was not observed visually above pH 7, the results of these tests showed that titanium is readily extracted and effectively separated from molybdenum and tungsten matrices by the above method. Complete recovery of the added titanium was obtained in all the tests, and analysis of the final solutions for the respective matrix elements showed that no tungsten and only small amounts of molybdenum (less than 100 $\mu$g) were co-extracted with the titanium. Because it was found that an excess of cupferron is not extracted from alkaline media, a pH of approximately 8 was employed in subsequent work.

### *Effect of diverse ions*

Starý and Smižanská[20] have shown that many metal ions form chloroform-extractable complexes with cupferron in neutral and alkaline media. Although EDTA and citrate or EDTA alone have been employed to complex some of these ions[21–24] during extraction or precipitation and filtration of titanium cupferronate from weakly acid media, no data have been found in the literature pertaining to the effectiveness of both ammonium tartrate and EDTA as masking agents during extraction from alkaline media. Because it was considered that some metal ions might interfere in the extraction of titanium, by forming extractable cupferronates under the conditions used, it was necessary to investigate those ions that could occur as impurities in samples of the two high-purity metals. Sodium sulphite was employed in these tests because it was found that low results were obtained for titanium when manganese(II) was present; this reagent prevents oxidation of manganese(II) to manganese(III) in alkaline EDTA media, which could cause incomplete extraction of the titanium, presumably because of its reduction to titanium(III). The results of these tests (Table I) show that for the quantity of each ion tested none affected the extraction of titanium by the proposed method. Although iron, zirconium, thorium, tin, aluminium and antimony are partially extracted under the proposed conditions, tests showed that up to at least 5 mg of these ions can be present in the solution taken for colour development without affecting the titanium result.

TABLE I.—EFFECT OF DIVERSE IONS ON THE EXTRACTION OF 250 $\mu g$ OF TITANIUM

| Diverse ion taken, (5 mg) | Ti found, *μg* | Diverse ion co-extracted with titanium, *mg* |
|---|---|---|
| Fe(III) | 254 | 0·15 |
| Cu(II) | 248 | None detected |
| Mn(II) | 253 | None detected |
| Ni(II) | 248 | None detected |
| Co(II) | 245 | None detected |
| Zn(II) | 245 | None detected |
| Cd(II) | 248 | None detected |
| Sn(IV) | 252 | 0·05 |
| V(V) | 250 | None detected |
| Al(III) | 248 | 0·50 |
| Zr(IV) | 249 | 0·51 |
| Th(IV) | 250 | 0·90 |
| Bi(III) | 249 | None detected |
| Sb(III) | 248 | 0·17 |

Several additional tests were carried out with solutions containing sodium orthophosphate because it was considered that phosphate might interfere in the proposed method by forming insoluble compounds with either tungsten or titanium. The results of these tests showed that up to at least 15 mg of phosphate ion do not affect the extraction of titanium from molybdenum and tungsten solutions.

### *Application to synthetic molybdenum and tungsten samples*

To determine the accuracy of the proposed method, it was applied to the analysis of a series of synthetic samples in which the added titanium was varied from 0·001 to 0·10%. The standard titanium solution was added directly to the powdered metal samples. The results obtained (Table II) agree favourably with the total calculated amount of titanium present.

## DISCUSSION

In the proposed method, isolation of titanium by extraction of its cupferronate from an alkaline tartrate–EDTA medium offers several advantages, besides providing

TABLE II.—RECOVERY OF TITANIUM BY THE PROPOSED METHOD FROM SYNTHETIC MOLYBDENUM AND TUNGSTEN SAMPLES

| Sample | Total Ti present, % | Ti found, % |
|---|---|---|
| Mo + 0·0010% Ti | 0·0013 | 0·0012 |
| Mo + 0·0050% Ti | 0·0053 | 0·0050 |
| Mo + 0·0100% Ti | 0·0103 | 0·0103 |
| Mo + 0·0250% Ti | 0·0253 | 0·0253 |
| Mo + 0·0500% Ti | 0·0503 | 0·0499 |
| Mo + 0·1000% Ti | 0·1003 | 0·1003 |
| W + 0·0010% Ti | 0·0010 | 0·0009 |
| W + 0·0050% Ti | 0·0050 | 0·0050 |
| W + 0·0100% Ti | 0·0100 | 0·0100 |
| W + 0·0250% Ti | 0·0250 | 0·0250 |
| W + 0·0500% Ti | 0·0500 | 0·0499 |
| W + 0·1000% Ti | 0·1000 | 0·1001 |

Duplicate determinations of titanium in these Mo and W metals by the proposed method gave average results of 0·0003 and none detected, respectively.

an effective means of separating small amounts of titanium from molybdenum and tungsten matrices. Titanium is also separated from certain ions [nickel, chromium(III) and (VI)] which interfere in its determination with diantipyrylmethane because of the colours imparted to the solution,[18] thus eliminating the necessity of correcting for background colour. Although iron(III) and vanadium(V) form complexes with diantipyrylmethane in hydrochloric acid media,[7] vanadium is not extracted under the proposed conditions; iron is partially extracted but its reaction with diantipyrylmethane is prevented by prior reduction to the bivalent state with ascorbic acid. A distinct advantage inherent in the proposed separation procedure is the fact that an excess of cupferron is not extracted at a pH above approximately 7. Consequently, after evaporation of the chloroform extract to dryness, the small amount of organic material in the titanium cupferronate residue is readily destroyed by oxidation with a mixture of hydrochloric and nitric acids.

In preliminary tests to determine the applicability of cupferron–chloroform extraction to the separation of titanium from molybdenum and tungsten matrices, slightly low results were obtained for the added titanium (500 $\mu$g) when an aliquot of the final solution (approximately 10% in sulphuric acid) was taken for analysis. Subsequent work showed that this error could be avoided by adding sufficient sulphuric acid to the aliquot so that approximately 2·5 ml of concentrated acid were present before colour development. Consequently, it was presumed that some hydrolysis of titanium occurs, probably during the neutralization process, if the sample solution, or aliquot, taken for analysis is not strongly acidic.

In the method described by Cheng,[22] titanium is determined by direct measurement of the 4-methyl-2-pentanone extract after a single-stage extraction of its cupferronate from an EDTA medium at pH 5·5. No attempt was made to apply this solvent or method of measurement in the present work because of the reported instability of the extract, the necessity for preparing calibration curves daily, and the lower molar absorptivity of the titanium cupferrate complex (620 $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 350 nm) compared to that of the diantipyrylmethane complex. Furthermore, direct measurement of the extract cannot be employed when titanium is extracted with either chloroform or 4-methyl-2-pentanone from alkaline tartrate–EDTA media containing iron because the co-extracted iron imparts a reddish-brown colour to the extract. A single-stage extraction will not remove titanium cupferronate quantitatively from alkaline media; consequently, because of its low density, 4-methyl-2-pentanone is not a convenient solvent to use in the proposed method.

The method presented in this paper is suitable for samples containing 0·0005–0·10% of titanium, but material containing larger amounts can also be analysed if smaller samples are taken. Smaller amounts cannot be accurately determined because of the titanium content of the reagent blank (approximately 4 $\mu$g).

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**Résumé**—On décrit une méthode pour déterminer 0,0005–0,10 % de titane dans le molybdène et le tungstène métalliques de haute pureté. Après dissolution de l'échantillon, on sépare le titane des substances de la matrice par extraction au chloroforme de son cupferronate à partir d'un milieu alcalin (pH 8) tartrate-EDTA, puis le dose spectrophotométriquement au diantipyrylméthane à 390 nm. On élimine l'interférence du manganèse pendant l'extraction par le sulfite de sodium. Les fer, zirconium, thorium, étain, aluminium et antimoine sont partiellement extraits dans les conditions proposées, mais des quantités modérées de ces éléments peuvent être présentes dans la solution de l'échantillon sans entraîner d'erreur dans les résultats. On élimine l'interférence du fer(III) durant le développement de la coloration par l'acide ascorbique. Les autres impuretés présentes dans les deux métaux de haute pureté décrits ne gênent pas dans la méthode proposée.

**Zusammenfassung**—Eine Methode zur Bestimmung von 0,0005–0,10% Titan in hochreinem metallischem Molybdän und Wolfram wird beschrieben. Nach Auflösen der Probe wird Titan von den Hauptbestandteilen durch Chloroformextraktion seines Kupferronats aus alkalischem (pH 8) Tartrat-EDTA-Medium getrennt und spektrophotometrisch bei 390 nm mit Diantipyrylmethan bestimmt. Die Störung durch Mangan bei der Extraktion wird mit Natriumsulfit eliminiert. Eisen, Zirkonium, Thorium, Zinn, Aluminium und Antimon werden unter den vorgeschlagenen Bedingungen teilweise extrahiert; mäßige Mengen dieser Elemente können jedoch in der Probelösung vorkommen, ohne Fehler bei den Ergebnissen hervorzurufen. Die Störung durch Eisen(III) bei der Farbentwicklung wird mit Ascorbinsäure beseitigt. Andere Verunreinigungen der beiden erwähnten hochreinen Metalle stören bei dem vorgeschlagenen Verfahren nicht.

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# ANALYSIS BY RELEASE OF RADIOACTIVITY BY INORGANIC ION-EXCHANGE AND RING OVEN TECHNIQUE—I

## DETERMINATION OF COPPER

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**Summary**—A sparingly soluble inorganic compound, fixed as a spot on filter paper, is used as an ion-exchanger in which the exchangeable ions are labelled with a radioactive isotope. These ions are replaced by the ions of the element to be determined but not by other accompanying ions. In this exchange an equivalent amount of the radioactive labelled ions is released from the ion-exchanger and separated from the spot by the ring oven technique. The activity of the ring is measured and compared with that of a standard processed in the same way. The determination of copper in amounts greater than 25 ng in the presence of a similar amount of lead and considerably greater amounts of cobalt, nickel, zinc, manganese and thallium is described.

RADIOMETRIC analysis, originally introduced by Ehrenberg,[1] is one of the important microanalytical methods because of its simplicity and high sensitivity. The typical procedure is based upon the formation of a radioactive compound by a stoichiometric reaction between the substance to be determined and a radioactive reagent with known specific activity and present in excess. The radioactive compound formed is markedly different in solubility from the original reacting substances. The activity of the resulting radioactive compound or of the unreacted radioactive reagent is measured and a simple calculation gives the amount of the substance in the unknown. Many variations of the method are possible.[2]

In a variation of this method worked out by us recently,[3] radioactively labelled silver was used as universal radio reagent for determining several metals. The metals are precipitated as sulphides and converted into an equivalent amount of silver sulphide, the activity of which is measured. All operations are carried out on filter paper. In the presence of accompanying elements forming sparingly soluble sulphides, corresponding separations must be carried out before application of the silver solution.

In this paper, a variation is described. It is based on the use of an inorganic compound of very low solubility, fixed on filter paper, as an ion-exchanger in which the exchangeable ions are radioactive, and also on the use of the ring oven technique.[4] By using various sparingly soluble and labelled inorganic compounds it is possible to work out procedures for selectively determining a certain element in the presence of other accompanying elements.

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### *Principle of the method*

A sparingly soluble inorganic compound, AX, is fixed as a spot in the centre of a round filter paper; A is cationic and X is anionic. In the determination of elements present in solution as cations, the component A is labelled with a suitable radioisotope (*AX). Assume that the solution to be analysed contains cations of the element of interest, B, which form a compound BX which is less soluble in the reaction medium than is AX. Assume also that it contains cations of other elements (C, D, . . .) which form with X compounds more soluble than AX. A small volume of the solution to be analysed (containing $x$ $\mu g$ of B) is placed on the *AX spot on the paper. Then a replacement reaction takes place with BX being formed in the solid phase and at the same time an equivalent amount of *A ions being released into solution. No ion-exchange takes place between the cations of other elements present in the analysed solution (C, D, . . .) and the substance *AX. The released *A cations are washed from the spot in the centre to a ring in the outer zone of the filter paper with a suitable solvent, by the ring oven technique (Fig. 1). The activity of the *A concentrated in the ring is then measured. A parallel experiment is carried out with a standard solution ($m$ $\mu g$ of B). A direct calculation gives the unknown amount $x$ of the element B:

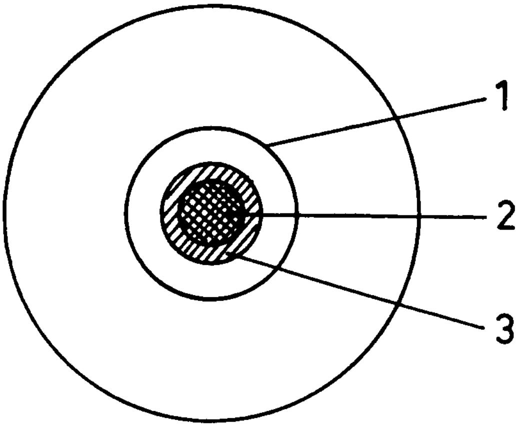

Fig. 1.—Schematic representation of the zones of the filter paper: 1-ring with the released radioactive labelled ions, 2-reaction zone, 3-spot of inorganic ion-exchanger.

$$x = m \cdot \frac{I_x}{I_m} \qquad (1)$$

where $I_x$ and $I_m$ are the measured activities of $*A$ in the ring when sample and standard are processed.

If the element to be determined is present in anionic form, Y, the anionic component, X, in compound AX will be labelled (A*X). The determination of Y is then based on the analogous replacement reaction.

It is possible to perform a determination in a similar way without using the ring oven. In this case, the released ions *A or *X are washed to the outer zone of the paper and the activity of *AX or A*X remaining in the spot is measured. A simple calculation will give the amount of element in question:

$$x = m \cdot \left\{\frac{I_{0s} - I_{xs}}{I_{0s} - I_{ms}}\right\} \tag{2}$$

where $I_{0s}$ is the original activity of the spot, and $I_{xs}$ and $I_{ms}$ are the activities remaining in the spot when the sample and standard solutions are processed.

This second variation without the use of the ring oven depends on the ratio *AX/B or A*X/Y. This diminishes the potentiality of the technique. The reproducibility when the ring oven technique is used is in every case considerably better.

The processing of the standard solution in the same way as the sample solution also makes it possible to use replacement reactions which do not proceed stoichiometrically, provided the ratio B/X is sufficiently constant.

The basis of the determination of copper described in this paper is the replacement of the cadmium ions in cadmium sulphide labelled with $^{109}$Cd, by copper(II) ions.

## EXPERIMENTAL

### *Reagents*

*Radiocadmium.* Dilute hydrochloric acid solution containing $^{109}$Cd carrier-free with a specific activity of 60 $\mu$Ci/ml was obtained from Kernforschungszentrum, Karlsruhe. Solutions were prepared from cadmium nitrate *p.a.* to contain the following amounts of carrier: 0·16, 0·32, 1·4 and 7 mg of Cd per ml. The corrsponding specific activities were 330, 147, 29 and 4 $\mu$Ci/mg Cd. Cadmium-109 disintegrates by orbital electron capture ($t_{1/2}$ = 470 d) producing $^{109m}$Ag, which emits gamma-rays ($t_{1/2}$ = 40 s) with energy of 88 keV. In addition, X-rays from silver with energy of 22 keV are emitted.

*Hydrogen sulphide.* Obtained in a pressure bottle from Gerling, Holz and Co., Hanau. All other reagents were of *p.a.* purity.

*Filter paper.* Round filter paper (55 mm diameter) MN 2260 from Macherey, Nagel and Co., Duren.

### *Procedure*

A 5-$\mu$l portion of a solution of radiocadmium is placed in the centre of each of three round filter papers. A suitable radiocadmium solution is chosen according to the following rule: if the sample solution contains a small amount of copper, the concentration of carrier cadmium must be low and the specific activity high; conversely, with large amounts of copper the concentration of carrier cadmium must be high and the specific activity can be low. The filter papers are placed in a stream of hydrogen sulphide gas in a simple glass apparatus. After a few minutes one drop of ethyl alcohol is placed on each cadmium sulphide spot and the precipitation is continued. This step is repeated once more. After precipitation is completed the cadmium sulphide spot is washed with a drop of 0·5% ammonium nitrate solution or 0·25% acetic acid and then with a drop of distilled water. The washing is best carried out on the "washing ring" described by West, Llacer and Cimerman,[5] with a capillary. After drying, 2 $\mu$l of the sample solution (containing $x$ $\mu$g of Cu$^{2+}$) are placed on the cadmium sulphide spot of the first paper. A similar volume of the standard solution (containing $m$ $\mu$g of Cu$^{2+}$) is applied to the second paper. Then 1 $\mu$l of distilled water is added to the spot in both cases. Because of the large surface area of the cadmium sulphide the replacement reaction takes place very quickly. After a few minutes the filter papers are placed one by one on the ring oven and the cadmium ions released are washed to the ring with 120–160 $\mu$l of 1% ammonium nitrate solution. The third filter paper, which is used for the blank test, is washed in the same way. After drying of the filter paper, a disc bearing the cadmium sulphide spot is punched out of the centre and the activity of the radiocadmium concentrated in the ring is measured. The X-rays from silver (22 keV) are used because the efficiency is more than 10 times that of detection of the gamma-rays of $^{109m}$Ag. The blank value (including the background) is then subtracted from the sample and standard counting data. From relationship (1) the amount of copper contained in 2 $\mu$l of sample solution is calculated.

## RESULTS AND DISCUSSION

Preliminary experiments showed that the dependence of the radiocadmium activity in the ring on the amount of copper(II) ions placed on the cadmium sulphide

TABLE I.—DETERMINATION OF COPPER IN THE ABSENCE OF OTHER IONS

| Taken<br>μg | Found<br>μg | Taken<br>μg | Found<br>μg |
|---|---|---|---|
| 0·025 | 0·029 | 0·80 | 0·78 |
| 0·050 | 0·044 | 1·00 | 1·05 |
| 0·100 | 0·109 | 4·00 | 4·17 |
| 0·200 | 0·183 | 8·00 | 8·20 |
| 0·400 | 0·370 | 10·00 | 9·55 |

spot is linear. The unknown amount of copper can therefore be determined by a direct comparison of the sample with a single standard.

The results of a number of determinations of copper obtained by this technique in the absence of other ions are given in Table I. Results for the determination of copper in the presence of $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Tl^{+}$ and $Pb^{2+}$ are summarized in Table II. For amounts of copper greater than 0·5 μg the relative standard deviation has been found to be less than 7% (0·5 ± 0·032 μg).

TABLE II.—DETERMINATION OF COPPER IN PRESENCE OF OTHER IONS

| Ion (Me) | Me:Cu | Copper, μg | | Ion (Me) | Me:Cu | Copper, μg | |
|---|---|---|---|---|---|---|---|
| | | Taken | Found | | | Taken | Found |
| Co(II) | 20 | 1·00 | 0·97 | Tl(I) | 20 | 1·00 | 0·95 |
| | 40 | 0·50 | 0·53 | | 40 | 0·50 | 0·54 |
| | 100 | 0·20 | 0·22 | | 100 | 0·20 | 0·16 |
| | 600 | 0·050 | 0·055 | | 600 | 0·050 | 0·056 |
| | 1200 | 0·025 | 0·019 | | 1200 | 0·025 | 0·032 |
| Ni(II) | 20 | 1·00 | 1·00 | Pb(II) | 20 | 1·00 | 1·09 |
| | 40 | 0·50 | 0·52 | | 0·5 | 0·50 | 0·48 |
| | 100 | 0·20 | 0·19 | | 2 | 0·50 | 0·52 |
| | 600 | 0·050 | 0·062 | | 40 | 0·50 | 0·56 |
| | 1200 | 0·025 | 0·030 | | 0·5 | 0·20 | 0·19 |
| Zn(II) | 20 | 1·00 | 1·03 | | 5 | 0·20 | 0·25 |
| | 40 | 0·50 | 0·49 | | 100 | 0·20 | 0·32 |
| | 100 | 0·20 | 0·23 | | 0·5 | 0·025 | 0·029 |
| | 600 | 0·050 | 0·037 | | 100 | 0·025 | 0·038 |
| | 1200 | 0·025 | 0·021 | | | | |
| Mn(II) | 20 | 1·00 | 0·96 | Co, Ni, | 20* | 1·00 | 0·94 |
| | 40 | 0·50 | 0·52 | Zn, Mn | 40* | 0·50 | 0·49 |
| | 100 | 0·20 | 0·19 | | | | |
| | 600 | 0·050 | 0·056 | Co, Ni, Tl, | 20* | 1·00 | 1·10 |
| | 1200 | 0·025 | 0·021 | Zn, Mn, Pb | 40* | 0·50 | 0·54 |

* For each ion.

From Table II it is evident that amounts of copper as low as 25 ng can be determined in the presence of 1200 times greater amounts of cobalt, nickel, manganese, zinc and thallium with satisfactory precision. Lead does not interfere markedly until it is present in nearly the same amount as copper (Cu/Pb up to 1/2). With ratios of Cu/Pb up to 1/20 slightly higher results are obtained but the errors exceed the standard deviation by only a small amount. With smaller ratios of Cu/Pb than 1/20 the results obtained are too high. Some additional experiments showed that the interference depends not only on the ratio of Cu/Pb but also on the absolute concentration of lead. At a constant ratio of Cu/Pb the interference increases slightly with the lead concentration. To obtain correct results it should not be higher than 2 μg/μl. This interference is due to the fact that the solubility of lead sulphide is only slightly greater than the solubility of cadmium sulphide, while that of the sulphides of other accompanying elements is considerably greater. Ziegler found[6] that lead ions would not replace cadmium in cadmium sulphide in 1% nitric acid solution. When this reaction medium was used under our experimental conditions the blank values obtained were many times higher and their reproducibility worse than when neutral or weakly acidic media were used. On the other hand, the assumption made by Koev[7] that lead ions replace cadmium on filter paper impregnated with cadmium sulphide at pH 1·5–2 could not be confirmed by our results.

Good results are obtained by this method when the precipitation of cadmium ions on the paper as cadmium sulphide is practically complete. This can be attained by using the precipitation procedure described above. Errors due to traces of unprecipitated cadmium as well as to the very low solubility of cadmium sulphide are sufficiently eliminated by the blank correction. It is necessary to remove the hydrogen sulphide adsorbed on the spot, otherwise incorrect results would be obtained. The cadmium sulphide has to be present on the paper in at least 3-fold excess in relation to the amount of copper. Moreover, the area of the cadmium sulphide spot must be greater than that of the sample solution spot.

The results indicate that this method can be used for a simple and relatively rapid determination of microgram and submicrogram amounts of copper in the presence of a great excess of other elements. The only conditions necessary are that the solution must be neutral or weakly acidic and that the acidity of sample solution and standard solution is nearly the same.

If no ring oven is used and the activities of the spots are measured [calculation using relationship (2)] it is necessary to know the approximate amount of copper in the solution. An amount of cadmium sulphide is then chosen on the basis of the copper content in order to get a measurable difference in activity $(I_{0s} - I_{xs})$. The errors of such determinations are, even under the optimal conditions, on the average twice as great as those obtained by the ring oven technique.

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**Zusammenfassung**—Eine schwerlösliche anorganische Verbindung, als Fleck auf Filtrierpapier festgelegt, wird als Ionenaustauscher verwendet, bei dem die austauschbaren Ionen mit einem radioaktiven Isotop markiert sind. Diese Ionen werden durch die Ionen des zu bestimmenden Elementes ersetzt, nicht jedoch durch andere Begleitionen. Bei diesem Austausch wird eine äquivalente Menge der radioaktiv markierten Ionen vom Austauscher freigesetzt und mit der Ringofentechnik vom Fleck getrennt. Die Aktivität des Rings wird gemessen und mit der eines ebenso behandelten Standards verglichen. Die Bestimmung von Kupfer in Mengen über 25 ng in Gegenwart ähnlicher Mengen Blei und wesentlich größerer Mengen Kobalt, Nickel, Zink, Mangan und Thallium wird beschrieben.

**Résumé**—Un composé inorganique difficilement soluble, fixé comme une tache sur papier filtre, est utilisé comme un échangeur d'ions dans lequel les ions échangeables sont marqués avec un isotope radioactif. Ces ions sont remplacés par les ions de l'élément à déterminer mais non par d'autres ions qui l'accompagnent. Dans cet échange, une quantité équivalente des ions marqués radioactivement est libérée de l'échangeur d'ions et séparée de la tache par la technique du four annulaire. L'activité de l'anneau est mesurée et comparée à celle d'un étalon traité de la même manière. On décrit la détermination du cuivre en quantités supérieures à 25 ng en la présence d'une quantité similaire de plomb et de quantités beaucoup plus grandes de cobalt, nickel, zinc, manganèse et thallium.

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# SELECTIVE TITRATION OF MICROGRAM AMOUNTS OF COPPER WITH PHOTOMETRIC END-POINT DETECTION

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**Summary**—The reaction of copper ions with pyridylazonaphthol is very suitable and sensitive for the photometric titration of copper. The titration is self-indicating, and at the 0·1-ppm level the standard deviation is 2·5%. The main interferences are caused by bismuth, iron, titanium and vanadium but can be overcome by suitable masking.

THE compound 1-(2-pyridylazo)-2-naphthol (PAN) was introduced into analytical chemistry in 1955 by Cheng and Bray.[1] Numerous applications of PAN and other azo compounds have since been published, and reviewed.[2,3]

We have carried out experiments with PAN as indicator in the complexometric titration of copper with EDTA, with photometric end-point detection; emphasis was placed on titration of low concentrations. We found that though the first break in the plot of absorbance *vs.* added EDTA was very sharp, the second break showed a pronounced rounding in all circumstances. As discussed by Reilley and Schmid[4] and by Flaschka and Khalafalla,[5] the first break in such a plot is sharp only if the product $K_{MI}c_M$ is large, while the second break is sharp only at large values of the ratio $K_{MY}:K_{MI}$, where $K_{MI}$ and $K_{MY}$ are the conditional stability constants of the metal-indicator and the metal-EDTA complexes respectively, and $c_M$ is the concentration of the metal titrated. The indicator in our titration apparently behaves as the so-called high sensitivity type, which is rather rare. This is in agreement with literature data[6] on the conditional equilibrium constants; *i.e.*, $\log K_{MI} = 7.8$ and $\log K_{MY} = 10.2$ for pH 4.0. If $c = 10^{-3}M$, it follows that $K_{MI}c_M = 10^{4.8}$ and $K_{MY}:K_{MI} = 10^{2.4}$.

For the determination of very small amounts of copper this situation is not very favourable. Because of the unsharpness of the second break, the first must be used for the location of the end-point. The determination of very small amounts of copper then becomes impossible, for the indicator correction is greater than the value of the copper titration and the first break disappears.

We chose PAN because of its strong affinity for copper, but for the complexometric titration of small amounts of copper with EDTA this affinity is rather a drawback. The conclusion was that PAN should be used as titrant rather than as indicator. Most indicators are unsuitable as titrants because of their poor stability in solution, but the solutions of PAN used in our investigation showed no decrease in titre after several weeks of standing.

The conditional constant given above for the copper–PAN complex was that obtained by Pease and Williams.[7] We have made an independent determination (see *Appendix*).

## EXPERIMENTAL

### *Reagents*

PAN (Eastman-Kodak) was not further purified. Analytical grade reagents were used throughout. Copper solutions were prepared by dissolving copper foil in dilute nitric acid.

### *Analytical procedure*

In photometric titrations the volume of the solution and the amount of the substance determined are strongly dependent on the characteristics of the photometric apparatus (cell dimensions, optimum for absorbance measurement). Therefore a detailed procedure is not given.

The solutions were buffered to about pH 4·0 by adding sodium acetate and acetic acid up to concentrations of about 0·01 and 0·05*M* respectively. The titrant used was 0·0001*M* PAN solution in methanol–water mixture (1:1). Absorbance was measured with a Zeiss Elko II and S 55 filter (maximum transmission at 550 nm; half-width about 20 nm). About 10 points before and after the end-point were plotted. For the technique of photometric titration with a substitution apparatus the publication by Groeneveld and den Boef[8] may be consulted.

## RESULTS

The spectra of PAN, the protonated species $PANH^+$, and the copper–PAN chelate are given in Fig. 1. The spectrum for uncharged PAN differs considerably from that published by Pease and Williams.[7] In our investigation, products from different manufacturers (Baker, Eastman-Kodak, Light) gave essentially the same spectrum, consisting of a broad maximum at 472 nm with molar absorptivity $1.7 \times 10^3$ $l.mole^{-1}.mm^{-1}$, and a very vague shoulder at about 420 nm. Above 550 nm the absorbance declined very rapidly. The spectrum obtained by Pease and Williams under practically the same conditions shows a shoulder at about 550 nm, which we suppose to be due to an impurity. The variation of the height of this shoulder with pH cannot be explained by the equilibrium with the protonated $PANH^+$. We therefore repeated the determination of the various stability constants (*Appendix*).

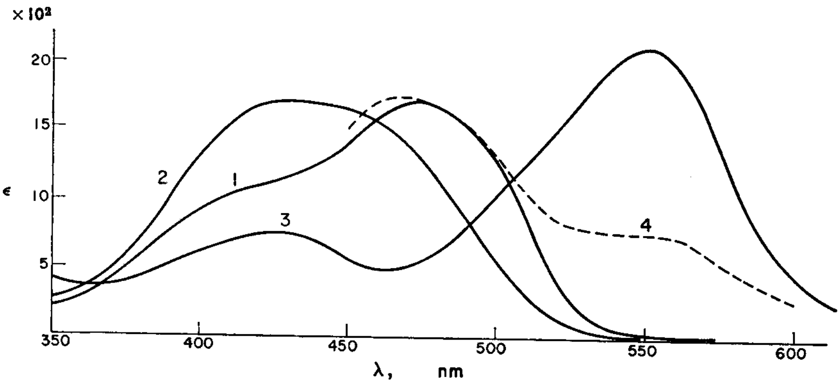

Fig. 1.—Absorption spectra of (1) PAN at pH = 4·40, (2) PAN at pH = 1·0, (3) Copper–PAN complex. The broken line (4) gives the absorption spectrum of PAN at pH = 4·2 as measured by Pease and Williams.

Two typical curves are shown in Fig. 2. In the titration of 0.4 μg of copper in about 25 ml the total change in absorbance is only 0.01. This result corroborates the conclusion reached by Groeneveld and den Boef[8] that photometric titrations with such small absorbance changes are possible if an appropriate instrument is used.

*Note.* The change in absorbance shown in Fig. 2 is opposite to the actual change in the solutions during the titrations. This stems from the principle of optical substitution used in the apparatus. The cell and the measuring attenuator are located in the same light-path. When during a titration the absorbance of the solution increases, the attenuator has to be opened in order to maintain balance of the two light-beams. As a consequence, a lower absorbance is read.

The experimental results on the reproducibility of the method are summarized in Table I. In the second series of titrations the standard deviation was determined in the presence of 100-fold amounts of Al, Cr(III), Cd, Co, Mn, Mo, W and Zn. These elements were chosen because they do not need to be masked. The selectivity is shown by Table II.

Standard alloys were analysed as an example of the application of the method. The results are given in Table III. Further fields of application could be trace analysis for copper in biological and water research.

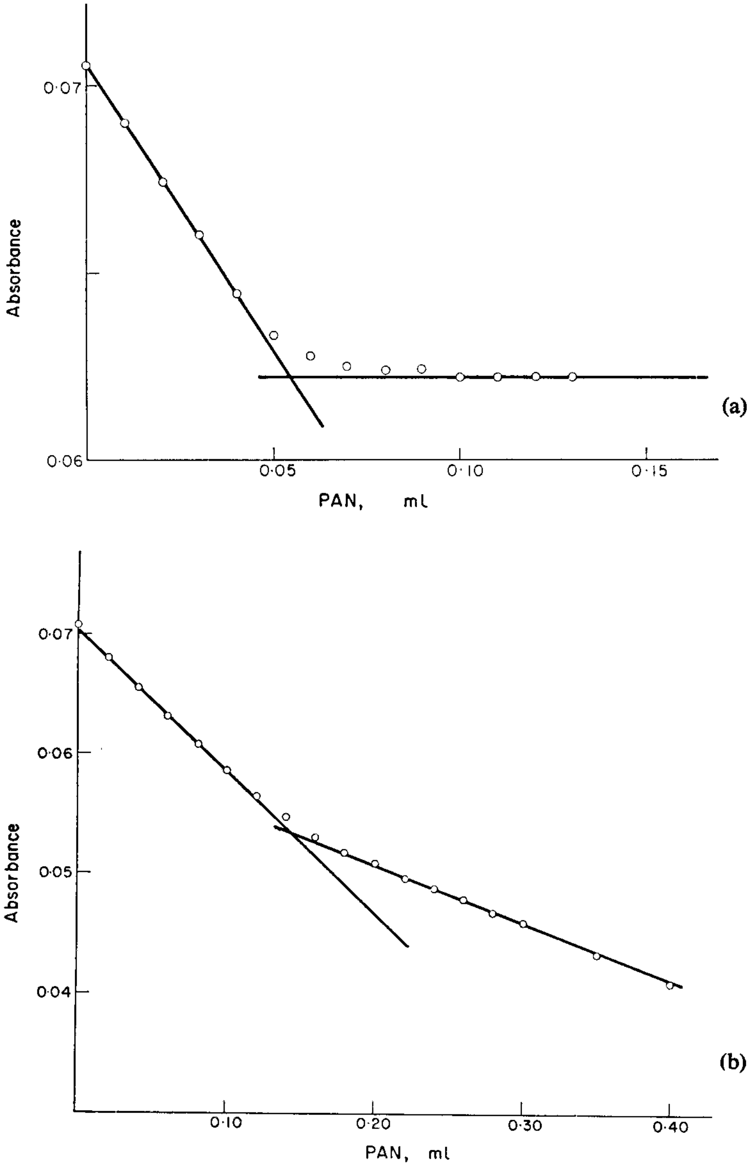

Fig. 2.—Photometric titration curve of (a) 0·4 μg of copper in 25 ml of solution; (b) 1 μg of copper in 25 ml of solution in the presence of 100-fold amounts of Al, Cr(III), Cd, Co, Mn, Mo, W, and Zn.

TABLE I.—DETERMINATION OF COPPER NEAR THE LIMIT OF DETECTION OF THE METHOD

| Series | Number of determinations | Titration volume, *ml* | Copper | | Standard deviation, $\mu g$ |
|---|---|---|---|---|---|
| | | | taken, $\mu g$ | mean found, $\mu g$ | |
| 1 | 5 | 25 | 0·953 | 0·954 | 0·025 |
| 2* | 10 | 25 | 0·953 | 0·958 | 0·032 |
| 3 | 10 | 10 | 0·244 | 0·221 | 0·008 |
| 4 | 10 | 10 | 0·162 | 0·157 | 0·010 |

* In the presence of 100-fold amounts of Al, Cr(III), Cd, Co, Mn, Mo, W and Zn.

TABLE II.—SELECTIVITY OF THE DETERMINATION OF COPPER

| Metal | Maximum ratio without masking | Masking agent and concentration | | Maximum ratio with masking |
|---|---|---|---|---|
| Ag | 1000* | — | | — |
| Al | 1000* | — | | — |
| As(III) | 1000* | — | | — |
| Bi | 10 | $Cl^-$ | 0·1*M* | 100 |
| Cd | 1000* | — | | — |
| Cr(III) | 10000 | — | | — |
| Co(II) | 400 | — | | — |
| Fe(III) | <100 | $F^-$ | 0·04*M* | 500 |
| | | $H_2PO_4^-$ | 0·02*M* | 2000 |
| Hg(II) | 1000* | — | | — |
| Mn(II) | 1000* | — | | — |
| Mo(VI) | 1000* | — | | — |
| Ni(II) | 100 | masking gives no improvement | | |
| Pb(II) | 10000* | — | | — |
| Sb(III) | 1000* | — | | — |
| Sn(II) | 1000* | — | | — |
| Ti(IV) | <10 | $H_2PO_4^-$ | 0·02*M* | 100 |
| V(V) | 3 | $H_2PO_4^-$ | 0·02*M* | 100 |
| V(IV) | <10 | $F^-$ | 0·08*M* | 13 |
| W(VI) | 1000* | — | | — |
| Zn | 5000* | — | | — |

* Highest ratio tried.

The metal–copper ratios are those at which the error exceeds 6% or at which the end-point is no longer discernable. The amount of copper was 1 $\mu g$, the titration volume about 25 ml. Solutions were buffered by 0·01*M* sodium acetate and 0·05*M* acetic acid. When masking agents were used the pH was restored to about 4·0.

## DISCUSSION

### *Limits of detection*

In comparing the method with other procedures for the determination of trace amounts of copper a clear distinction should be made between sensitivity and limit of detection.

The term sensitivity is recommended for the slope of the calibration curve. In spectrophotometry the significant parameter for the sensitivity is the molar absorptivity. The lower limit of detection, which is of final importance in trace analysis, is a function of both this sensitivity and the level of disturbing influence (the noise). In spectrophotometry noise may originate from a host of causes, ranging from airborne contamination to fluctuations in light-source intensity. It is common practice to assume that an absorbance change of 0.001 is the minimum detectable.[9] This figure thus defines the noise level and is, of course, an arbitrary limit. However, the figure

TABLE III.—DETERMINATION OF COPPER IN STANDARD ALLOYS

| Alloy | Copper content, % | | Composition, % | Masking agent |
|---|---|---|---|---|
| | given | found | | |
| BCS 173 | 4·73 | 4·36 | C 3·06, Si 2·26, Mn 1·01, | |
| | | 4·75 | S 0·031, Ni 13·45, Cr 3·97, Cu 4·73, | fluoride |
| | | 4·40 | P 0·119, Fe rest | |
| BCS 251 | 0·090 | 0·089 | Si 0·013, Mn 0·165, Ni 5·15, | fluoride |
| | | 0·089 | Cr 0·044, Mo 0·18, V 0·034, Cu 0·090, | fluoride |
| | | | Sn 0·007, Co 0·070, Fe rest | |
| BCS 256/1 | 0·16 | 0·164 | Si 0·23, Mn 1·02, Ni 0·19, | fluoride |
| | | 0·164 | Cr 2·33, Mo 0·53, V 0·18, Cu 0·16, Fe rest | fluoride |
| BCS 280 | 0·04 | 0·052 | Mn 80·4, Fe 16·0, C 0·47, Si 2·01, P 0·31, | fluoride |
| | | 0·036 | Cr 0·56 | fluoride |
| | | 0·040 | | fluoride |
| NBS 85 B | 3·99 | 4·05 | Mg 1·49, Mn 0·61, Fe 0·24, | phosphate |
| | | 3·78 | Cr 0·211, Si 0·18, Ni, Zn, Ti, Pb, Ga, V 0·2, | fluoride |
| | | 3·94 | Al rest | fluoride |

Titration conditions as in Table I. Results are the mean of 4 titrations from the same weighing. The amount of copper in each titration was 1–2 μg.

is a pretty optimistic estimate. Emptying and refilling cells with the same solution, for instance, often leads to variations of this order of magnitude. Moreover, many photometers are not stable enough to detect such small changes.

The molar absorptivity of the copper–PAN chelate, about $2.2 \times 10^3$ l.mole$^{-1}$.mm$^{-1}$, is very favourable. Of the more commonly employed copper reagents mentioned by Sandell,[9] only dithizone, oxalyldihydrazide in combination with acetaldehyde, and salicylaldoxime show a greater sensitivity.

With respect to noise level, two points are of vital importance in the present case. First, the colour-forming reaction is used in a photometric titration procedure; this means that cell errors, dust and scratches on the cell faces, and foreign absorbing substances in the sample solutions do not lead to any uncertainty in the results, because the absolute value of the absorbance is of no importance. Secondly, the apparatus used, the Zeiss Elko II, has a very high optical and electrical stability, as shown by Specker *et al.*,[10] and (for photometric titrations) by Groeneveld and den Boef.[8] This makes it possible to carry out titrations at an absorbance level of 0.01 and to read the absorbance to the fourth decimal place.*

For a titration of the self-indicating type with this apparatus under similar conditions, Groeneveld and den Boef[8] estimate the error due to instrumental causes to be about 0.6% if the total change in absorbance is 0.01. We find in series 4 of Table I a relative standard deviation of 6% for an absorbance change of 0.011. This shows that the error is mainly determined by chemical phenomena. However, this titration would hardly be possible on even a good deflection-type instrument.

From Table I the very low limit of detection can be inferred. A value of 0.01 μg in 10 ml of solution for the standard deviation compares well with figures obtained with

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* *Note.* With this high stability two drawbacks have to be taken into account. First there is the use of filters (half-bandwidth about 25 nm) instead of a monochromator. Secondly, when working with great precision or with small absorbance changes it is necessary to read the transmission scale and to convert into absorbance units by means of a nomogram. On this second point, however, a remark by Ringbom[14] is important.

other absorptiometric procedures. Gottschalk,[11] who tested the diethyldithiocarbamate method statistically, obtained a standard deviation of 0.1 μg in 15 ml of aqueous solution. Knizek and Pecenkova[12] determined copper with neocuproine and obtained a standard deviation of 0.06 μg in 5 ml of solution. For other reagents we could not find statistical figures in the literature. The investigation by Butler and Forbes[13] cannot be compared with ours, because their procedure included destruction of organic matter.

### *Selectivity*

The selectivity of our method is poorer, of course, than that of methods involving an extraction. However, the values in Table II show that for most elements a reasonable selectivity can be obtained.

This selectivity is due in part to the use of a titration procedure. All transition metals form complexes with PAN, and by use of direct spectrophotometry with addition of excess of PAN, a selective determination of copper would only be possible if a wavelength could be found where only the complex of copper absorbs, or a medium (masking, choice of pH) could be found in which the complex of copper is quantitatively formed and the other metals are not complexed. The first condition cannot be fulfilled, for all spectra of PAN chelates resemble each other. The second condition can only be fulfilled if the ratio of the conditional stability constants of the PAN complexes of copper and the interfering metal is about $10^4$ (assuming equal amounts of the two metals). In photometric titrations a ratio of $10^3$ is enough (as shown by Ringbom's methods[6]). Moreover, a kinetic effect is sometimes advantageous in photometric titrations. This is the case here for nickel. The complex of this metal with PAN is formed so slowly that in a titration of copper in the presence of a 100-fold amount of nickel a clear break in the titration curve is observed after all the copper has been complexed. When the titration is done extremely slowly, the break disappears, because then the nickel complex has time to form nearly quantitatively. In normal spectrophotometry nickel would interfere, of course.

The main interferences in the proposed procedure are caused by bismuth, iron, titanium and vanadium. The interference by 0.1 mg of bismuth in the determination of 1 μg of copper can be overcome by masking with $0.1M$ chloride. Bismuth also interferes in the diethyldithiocarbamate method, which is otherwise very selective. Using the lead complex of the reagent effectively overcomes this last difficulty, however, as Gottschalk showed.[11] The largest amount of iron(III) which can be tolerated in the titration can be increased by masking with phosphate or fluoride. The maximum ratio of iron to copper then becomes 2000, so that a copper content of 0.05% in iron can be determined as long as other elements do not interfere to a greater extent. The determination of copper in the presence of titanium and vanadium is also best carried out in a phosphate or fluoride medium. For vanadium(IV) the selectivity remains poor. When vanadium is present, a treatment with an oxidant (fuming with nitric acid) is advisable.

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## APPENDIX

The equilibrium constant of the protolysis of PAN in acid medium and the formation constant of the copper-PAN complex were measured spectrophotometrically in dioxan–water solutions (20% v/v), made up to ionic strength 0·1 with potassium nitrate. For the hydrogen ion concentration in the equilibrium expressions the concentration of the nitric acid was taken.

The p$K_a$ values were calculated from the formula:

$$\mathrm{p}K_a = -\log c_{\mathrm{HNO_3}} + \log(A_b - A) - \log(A - A_d),$$

where $A$ is the absorbance, $A_a$ is the absorbance in very acid solution and $A_b$ is the absorbance in neutral solution. From 12 results (4 results each at 425, 472 and 500 nm) a mean value was obtained for p$K_a$, of 2·35 ± 0·02 (95% confidence limits).

The equilibrium constant of the complexation reaction was measured at 0·1, 0·01 and 0·001*M* nitric acid concentrations by means of a spectrophotometric titration technique. Allowance was made for the small absorption caused by the uncomplexed PAN. Table IV gives the values for the conditional constants obtained in this way. The last column of this table gives the values for the real constant of the reaction

$$\mathrm{Cu^{2+} + HL \rightleftharpoons CuL + H^+}$$

where HL stands for the neutral PAN molecule.

TABLE IV.—DETERMINATION OF THE EQUILIBRIUM CONSTANT OF THE COMPLEXATION OF COPPER WITH PAN IN 20% (v/v) DIOXAN–WATER, IONIC STRENGTH 0·1

| Concentration of nitric acid, *M* | Wavelength, *nm* | Conditional constant | Log of equilibrium constant |
|---|---|---|---|
| 0·1 | 525 | $1{\cdot}08 \times 10^4$ | 4·40 |
| 0·1 | 550 | $1{\cdot}06 \times 10^4$ | 4·40 |
| 0·1 | 575 | $1{\cdot}19 \times 10^4$ | 4·45 |
| 0·01 | 525 | $1{\cdot}01 \times 10^6$ | 4·51 |
| 0·01 | 550 | $1{\cdot}01 \times 10^6$ | 4·51 |
| 0·01 | 575 | $0{\cdot}80 \times 10^6$ | 4·41 |
| 0·001 | 550 | $1{\cdot}92 \times 10^7$ | 4·37 |
| 0·001 | 546 | $2{\cdot}51 \times 10^7$ | 4·49 |

Mean value for log $K$ 4·44 ± 0·05 (95% confidence limits).

To convert the results for the equilibrium constants into figures for the "mixed" constants which are more usual in indicator research, a correction of 0·17 (estimated experimentally) is to be applied. The result is 2·52 for the log of the protolysis constant and 4·27 for the log of the complexation constant.

The latter result may be compared with those obtained by Pease and Williams[7] (3·81, spectrophotometry, 20% dioxan, $\mu = 0{\cdot}1$), Wada and Nakagawa[15] (4.03, spectrophotometry, 3–10% dioxan, $\mu = 0.1$) and Betteridge *et al.*[16] (1·4, solvent extraction, water phase of a water–chloroform system, $\mu = 0{\cdot}1$).

**Zusammenfassung**—Die Reaktion von Kupferionen mit Pyridylazonaphthol ist für die photometrische Titration von Kupfer gut geeignet und sehr empfindlich. Die Titration zeigt ihren Endpunkt selbst an; im 0,1 ppm-Bereich beträgt die Standardabweichung 2,5 %. Störungen kommen hauptsächlich von Wismut, Eisen, Titan und Vanadium; sie können jedoch durch geeignete Maskierung unwirksam gemacht werden.

**Résumé**—La réaction des ions cuivre avec le pyridylazonaphtol est très convenable et sensible pour le titrage photométrique du cuivre. Le titrage est auto-indicateur, et au niveau 0,1 p.p.m. l'écart type est 2,5 %. Les principales interférences sont causées par les bismuth, fer, titane et vanadium mais peuvent être surmontées par une dissimulation convenable.

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# ANALYTICAL APPLICATION AND SPECTROPHOTOMETRIC STUDY OF THE SCANDIUM-INDOFERRON COMPLEX

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**Summary**—A new spectrophotometric method for microgram amounts of scandium with indoferron is described. The molar absorptivity is 960 l. mole$^{-1}$.mm$^{-1}$ at 600 nm. Uranium and the rare earths do not interfere, if present in amounts less than 50 $\mu$g. Scandium in silicate rocks can be determined by the procedure after separation of the scandium by a three-stage ion-exchange chromatographic technique. The acid dissociation constants of indoferron and conditional formation constants of the 1:2 complex have been determined spectrophotometrically.

INDOFERRON (2,6-dibromoindo-3′-methyl-5′-*N*,*N*-dicarboxymethylaminomethylphenol) was proposed by Körbl *et al.*[1,2] as a metal indicator for chelometric titration of metal ions, including bismuth, scandium and thorium. The reagent has not been widely applied to the spectrophotometric determination of metal ions, and its proton and metal ion formation constants have not been properly determined.

This study was concerned with applying the reagent to the spectrophotometric determination of traces of scandium, especially in rocks, and the determination of acid dissociation constants of the reagent and stability constant of the scandium-indoferron complex.

## EXPERIMENTAL

### *Reagents*

*Scandium stock solution.* A stock solution containing 0·919 mg of scandium per ml of 0·1*M* hydrochloric acid was prepared and used after appropriate dilution.

*Indoferron solution.* A 0·2% solution was prepared by dissolving indoferron in demineralized water.

*Acetate buffer solution, pH* 4·1. Acetic acid (1*M*) and sodium acetate solution (1*M*) were mixed in the proportions of 4:1.

*Buffer solutions.* Hydrochloric acid–potassium chloride, acetic acid–acetate and ammonia–ammonium chloride mixtures were used for absorbance–pH investigations.

All other reagents used were of analytical reagent grade purity.

### *Recommended procedure for scandium*

Place an aliquot of solution, containing 10–90 $\mu$g of scandium, in a 25-ml volumetric flask, and add 5 ml of the acetate buffer solution (pH 4·1) and 1·0 ml of 0·2% indoferron solution. Dilute to the mark with demineralized water and mix. Measure the absorbance of the solution at 600 nm against a reagent blank as reference.

## RESULTS AND DISCUSSION

### *Spectrophotometric study for the determination of scandium with indoferron*

*Absorption spectra and characteristics.* The spectra of solutions of indoferron at various pH values, Fig. 1, have absorption maxima at 480, 490, 620 and 580 nm in

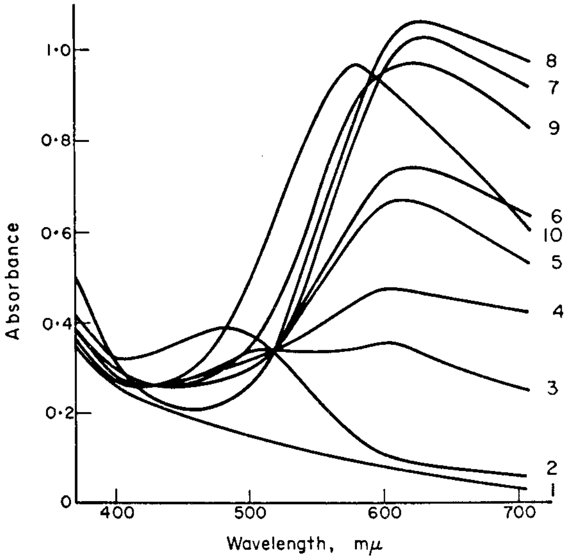


Fig. 2.—Absorption spectra for indoferron plus scandium at various pH values against water.
Indoferron 1·69 × $10^{-4}M$, scandium: 3·27 × $10^{-5}M$.
(1) pH 0·25, (2) pH 2·16, (3) pH 4·23, (4) pH 4·78, (5) pH 5·48, (6) pH 5·65, (7) pH 7·22, (8) pH 7·93, (9) pH 8·68, (10) pH 10·15.

Table I.—Effect of diverse ions on determination of 36·7 μg of scandium

| Ion | Amount added, μg | Sc found, μg | Ion | Amount added, μg | Sc found, μg |
|---|---|---|---|---|---|
| Al(III) | 100 | 52·3 | Tl(I) | 100 | 36·0 |
| Al(III) | 50 | 37·2 | Th(IV) | 50 | 48·0 |
| Bi(III) | 50 | 43·8 | Th(IV) | 10 | 37·5 |
| Bi(III) | 10 | 37·5 | U(VI) | 100 | 36·0 |
| Ce(IV) | 50 | 42·2 | U(VI) | 50 | 36·0 |
| Ce(IV) | 10 | 37·5 | W(VI) | 100 | 36·0 |
| Cr(III) | 50 | 36·0 | Y(III) | 100 | 38·4 |
| Cu(II) | 50 | 36·0 | Y(III) | 50 | 37·0 |
| Dy(III) | 100 | 38·6 | Yb(III) | 100 | 41·6 |
| Dy(III) | 50 | 37·1 | Yb(III) | 50 | 36·5 |
| Fe(III) | 50 | 63·6 | Zn(II) | 100 | 38·0 |
| Fe(III) | 10 | 43·1 | Zn(II) | 50 | 36·5 |
| Ga(III) | 100 | 41·5 | Zr(IV) | 50 | 60·6 |
| Ga(III) | 50 | 37·2 | Zr(IV) | 10 | 43·6 |
| Gd(III) | 100 | 37·6 | Sulphate | 100 | 36·6 |
| Gd(III) | 50 | 36·6 | Chloride | 100 | 36·6 |
| In(III) | 50 | 67·6 | Borate | 100 | 36·5 |
| In(III) | 10 | 43·6 | Thiocyanate | 100 | 36·7 |
| La(III) | 100 | 36·4 | Tartrate | 100 | 36·6 |
| Mo(VI) | 100 | 39·0 | Phosphate | 100 | 17·0 |
| Mo(VI) | 50 | 37·3 | Phosphate | 50 | 30·0 |
| Sm(III) | 100 | 36·4 | Phosphate | 10 | 36·5 |

Because of the many interferences, a preliminary separation is necessary before the determination of scandium, and this may be effected by a specific anion-exchange chromatographic method in dilute acid ammonium sulphate media.[3] In this method

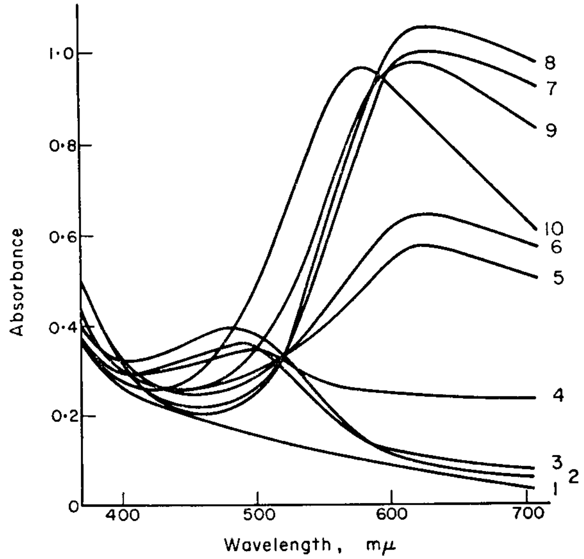


Fig. 1.—Absorption spectra for indoferron at various pH values against water. Indoferron 1·69 × $10^{-4}M$.
(1) pH 0·25, (2) pH 2·11, (3) pH 4·07, (4) pH 4·77, (5) pH 5·48, (6) pH 5·66, (7) pH 7·22, (8) pH 8·03, (9) pH 8·76, (10) pH 10·12.

pH ranges 2·0–3·0, 3·5–4·8, 5·0–8·5 and $>10$ respectively, but none at pH $< 0·7$. The spectra of indoferron in strongly acidic (pH $< 2·0$) or basic (pH $> 7·5$) media are scarcely changed by the addition of scandium, Fig. 2. Over the pH range 2·5–7·0, however, the absorbance of the mixture at 600 nm increases, indicating formation of a scandium-indoferron complex.

The absorbance is nearly constant over the pH range 3·5–4·5.

The indoferron concentration has no effect on the absorbance when 0·8–1·2 ml of 0·2% indoferron solution are added to 25 ml of buffer solution (pH 4·1) containing 73·5 μg of scandium.

At pH 4·1 the absorbance of the complex is constant when less than 7 ml amounts of the acetate buffer solution are added, but decreases on further addition, the final volume of the solution being kept at 25 ml.

The complex forms instantly at pH 4·1 and the absorbance at 600 nm remains constant for at least 2 hr.

*Conformity to Beer's law.* The absorbance of the scandium–indoferron system at pH 4·1 and 600 nm obeys Beer's law over the range 0.6–3·2 ppm of scandium in the final solution. The molar absorptivity is 960 $1.mole^{-1}.mm^{-1}$ at 600 nm.

*Effect of diverse ions.* Table I summarizes the results of the interference study for the determination of scandium under the conditions used in the procedure above. Bismuth(III), cerium(IV), indium(III), iron(III), thorium and zirconium interfere seriously, but aluminium, copper(II), gallium, molybdenum(VI), the rare earths(III) and zinc, if present in amounts less than 50 μg do not interfere with the determination of 36.7 μg of scandium. Chromium(III), thallium(I) and uranium(VI) in amounts less than 100 μg also do not interfere. Borate, chloride, nitrate, sulphate, tartrate and thiocyanate do not interfere, but phosphate must be absent.

scandium can be selectively removed by elution with 0·1*M* ammonium sulphate–0·025*M* sulphuric acid from a Dowex-1 (sulphate form) column. Scandium, 36·7–73·5 μg, mixed with 1-mg amounts of Al, Bi, Cu(II), Fe(III), Ga, In(III), Mo(VI), lanthanides (III), Th, Y, Zn and Zr, was satisfactorily determined spectrophotometrically with indoferron after the separation by the anion-exchange technique.

*Application to the determination of scandium in silicate rocks*

A complete ion-exchange chromatographic procedure for the separation of scandium in a variety of silicate rocks has been established.[4] After the decomposition of samples by means of perchloric–hydrofluoric acid digestion, traces of scandium can be separated from all interferences by a successive cation- and anion-exchange chromatographic technique in acid–ammonium sulphate media and anion-exchange in hydrochloric acid. This procedure was used to separate scandium from three types of silicate rocks before spectrophotometric determination with indoferron. The results of duplicate determinations are given in Table II, and they are compared with those obtained by an established arsenazo method.[4] There is no significant difference between values obtained by the two methods.

TABLE II.—DETERMINATION OF SCANDIUM IN SILICATE ROCKS

| Rock sample | Sc, *ppm* | |
|---|---|---|
| | Indoferron method | Arsenazo method |
| Basalt | 33·3, 33·2 (av. 33·3 ± 0·1*) | 34·7 ± 1·2* (av. of 8 detns.) |
| Andesite | 18·5, 18·8 (av. 18·7 ± 0·3*) | 20·7 ± 1·3* (av. of 12 detns.) |
| Quartz diorite | 11·6, 12·9 (av. 12·3 ± 1·1*) | 11·9 ± 1·2* (av. of 8 detns.) |

* Standard deviations based on range.

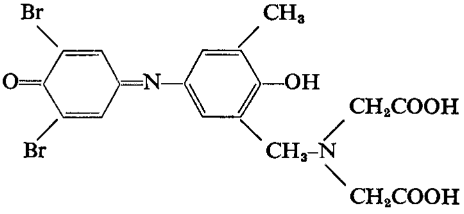
## ACID DISSOCIATION CONSTANTS OF INDOFERRON

Absorbance-pH curves of solutions of indoferron were obtained (Fig. 3) and the acid dissociation constants were calculated from them in the usual way. Above pH 2·0, dissociation of indoferron may be represented by

$$H_3A \underset{K_1}{\rightleftharpoons} H_2A^- + H^+ \underset{K_2}{\rightleftharpoons} HA^{2-} + 2H^+ \underset{K_3}{\rightleftharpoons} A^{3-} + 3H^+$$

where

$H_3A$ represents



Indoferron may be protonated in strongly acid solution below pH 0·5. The values of p$K_1$, p$K_2$ and p$K_3$ were found to be 3·01, 5·49 and 9·20 respectively.

## COMPOSITION AND STABILITY CONSTANT OF SCANDIUM-INDOFERRON COMPLEX

The ratio of scandium to indoferron in the complex at pH 4·1, ionic strength 0·1 and temperature 25 ± 0·5° was found by Job's method[5] to be 1:2. An apparent

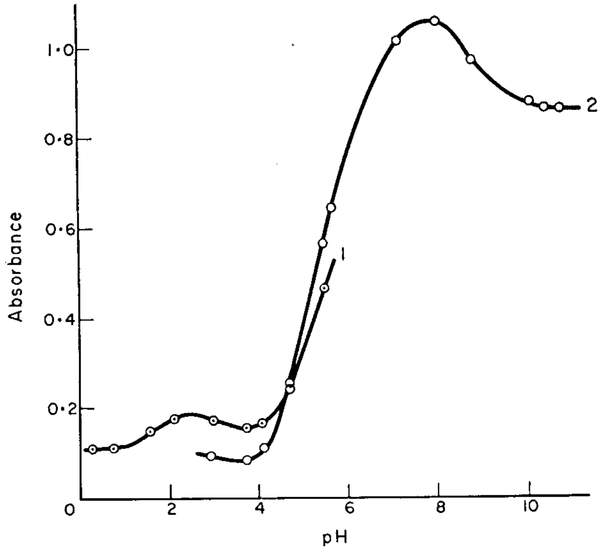


FIG. 3.—Absorbance of indoferron at various pH values.
Indoferron $1{\cdot}69 \times 10^{-4}M$; ionic strength: $0{\cdot}1M$; temp.: 25 ± 5°C.
(1) at 570 nm, (2) at 620 nm.

stability constant of the complex as calculated from the Job's plot and the equation $\beta_{12} = (1 - C)/4C^2\alpha^3$, where $\alpha = (A_m - A_s)/A_m$ and $A_m$ and $A_s$ are the theoretical and observed absorbance maxima, was found to be $5{\cdot}5 \times 10^{10}$. The molar-ratio[6] and the slope-ratio methods[7] also indicated the formation of a 1:2 complex under the same conditions; results from the molar-ratio method gave a value of $\beta_{12}$ of $5{\cdot}8 \times 10^{10}$.

Indoferron exists predominantly as the species $H_2A^-$ at pH 3·8–4.5. In the solution containing scandium and indoferron at 1:2 mole ratio, the reaction can be written

$$Sc^{3+} + 2\,H_2A^- \rightleftharpoons ScH_nA_2^{n-3} + (4 - n)H^+$$

where $n = 0, 1, 2, 3, 4$.

The equilibrium constant, $K$, is defined as

$$K = [ScH_nA_2^{n-3}][H^+]^{4-n}/[Sc^{3+}][H_2A^-]^2$$

Designating the complex as $ScL_2$, the absorbance, $A_s$, can be written as

$$A_s = \varepsilon_c[ScL_2] + \varepsilon_l C_L$$

where $C_L$ is the total concentration of all free reagent species, and $\varepsilon_c$ and $\varepsilon_l$ are the molar absorptivities of the complex and free reagent, respectively. If the total concentrations of scandium and indoferron are represented by $C_{Sco}$ and $C_{Lo}$,

$$[ScL_2] = (A_s - \varepsilon_l C_{Lo})/(\varepsilon_c - 2\varepsilon_l)$$

and the apparent stability constant, $\beta_{12}$, is defined by

$$\beta_{12} = [ScL_2]/4(C_{Sco} - [ScL_2])^3$$

At a suitable pH value, the apparent stability constant, $\beta_{12}$, may be related to the equilibrium constant, $K$, through

$$-\log K = -\log \beta_{12} + (4 - n)\text{pH}$$

A plot of log $\beta_{12}$ against pH should be linear with a slope of $(4 - n)$ and an intercept at log $K$.

Log $\beta_{12}$ was determined as a function of pH and the results are shown in Fig. 4, the slope of which is 0·97, giving $n = 3{\cdot}03$. On the basis of these observations it can be seen that the complex $ScH_3A_2$ may be formed by the reaction between one scandium and two indoferron ions at pH values ranging from 3·5 to 4·7. If it is assumed that the complex, $ScH_3A_2$, is formed by the reaction,

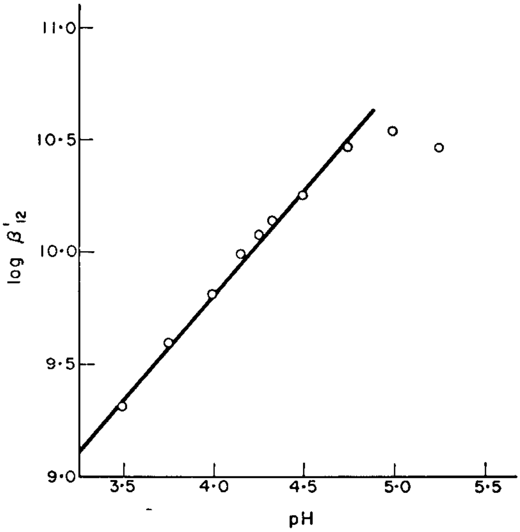


FIG. 4.—Relationship between pH and the apparent stability constants of scandium–indoferron complex.
Scandium: $7{\cdot}2 \times 10^{-5}M$; indoferron: $1{\cdot}63 \times 10^{-4}M$; ionic strength: $0{\cdot}1M$; temperature: $25{\cdot}0 \pm 0{\cdot}5°C$.

$$Sc^{3+} + H_2A^- + HA^{2-} \rightleftharpoons ScH_3A_2$$

the formation constant $\beta_{132}$, is defined as

$$\beta_{132} = [ScH_3A_2]/[Sc^{3+}][H_2A^-][HA^{2-}]$$

Total concentrations of scandium and indoferron are given by

$$C_{Sc_0} = C_{Sc} + [ScH_3A_2]$$

and

$$C_{L_0} = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}] + 2[ScH_3A_2]$$

The acid dissociation constants of indoferron are related to the formation constant of the complex,

$$\beta_{132} = \frac{[ScH_3A_2]}{4[(C_{Sc_0} - [ScH_3A_2])^3}\left\{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} + \frac{K_2K_3}{[H^+]^2}\right\}\left\{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1 + \frac{K_3}{[H^+]}\right\}$$

The constant, log $\beta_{132}$, was estimated to be 10·43 at pH 4·1 and 10·35 at pH 4·5.

*Acknowledgement*—The authors are greatly indebted to Professor R. Kuroda, University of Chiba, for many helpful discussions and suggestions during this study.

**Zusammenfassung**—Eine neue spektrophotometrische Analysenmethode für Mikrogrammengen Scandium mit Indoferron wird beschrieben. Der molare Extinktionskoeffizient beträgt 960 l. $mol^{-1}$ . $mm^{-1}$ bei 600 nm. Uran und die seltenen Erden stören nicht, wenn sie in kleineren Mengen als 50 μg vorkommen. Scandium in Silikatgesteinen kann mit dem Verfahren bestimmt werden, wenn es vorher durch dreistufige Ionenaustauschchromatographie abgetrennt wurde. Die Säuredissoziationskonstanten von Indoferron und die Bildunsgkonstanten des 1:2-Komplexes unter den betreffenden Bedingungen wurden spektrophotometrisch ermittelt.

**Résumé**—On décrit une nouvelle méthode spectrophotométrique pour le dosage de quantités de scandium de l'ordre du microgramme avec l'indoferron. Le coefficient d'absorption moléculaire est de 960 l. $mol^{-1}$ . $mm^{-1}$ à 600 nm. L'uranium et les terres rares ne gènent pas, s'ils sont présents en quantités inférieures à 50 μg. On peut, par la technique, déterminer le scandium dans les roches aux silicates après séparation du scandium par une technique chromatographique d'échange d'ions en trois stades. On a déterminé spectrophotométriquement les constantes de dissociation acide de l'indoferron et les constantes de formation conditionnelles du complexe 1:2.

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# CO-PRECIPITATION OF METAL DIMETHYLGLYOXIMATES GENERATED FROM BIACETYL MONOXIME OR BIACETYL AND HYDROXYLAMINE

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**Summary**—A study has been made of some aspects of the co-precipitation of gold and platinum(II) and (IV) with palladium(II) precipitated from homogeneous solution initially containing biacetyl and hydroxylamine in 0·3*M* hydrochloric acid. The co-precipitation of nickel(II) with palladium(II) and *vice versa* from near neutral solutions initially containing biacetyl and hydroxylamine was also explored; the solid is enriched in the minor constituent in both cases. As with biacetyl monoxime-hydroxylamine systems, both nickel(II) and palladium(II) promote formation of dimethylglyoxime from such solutions between pH 7 and 8. Factors leading to this unusual behaviour in co-precipitation are discussed and a qualitative explanation tentatively advanced. The co-precipitation of nickel and palladium(II) is different when biacetyl monoxime solutions are used; the former comes out of solution faster than the latter irrespective of their concentration ratio. This disparity in the reaction rates can be used to separate nickel directly from palladium(II) by precipitation or extraction of the dimethylglyoximate into chloroform.

BIACETYL MONOXIME and biacetyl react with hydroxylamine in aqueous solution to give dimethylglyoxime. The reaction carried out in the presence of either nickel(II) or palladium(II) gives rise to methods for the precipitation of the respective bisdimethylglyoximates from homogeneous solution as shown by Gordon and his coworkers[1–7].

In the work described in this paper the co-precipitation of gold and platinum with palladium(II) precipitated from 0·3*M* hydrochloric acid by the homogeneous solution method starting from biacetyl is compared with the products from other methods of precipitation. Aspects of the behaviour of nickel and palladium(II) in precipitation and co-precipitation from biacetyl monoxime–hydroxylamine and biacetyl–hydroxylamine media in the pH range 7–8 and occasionally beyond, are also examined. Various factors contributing to the observed results have been investigated qualitatively.

## EXPERIMENTAL

### *Reagents*

Reagent grade chemicals were used unless otherwise stated.

*Nickel and palladium.* Aqueous solutions containing 3 mg of nickel(II) and 2·7 mg of palladium(II) per ml were prepared from hydrated nickel sulphate and palladium(II) chloride respectively. The palladium salt was dissolved in 0·005*M* hydrochloric acid; when necessary the pH was adjusted by the addition of dilute ammonia.

The nickel and palladium solutions were standardized gravimetrically with dimethylglyoxime.

*Platinum*-197, specific activity 15 mCi/g, was obtained by thermal neutron irradiation of platinum. It contained some gold-199 which was removed by extraction into ethyl acetate.[8]

*Gold*-198, from neutron irradiation of gold, had a specific activity of 5 Ci/g.

The irradiated gold and platinum were dissolved separately in *aqua regia* and oxides of nitrogen were expelled by repeated evaporation with hydrochloric acid. Solutions containing labelled platinum(II) were prepared by reduction of the platinum(IV) solution with sulphur dioxide.[9]

Stock solutions of the platinum-197 and gold-198 were prepared in 1*M* hydrochloric acid. Both were measured with a well-type NaI(Tl) scintillation detector.

*Palladium*-103. This was obtained containing substantial amounts of inactive palladium, by irradiation of palladium in a thermal neutron flux; the purification from silver was effected by successive precipitations of added silver ion as silver chloride or by the ion-exchange method previously described.[10] A labelled stock solution prepared from the purified palladium was standardized gravimetrically. X-Rays, resulting from the electron capture process in the decay of this isotope, were measured by NaI(Tl) scintillation detectors.

*Hydroxylamine hydrochloride.* A 1·8% w/v stock solution was prepared.

*Biacetyl monoxime* (Puriss. grade, Koch-Light) was further purified by triple sublimation.

Nickel-63, biacetyl, other substances and the methods of investigation used have been described[11] except in the case of the experiment with gold; in these measurements the gold in the precipitate was determined radiometrically (*via* gold-198) as the fraction of the total gold initially present, and "completeness" of precipitation of palladium was checked by examination of the filtrate.

## RESULTS AND DISCUSSION

### *Co-precipitation of gold and platinum with palladium from a biacetyl system*

Gold ions in solution tend to be reduced to the element in the presence of dimethylglyoxime[12] while platinum(II) has been claimed[13] to give a bisdimethylglyoximate isomorphous with those of palladium(II) and nickel(II). Complete precipitation of palladium(II) in the presence of gold [initially added as gold(III)] and platinum(II) and (IV) [present as chloro-complexes] gave rise to the results presented in Tables I and II.

TABLE I.—CO-PRECIPITATION OF GOLD FOR COMPLETE OR NEAR COMPLETE PRECIPITATION OF PALLADIUM(II) FROM 0·3*M* HYDROCHLORIC ACID SOLUTION AT 23°C

| Init. conc. of gold, *M* | Gold pptd., % | Reaction time, *min* | Method |
|---|---|---|---|
| $5{\cdot}2 \times 10^{-8}$ | 34·6 | 120 | A |
| $5{\cdot}2 \times 10^{-8}$ | 15·1 | 60 | A |
| $5{\cdot}2 \times 10^{-8}$ | 4·5 | 20 | A |
| $1{\cdot}0 \times 10^{-3}$ | 93·7 | 120 | A |
| $1{\cdot}0 \times 10^{-3}$ | 88·5 | 120 | A |
| $5{\cdot}2 \times 10^{-8}$ | 13·6 | 60 | B |
| $5{\cdot}2 \times 10^{-8}$ | 17·1 | 80 | B |
| $5{\cdot}2 \times 10^{-8}$ | 39·1 | 960 | C |
| $5{\cdot}2 \times 10^{-8}$ | 25·6 | 300 | C |
| $5{\cdot}2 \times 10^{-8}$ | 23·2 | 200 | C |
| $5{\cdot}2 \times 10^{-8}$ | 18·4 | 120 | C |
| $2{\cdot}5 \times 10^{-4}$ | 4·9 | 960 | C |
| $2{\cdot}5 \times 10^{-4}$ | 5·1 | 960 | C |
| $2{\cdot}5 \times 10^{-4}$ | 18·2 | 1200 | C |
| $2{\cdot}5 \times 10^{-4}$ | 17·1 | 1200 | C |
| $2{\cdot}5 \times 10^{-4}$ | ~4 | 1200 | D |

Initial palladium(II) concentration, $1{\cdot}01 \times 10^{-3}M$, total volume of solution 200 ml.

A, addition of 15 ml of 1% w/v ethanolic solution of dimethylglyoxime (HD) to the aqueous palladium(II).

B, addition of 15 ml of 1% w/v acetone solution of HD to a 1:3 v/v acetone–aqueous solution of palladium(II).

C, precipitation from homogeneous solution; initial concentrations: $6 \times 10^{-3}M$ biacetyl and $2{\cdot}3 \times 10^{-2}M$ hydroxylamine.

D, palladium(II) and biacetyl absent, otherwise as in C.

Substantial fractions of the gold precipitate following the direct addition of dimethylglyoximate (Table I); the fraction increases with the reaction time. It is likely that the gold is reduced rather slowly at room temperatures by the dimethylglyoxime to the elemental form and is thus collected on the palladium precipitate; as long as palladium(II) remains in the solution, however, the gold ions will be forced

TABLE II.—CO-PRECIPITATION OF PLATINUM FOR COMPLETE PRECIPITATION OF PALLADIUM BY VARIOUS METHODS

| Platinum co-pptd., % | | | | |
|---|---|---|---|---|
| *a* | *b* | *c* | *d* | *e* |
| 4·23 | 0·15 | 4·15 | 5·95 | 0·79 |
| 3·06 | 0·17 | 3·80 | 5·79 | 0·69 |
| 3·16 | 0·16 | 3·10 | 4·80 | 0·67 |

Initial concentrations: palladium 1·01 × $10^{-3}M$, platinum 2·4 × $10^{-6}M$, biacetyl 6·0 × $10^{-3}M$, and hydroxylamine 2·3 × $10^{-2}M$.

Addition of 15 ml of 1% w/v ethanolic dimethylglyoxime to 200 ml of aqueous palladium(II) containing (*a*) platinum(II) or (*b*) platinum(IV). (*c*) Platinum(II) in 25% v/v aqueous acetone containing the palladium(II).

Application of the method of Kanner, Salesin and Gordon[3] to solutions containing palladium(II), biacetyl, hydroxylamine and (*d*) platinum(II) or (*e*) platinum(IV).

Each solution was 0·3*M* in hydrochloric acid; precipitates from *a*, *b* and *c* were collected 2 hr, from *d* and *e* 16 hr, after mixing of the components.

to compete for dimethylglyoxime. Hence the standing time and the excess of dimethylglyoxime added will largely determine the extent of the gold co-precipitation with palladium(II). In precipitation from homogeneous solution, the most important single factor in determining the extent of co-precipitation of gold is probably the standing time. Other substances present in the solution and having reducing properties, such as hydroxylamine, may contribute to reduction of the gold, and the method of precipitation from homogeneous solution thus suffers from the relatively long time (16 hr) required for complete precipitation of palladium(II). Nevertheless from a $10^{-3}M$ solution containing a 4:1 molar ratio of palladium to gold only a few per cent of the latter are collected with the palladium (Table I).

Platinum(II) co-precipitates to a greater extent than does platinum(IV) at low concentrations, as might be expected since the latter is not precipitated directly by dimethylglyoxime under the conditions employed for palladium precipitation. Kanner, Salesin and Gordon[6] have studied the precipitation of palladium from solutions containing appreciable amounts of platinum and so this system was not studied further. Neither of the two limiting laws[14] describing co-precipitation as a function of fractional precipitation of carrier applicable to gold or platinum carried down by palladium dimethylglyoximate precipitated from homogeneous solution.

### *Co-precipitation of palladium and nickel from biacetyl monoxime and biacetyl systems*

Palladium and nickel give rise to nearly isostructural dimethylglyoximate crystals.[15] At 23° and also 50° trace component enrichment in the solid phase from biacetyl solution is observed irrespective of whether the carrier is nickel or palladium (Figs. 1 and 2). This is in contrast to systems in which biacetyl monoxime and hydroxylamine provide the dimethylglyoxime (Fig 3). Neither limiting law[14] describing co-precipitation behaviour applies to these systems. Previous studies of co-precipitation of purely inorganic substances have shown[14] that change of the molar ratio of the metal ions over wide ranges did not affect *D* or $\lambda$ coefficients (which determine enrichment) from these laws. To the best of our knowledge the behaviour shown by nickel(II) and palladium(II) in Figs. 1 and 2 has not been observed for any other

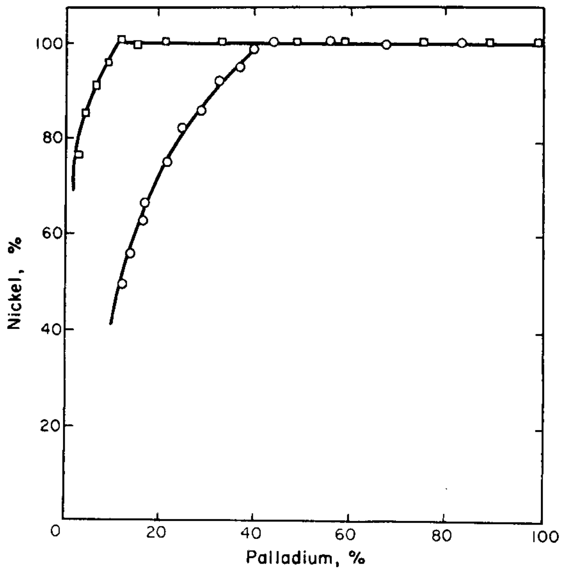

FIG. 1.—Co-precipitation of nickel(II) tracer with palladium(II) carrier. □ At 23°C, ○ at 50°C. Initial concentrations: $3\cdot8 \times 10^{-8}M$ nickel(II), $1\cdot01 \times 10^{-3}M$ palladium(II), $6\cdot0 \times 10^{-3}M$ biacetyl and $2\cdot3 \times 10^{-2}M$ hydroxylamine. Initial pH 7·6.

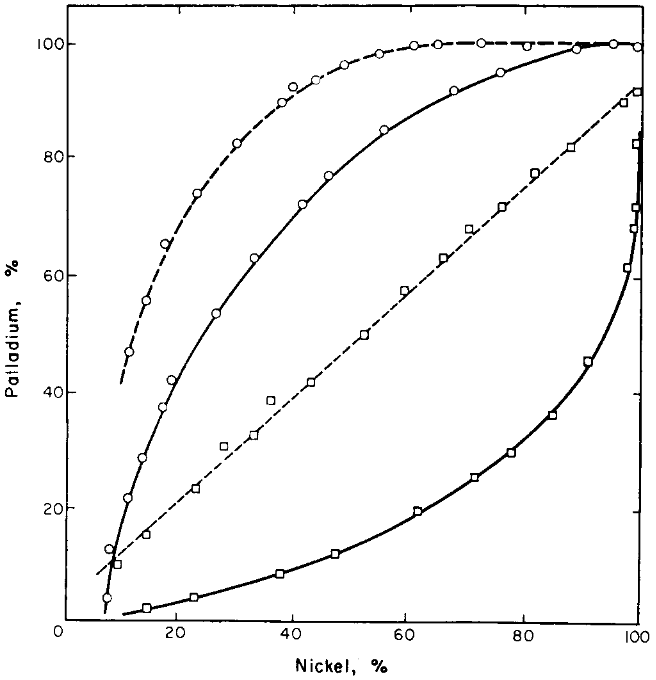

FIG. 2.—Co-precipitation of palladium(II) with nickel(II);
○ Palladium initially $9\cdot5 \times 10^{-6}M$ and nickel initially $2\cdot56 \times 10^{-3}M$; □ palladium(II) and nickel(II) each initially $1\cdot28 \times 10^{-3}M$. Broken lines represent data at 50°C and full lines 23°C. Initial pH 7·6.

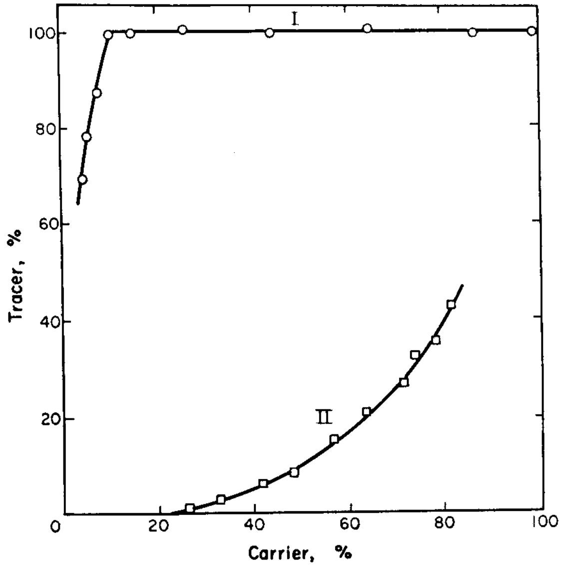

FIG. 3.—Co-precipitation of nickel(II) (traces) with palladium(II) carrier (curve I) and palladium (traces) with nickel(II) carrier (curve II) at 23°.
Initial concentrations: nickel(II) and palladium(II), 2·82 × $10^{-6}M$ as trace components; nickel(II) and palladium(II), 1·28 × $10^{-3}M$ as carriers; biacetyl monoxime, 2·5 × $10^{-3}M$ and hydroxylamine 3·6 × $10^{-2}M$. Initial pH 7·6.

system. A 1 : 1 molar ratio of palladium(II) to nickel(II) gives precipitates with nickel enrichment at 23°, but at 50° enrichment is much reduced. At trace levels it is seen from Figs. 1 and 2 that at 50° nickel enrichment is decreased and palladium increased relative to the respective carrier.

Some studies on systems containing only one of the two metals were carried out to obtain data on the relative importance of the various factors contributing to precipitation.

A study of the effect of temperature revealed that the mean rate of precipitation of palladium is more temperature-sensitive than that of nickel, a result in qualitative accord with the co-precipitation data (Figs. 1 and 2). At 23°, hydroxyl ion influences the mean rate of precipitation of nickel more than that of palladium. For biacetyl monoxime and biacetyl systems the hydroxyl ion concentration measured as a function of time initially increases steeply in the presence of palladium(II) and passes through a broad maximum, whereas it decreases from the beginning in the presence of nickel(II) [see for example Fig. 4]. The increase probably arises from reactions involving ions such as $Pd(NH_3)_4^{2+}$, $Pd(NH_3)_3Cl^+$ or $Pd(NH_3)_3OH^+$ which lose ammonia and hydroxyl ion by biacetyl monoxime or biacetyl substitution or in the formation of reaction intermediates leading to dimethylglyoxime. A hydrated metal ion, *e.g.*, $Ni_{aq}^{2+}$ would be expected to give a continuous decrease in hydroxyl ion concentration as its dimethylglyoximate precipitates.

From experiments carried out under controlled conditions it was found that the rate of precipitation of either metal dimethylglyoximate was a function of the formal metal ion concentration in solution. Evidence was thus obtained for the participation of nickel and palladium(II) ions in the formation of the dimethylglyoxime (see for

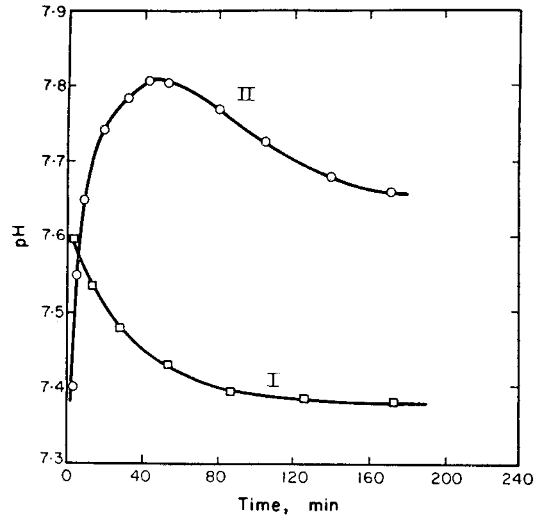

FIG. 4.—pH plotted as a function of time for a solution as 23° initially containing $1{\cdot}28 \times 10^{-3}M$ nickel(II) [curve I] or palladium(II) [curve II], $2{\cdot}5 \times 10^{-3}M$ biacetyl monoxime and $3{\cdot}6 \times 10^{-2}M$ hydroxylamine.

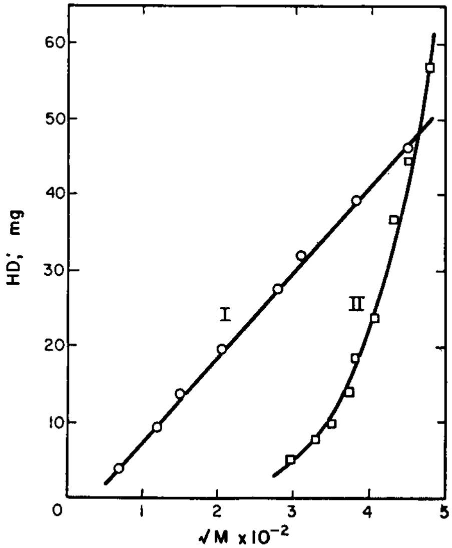

FIG. 5.—The effect of the mean formal metal ion concentration in solution on the formation of dimethylglyoxime (HD) in 25 min at 23°C.
Initial concentrations: $1{\cdot}05 \times 10^{-2}M$ biacetyl and $5{\cdot}14 \times 10^{-2}M$ hydroxylamine. pH 7·6. Nickel(II) [curve I], palladium(II) [curve II].

example Fig. 5). The results recorded in Table III illustrate well the effect of the metal ion above pH 7 for a biacetyl monoxime system. When both nickel(II) and palladium(II) are present in solutions containing biacetyl, the precipitation of the latter metal ion is enchanced roughly by a factor of two under the conditions of the experiments (Table IV). Owing to the complex manner in which the pH changes, a sufficiently reliable measure of the amount of nickel expected in the absence of interference

TABLE III.—FORMATION OF DIMETHYLGLYOXIME, HD, AT 23°C IN 21 MINUTES FROM MIXING THE REACTANTS AT THE pH RECORDED

| pH | 9·40* | 8·32* | 7·71* | 7·24* | 7·90 | 7·85 | 7·65 | 7·50 | 7·26 | 7·20 |
|---|---|---|---|---|---|---|---|---|---|---|
| HD, mg. | 0·20 | 0·18 | 0·18 | 0·20 | 40·8 | 39·1 | 28·4 | 24·2 | 15·7 | 10·2 |

Initial concentration in 200 ml: biacetyl monoxime $2·5 \times 10^{-3}M$, hydroxylamine $3·6 \times 10^{-2}M$, nickel(II) $1·28 \times 10^{-3}M$.

* Nickel(II) absent, but at the end of the reaction period the pH was quickly reduced to 7·2 and nickel(II) was added to determine the amount of HD formed.

from palladium(II) is not readily obtained; it was only possible to give limits below which the nickel bisdimethylglyoximate yield is expected to lie. These limits were read from a curve giving the amount of nickel precipitate formed in 25 min, plotted against the final pH values over the required range for solutions of initial biacetyl, hydroxylamine and nickel(II) concentrations as given in Table IV. The values quoted suggest that palladium(II) gains at the expense of nickel(II), probably by metal-ion exchange at some stage or stages in the formation of the dimethylglyoxime, or with nickel(II) monodimethylglyoximate. [Exchange with nickel(II) bisdimethylglyoximate was found to be very slight.]

TABLE IV.—PRECIPITATION OF PALLADIUM(II) BISDIMETHYLGLYOXIMATE EITHER IN THE ABSENCE OR PRESENCE OF NICKEL(II) FROM 200 ml OF SOLUTION AT 23°C

| $[\mathrm{Ni}^{2+}]$, $10^{-4}M$ | Reaction time, *min* | Initial pH | Final pH | $\mathrm{PdD_2}$ found, *mg* | $\mathrm{NiD_2}$ found, *mg* | $\mathrm{NiD_2}$ estimated, *mg* |
|---|---|---|---|---|---|---|
| 0·00 | 25 | 7·28 | 7·47 | 2·8 | 0·0 | 0·0 |
| 5·16 | 25 | 7·25 | 7·36 | 6·2 | 15·2 | <18 |
| 0·00 | 25 | 7·50 | 7·65 | 4·3 | 0·0 | 0·0 |
| 5·16 | 25 | 7·50 | 7·58 | 6·9 | 25·0 | <30 |
| 0·00 | 25 | 7·37 | 7·52 | 3·1 | 0·0 | 0·0 |
| 5·16 | 25 | 7·37 | 7·47 | 5·0 | 17·1 | <24 |

Initial concentrations: hydroxylamine $5·14 \times 10^{-2}M$, biacetyl $1·04 \times 10^{-2}M$, palladium(II) $1·10 \times 10^{-3}M$.

D is the dimethylglyoximate ion.

The observed co-precipitation phemomena for trace component and carrier systems starting from biacetyl may be explained qualitatively as set out below.

1. Nickel(II) promotes the production of dimethylglyoxime faster than does palladium(II) [see Fig. 5]. When nickel(II) is present as the minor constituent it will lose by exchange with palladium(II) but gain in rate relative to the carrier by the increase in pH as palladium precipitates.

2. When palladium(II) is the minor component and nickel(II) the carrier, the pH decreases as nickel(II) reacts, to the advantage of the palladium. In addition the relatively high concentration of nickel intermediates such as the monodimethylglyoximate will enhance the rate of metal ion exchange in favour of palladium(II).

As the ratios of nickel(II) to palladium(II) become closer to unity pH changes will tend to cancel each other and metal-ion exchange is also likely to be less important; nickel(II) again dominates at ratios above 1:1 at 23° (Fig. 2).

This explanation needs modification in considering co-precipitation from homogeneous solution starting from biacetyl monoxime; the difference in rates of formation of metal bisdimethylglyoximate remains in favour of nickel over wide ratios of nickel to palladium(II) concentrations. This may be due to a more limited opportunity for metal-ion exchange to occur in reaction intermediates.

The disparity in the rates (estimated to be more than an order of magnitude) at which nickel(II) and palladium(II) form bisdimethylglyoximates above pH 7 can be used to separate the former directly from the latter either by precipitation or, for micro amounts, by liquid–liquid extraction. Tables V and VI give some data on typical separations achieved under different conditions. Clearly optimum conditions depend on the concentration ratios of metal ions present initially but in general an increase in pH or in hydroxylamine concentration enhances the nickel reaction relative to that of palladium. The amount of palladium co-extracted was checked and found to be less than 0·1% of the total palladium present. Hydroxylamine is known[16] to coordinate to palladium(II) and hence in the present context it may have a partial masking effect on the palladium.

Table V.—The separation of nickel(II) by precipitation in the presence of palladium(II) from biacetyl monoxime-hydroxylamine solution at about 20°C

| Reagents | | Initial concentrations | | Nickel precipitated, % | Reaction time, *min* | Initial pH | Notes |
|---|---|---|---|---|---|---|---|
| [HM] $10^{-2}M$ | [HX] $10^{-2}M$ | [$Pd^{2+}$] $10^{-3}M$ | [$Ni^{2+}$] $10^{-3}M$ | | | | |
| 1·00 | 7·1 | 1·28 | 2·56 | 98·7 | 4 | 8·1 | — |
| 1·00 | 7·1 | 1·28 | 1·28 | 99·1 | 3 | 7·9 | — |
| 1·00 | 7·1 | 1·28 | 1·28 | 98·7 | 2 | 7·8 | — |
| 1·00 | 7·1 | 2·56 | 1·28 | 96·3 | 3 | 7·9 | 7% Pd co-pptd. |
| 1·00 | 10·5 | 1·00 | 1·28 | 99·1 | 2 | 7·9 | — |
| 1·00 | 10·5 | 1·00 | 1·28 | 99·6 | 4 | 8·0 | — |
| 0·81 | 7·1 | 0·8 | 1·28 | 99·3 | 5 | 7·9 | — |
| 0·81 | 7·1 | 0·8 | 1·28 | 101·3 | 12 | 7·9 | 1% Pd. co-pptd. |
| 0·45 | 5·1 | 0·2 | 1·28 | 99·8 | 5 | 7·9 | — |
| 0·81 | 5·1 | 1·00 | 0·26 | 99 | 2 | 7·9 | — |
| 1·2 | 15·0 | 2·70 | 0·26 | 100 | 5 | 9·0 | 1% Pd co-pptd. |
| 0·7 | 15·0 | 2·70 | 0·26 | 99 | 4 | 9·0 | — |
| 0·5 | 15·0 | 2·70 | 0·26 | 100 | 5 | 9·0 | — |
| 0·5 | 15·0 | 2·70 | 0·26 | 98 | 4 | 9·0 | — |

Table VI.—Separation of nickel from palladium by extraction of the former from aqueous biacetyl monoxime–hydroxylamine at pH 8·7–9·0 into chloroform

| [HM] $10^{-2}M$ | [HX] $10^{-2}M$ | [$Pd^{2+}$] $10^{-3}M$ | [$Ni^{2+}$] $10^{-5}M$ | $Ni^{2+}$ extracted*, % |
|---|---|---|---|---|
| 0·5 | 15·0 | 2·70 | 5·4 | 98 |
| 0·5 | 15·0 | 2·70 | 1·8 | 97 |
| 0·5 | 15·0 | 2·70 | 1·8 | 100 |
| 0·3 | 7·6 | 2·70 | 1·8 | 96 |
| 0·25 | 7·6 | 2·70 | 0·9 | 99 |

* The nickel was labelled with nickel-63 and determined by liquid-scintillation counting after 1–2 min shaking. Aqueous phase 100 ml, chloroform phase 50 ml.

**Zusammenfassung**—Teilaspekte der Mitfällung von Gold und Platin(II) and -(IV) mit aus homogener Lösung mit Biacetyl und Hydroxylamin in 0,3$M$ Salzsäure gefälltem Palladium(II) wurden untersucht. Die Mitfällung von Nickel(II) mit Palladium(II) und umgekehrt aus etwa neutralen Lösungen, die anfangs Biacetyl und Hydroxylamin enthielten, wurde ebenfalls untersucht: der Festkörper ist beidesmal mit dem geringeren Bestandteil angereichert. Wie bei Systemen aus Biacetylmonoxim und Hydroxylamin fördern Nickel(II) und Palladium(II) die Bildung von Dimethylglyoxim in Lösungen zwischen pH 7 und 8. Die zu solch ungewöhnlichem Verhalten bei der Mitfällung beitragenden Faktoren werden diskutiert und eine vorläufige qualitative Erklärung gegeben. Die Mitfällung von Nickel und Palladium(II) verläuft anders, wenn von Biacetylmonoxim verwendet werden; Nickel fällt schneller aus als Palladium, unabhängig vom Konzentrationsverhältnis. Dieser Unterschied in den Reaktionsgeschwindigkeiten kann zur direkten Trennung von Nickel und Palladium(II) dienen, indem man das Dimethylglyoximat fällt oder in Chloroform extrahiert.

**Résumé**—On a effectué une étude de quelques aspects de la coprécipitation de l'or et du platine(II) et (IV) avec le palladium(II) précipité d'une solution homogène contenant initialement du diacétyle et de l'hydroxylamine en acide chlorhydrique 0,3$M$. On a aussi examiné la coprécipitation du nickel(II) avec le palladium(II) et *vice versa* de solutions voisines de la neutralité contenant initialement du diacétyle et de l'hydroxylamine; dans les deux cas, le solide est enrichi en le constituant mineur. Comme avec les systèmes diacétylemonoxime–hydroxylamine, le nickel(II) et le palladium(II) favorisent tous deux la formation de diméthylglyoxime à partir de telles solutions entre pH 7 et 8. On discute des facteurs menant à ce comportement inhabituel dans la coprécipitation et l'on suggère une explication qualitative. La coprécipitation du nickel et du palladium(II) est différente lorsqu'on utilise des solutions de diacétylemonoxime; le premier se sépare de la solution plus rapidement que le dernier, quel que soit leur rapport de concentrations. Cette disparité dans les vitesses de réaction peut être utilisée pour séparer directement le nickel du palladium(II) par précipitation ou extraction du diméthylglyoximate en chloroforme.

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# ALKALINE ERRORS OF GLASS ELECTRODES IN NON-AQUEOUS SOLVENTS

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**Summary**—Alkaline errors of glass electrodes in isopropanol were obtained from a comparison with the hydrogen electrode. Electrode glasses which show low alkaline errors in water are also more ideal in isopropanol. Univalent metal ions cause larger deviations than bivalent. Hysteresis effects were found in going from alkaline to acid solutions but not for the reverse direction.

SINCE its introduction the glass electrode has been an object of critical studies and investigations. It was soon shown to be non-ideal in acidic, basic and non-aqueous media. The behaviour in non-aqueous solutions exposed irregularities that cast doubt on the applicability of the glass electrode in these media. Dole[1] placed the non-aqueous solution errors in a group of apparent negative errors. The Corning 015 glass used in most early studies was successively replaced by lithia glass compositions which had much lower alkaline errors. These new electrodes were used with some success for titrations in organic solvents as shown by the large number of publications. In spite of this very little is known about the exact behaviour of the glass electrode in non-aqueous solutions. In some organic solvents an almost ideal response has been reported.[2,3]

Harlow[4] has studied the influence of small amounts of potassium ion in a titrant (0·25*M* tetrabutylammonium hydroxide) in 80% pyridine and 20% isopropanol. Potassium ions decreased the sensitivity to changes in acidity. The size of the effect varied from one electrode to another and was dependent on pretreatment. The changes in medium which occurred during a run prevented a quantitative evaluation of the results.

Rechnitz and co-workers[5,6] have made measurements with cation-selective electrodes in partially aqueous media. The electrodes showed anomalous behaviour for $H^+$ in ethanol–water mixtures. The electrode response to alkali metal cations was supposed to be solvent-independent for a given concentration and type of solute. McClure and Reddy[7] have reported cationic glass electrode response to alkali metal ions in propylene carbonate, acetonitrile, and dimethylformamide. They noted that the glass electrode ceased to respond in acetonitrile after three months. The response time in the solvents was short, being from 5 to 10 sec.

There seems to be insufficient information concerning glass electrode behaviour in non-aqueous solvents. The present study was therefore undertaken to obtain a quantitative measure of the cation response. Glass electrodes were compared directly against hydrogen electrodes and the difference was taken as a measure of the non-ideality of the glass electrode. Isopropanol was selected as a medium mainly because other studies of electrode behaviour have been made in this solvent.

## EXPERIMENTAL

Buffer solutions were prepared by partially titrating 0·02*M* di-isopropylamine with perchloric acid. The water content of the isopropanol (Merck, *p.a.*) was less than 0·1% and in the making of the buffer it did not increase by more than another 0·1% from water in the perchloric acid. The exact amount of amine in each buffer was determined by titration to the end-point. In the latter procedure an Ag/AgCl reference electrode, separated from the test solution by a sintered-glass disc, was used instead of the hydrogen electrodes. These buffer solutions also contained a known amount of either sodium, lithium or barium perchlorate (dried at 130°). In the selection of a base for the buffers several aspects must be considered. Tetraethylammonium hydroxide was rejected because of the low solubility of the perchlorate in isopropanol, and diphenylguanidine because it is reduced in the presence of hydrogen-saturated platinum black.

Potentiometric measurements were made at 25° with a Radiometer pH Meter 4d. Three wash-bottles for the hydrogen gas were used, the first containing pure isopropanol and the others portions of the test solution in question. The titration vessel could accommodate three glass electrodes and two hydrogen electrodes. Titrations were made with a Metrohm piston burette E 274. An electrode selector permitted fast and easy readings. Two readings were made for every possible combination of glass electrode and hydrogen electrode.

The glass electrodes were stored in distilled water when not in use. Before measurement they were rinsed in isopropanol and immersed in a portion of the actual test solution for at least 15 min. After transfer to the test solution they were allowed to stabilize for a further 10 min. No drift was observed when the electrodes were treated in this way. Prolonged storing in isopropanol was avoided since some buffer substances can cause a slow response.

A Hildebrand-type hydrogen electrode with two platinum foils was employed. The old coating was removed with *aqua regia*. After treatment with concentrated nitric acid and cathodic electrolysis in diluted sulphuric acid as a check of careful cleaning, the foils were platinized without delay according to the method described by Bates.[8] The electrodes were then thoroughly rinsed in isopropanol and stored in a portion of the test solution for 15 min with the hydrogen gas stream turned on. The potential difference was followed until it became zero, which usually took less than 10 min. Fresh hydrogen electrodes were prepared at least once a day. The hydrogen electrode has previously been used in water–isopropanol mixtures[9,10] but information for its use in pure isopropanol is scanty.

The silver–silver chloride electrode has commonly been used in non-aqueous solvents and the behaviour in isopropanol has been studied.[3] The use of reference electrodes in non-aqueous solutions has been summarized by Ives and Janz.[11]

## RESULTS

The base di-isopropylamine dissociates[3] in isopropanol according to

$$B + H^+ \rightleftharpoons BH^+ \tag{1}$$

If $P$ is the per cent of base titrated, $\log P/(100 - P)$ can be taken as a measure of the acidity. Figure 1 shows the potential of the hydrogen electrode with respect to the Ag/AgCl electrode plotted against this function. A definite curvature shows that equation (1) is not sufficient to explain the behaviour of the amine, provided the hydrogen electrode response can be taken as a true measure of acidity. Glass electrodes gave similar curves in buffers containing barium perchlorate. Such curvature can also be seen in the results of ref. 3 and is probably due to association. The function $\log P/(100\text{-}P)$ was therefore only used as a means of relating the hydrogen and glass electrode potentials. Interpolation between experimental points gave potentials for all the series at the same acidities.

In order to measure glass electrode deviations an ideal Nernstian line must be found. This ideal line should be obtained from measurements in an acidity range where the deviations are negligible, that is the medium range. The glass electrode potential referred to the hydrogen electrode in this range is denoted by $E'$. Few buffer substances were suitable so it was not possible to cover the whole of the acidity range. Measurements could be made on the acid side and in the region of non-ideality but not between. Extrapolation of a line over such a distance proved to be unreliable so another procedure was adopted. The most acid point in the alkaline buffer, where $\log P/(100 - P) = 1$, had a small unknown error. This error was

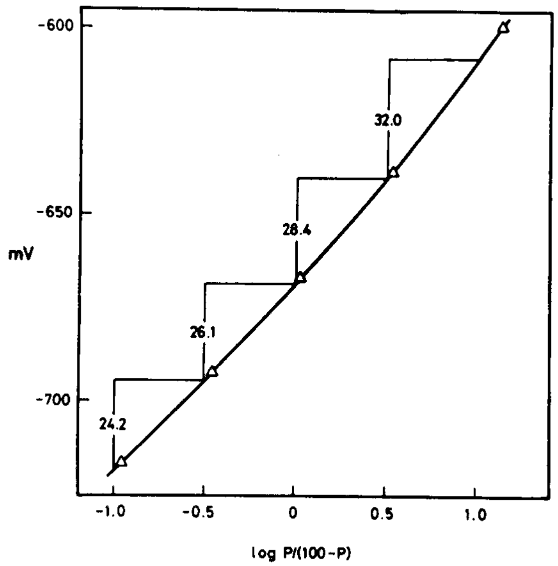

FIG. 1.—Hydrogen electrode potential *vs.* Ag/AgCl as a function of log $P/(100\text{-}P)$.

arbitrarily set at zero and the deviations from a line of ideal slope were tabulated for several types and makes of glass electrode (see Table I). The table shows that the deviations are larger in the presence of lithium and sodium ions than in the presence of barium. The solubility of potassium perchlorate was too low to allow a complete series of measurements but data obtained in dilute solutions show that the deviations in potassium salt solutions are of the same order as those for lithium and sodium.

The effect of various salt concentrations was studied at log $P/(100 - P) = -1$. The differences in potential between the glass and the hydrogen electrodes were measured and $E'$ for each electrode subtracted. The results are plotted in Fig. 2 which illustrates the sodium ion response at almost constant alkalinity. The hydrogen electrode was used here as a reference electrode for checking the metal ion function.

If the alkalinity is sufficiently high the efficiency as a cation-selective electrode may be found provided that the ion activity can be calculated. Neither of these conditions was fulfilled in Fig. 2. The tangential slope for the sodium response of the MacInnes and the low temperature glasses, however, approaches 59 mV/decade.

Figure 2 together with Table I show that the glass composition is very important. Glass electrodes intended for use in water up to pH 14, *i.e.*, those which have a low alkaline error in water, also show a low alkaline error in isopropanol.

A peculiar dependence on the direction of the titration was observed during the measurements described above. In Fig. 3, curve A, a titration producing a solution of continuously increasing acidity is shown. The curve is smooth as expected. Curves B and C show an irregularity, the expected course being given by the broken line. It was found that there was a slow drift from the upper line towards the lower broken line and the drift was more rapid the more acidic the solution. Curve A was obtained with an electrode which had a low alkaline error but curves B and C with electrodes of high alkaline error. Curve D, on the other hand, was obtained with the same electrode as in curve B but the titration was made with base.

TABLE I.—DEVIATIONS IN mV FOR SOME GLASS ELECTRODES IN ISOPROPANOL SOLUTIONS AT FOUR VALUES OF THE ACIDITY FUNCTION log $P/(100\text{-}P)$. THE DEVIATION IS SET AT ZERO WHEN log $P/(100\text{-}P) = 1$.

| | 0·036*M* $Na^+$ | | | | 0·050*M* $Li^+$ | | | | 0·050*M* $Ba^{2+}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | log $P/(100\text{-}P)$ | | | | | | | | | | | |
| | 0·5 | 0 | −0·5 | −1 | 0·5 | 0 | −0·5 | −1 | 0·5 | 0 | −0·5 | −1 |
| *Full-range electrodes* | | | | | | | | | | | | |
| Beckman type E-2 | 0·9 | 2·5 | 4·4 | 6·6 | 3·0 | 8·1 | 16·0 | 26·9 | 0·3 | 0·8 | 1·5 | 2·3 |
| Fisher, full range | 0·8 | 1·1 | 2·3 | 3·4 | 1·2 | 3·6 | 8·1 | 14·9 | 0·4 | 0·9 | 1·7 | 4·0 |
| Ingold 201 | 8·4 | 21·1 | 34·4 | 50·9 | 3·1 | 8·8 | 17·9 | 31·0 | 0·1 | 0·3 | 0·8 | 2·7 |
| Metrohm EA 107 UX | 0·9 | 3·0 | 4·8 | 7·8 | 1·5 | 4·1 | 8·6 | 15·3 | 0·1 | 0·5 | 1·3 | 3·5 |
| *Low-temperature electrodes* | | | | | | | | | | | | |
| Beckman type 42 | 14·5 | 32·4 | 52·1 | 73·2 | 7·2 | 17·4 | 30·7 | 46·8 | 0·1 | 0·3 | 1·0 | 3·0 |
| Ingold LoT 201 | 22·1 | 46·3 | 71·7 | 97·3 | 8·6 | 20·5 | 36·1 | 54·4 | 0·1 | 0·2 | 0·4 | 0·6 |
| Metrohm EA 107 T | 16·9 | 36·7 | 58·4 | 79·5 | 9·3 | 22·8 | 40·7 | 61·3 | 0·0 | 0·1 | 0·2 | 0·5 |
| Philips GT 130 | 18·5 | 39·9 | 63·9 | 87·3 | 9·1 | 22·0 | 40·8 | 62·1 | 0·1 | 0·4 | 0·9 | 3·0 |
| *Corning 015 electrode* | | | | | | | | | | | | |
| Radiometer | 20·9 | 43·8 | 68·1 | 91·7 | 10·0 | 23·9 | 41·6 | 62·5 | 0·4 | 1·2 | 2·8 | 6·2 |

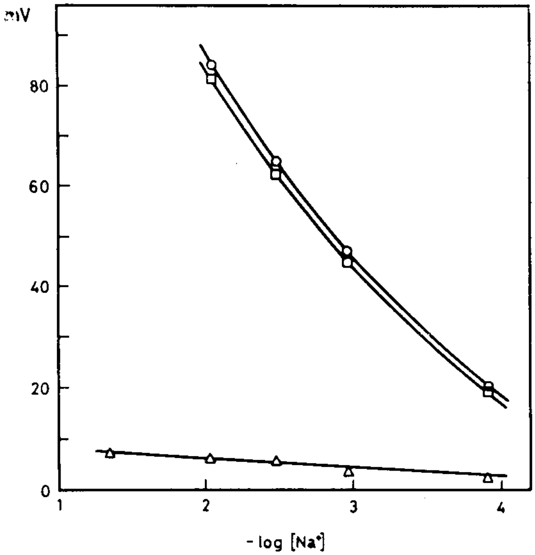

FIG. 2.—Glass electrode potential deviation plotted *vs.* $-\log [Na^+]$.
The deviation is defined as zero in an isopropanol solution containing no $Na^+$. The acidity corresponds to $\log P/(100\text{-}P) = -1$.

Electrode types:

△ pH range 0–14
□ Corning 015
○ Low temperature

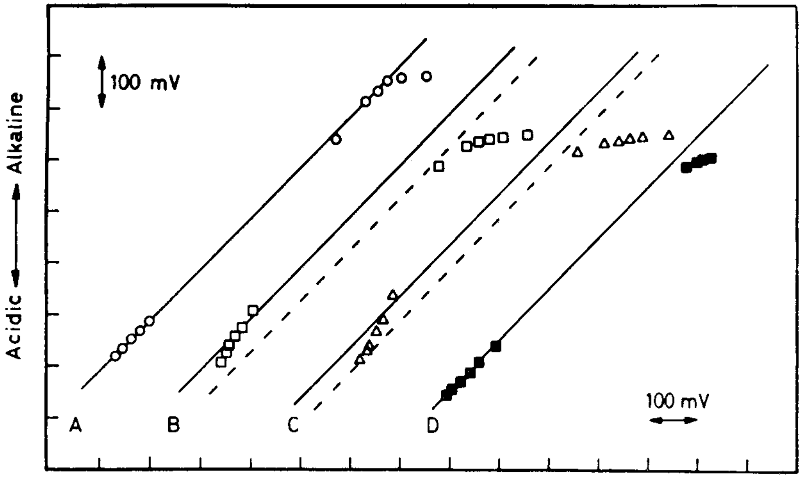

FIG. 3.—Glass electrode potential plotted *vs.* the hydrogen electrode potential. $0{\cdot}1M$ $Li^+$ in isopropanol. Reference electrode: Ag/AgCl.

Base can obviously enter into or be adsorbed at the electrode surface of some glass compositions thus causing an error. The excess of base will slowly equilibrate with the solution during times of the order of hours. A closer investigation of this adsorption effect has been started.

## DISCUSSION

Glass electrode deviations in non-aqueous solvents are very similar to the alkaline errors in water. The simplest equation, first given by Dole,[1] which describes the electrode potential is

$$\Delta E = \frac{RT}{F} \ln \left[1 + K\frac{a_{\mathrm{M}^+}}{a_{\mathrm{H}^+}}\right] \tag{2}$$

$$\Delta E = E_{\mathrm{G}} - E_{\mathrm{H}} - E' \tag{3}$$

where $K$ is a constant, $E_{\mathrm{G}}$ is the glass electrode potential and $E_{\mathrm{H}}$ the hydrogen electrode potential measured against any suitable reference. $E'$ is a term used to normalize the electrodes, so that an ideal glass electrode shows $\Delta E = 0$. Equation (2) applies accurately in ranges of pure hydrogen ion or pure metal ion response but only approximately in the transition region. Several attempts have been made, *e.g.*, by Oláh,[12] Schwabe *et al.*,[13] Nicolsky *et al.*[14,15] and Eisenman *et al.*[16,17] to derive equations which hold even in the range of mixed response. The derivations contain one or more constants which cannot be measured independently and which change with the nature of the metal ion and with glass composition. In practice this is equivalent to adjusting arbitrary constants until a fit is obtained. Measurements in non-aqueous solvents represent a new approach to the investigation of the alkaline error. The experimental results presented in Table I can be fitted to equation (2) but $K$ will not be a true constant as is the case in aqueous solution. Oláh's simplest formula, which differs from equation (2) in the prelogarithmic term, $(RT/2F)$, cannot provide good agreement either. No attempts were made to fit the data to equations containing additional arbitrary constants.

## CONCLUSIONS

Glass electrodes are subject to the same type of alkaline errors in isopropanol as in water. Electrode types which show low alkaline errors in water are more ideal in non-aqueous solvent. Even the best electrode types can deviate significantly from ideal behaviour in the most alkaline region if the concentration of univalent metal ions is high. As the solubility of *e.g.*, barium perchlorate is high it might provide a better choice in many cases. Titrations should, if possible, be made from acidic towards basic values to avoid hysteresis effects.

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**Zusammenfassung**—Durch Vergleich mit der Wasserstoffelektrode wurden Alkalifehler von Glaselektroden in Isopropanol ermittelt. Elektrodengläser, die in Wasser geringe Alkalifehler zeigen, sind auch in Isopropanol günstiger. Einwertige Metallionen geben größere Abweichungen als zweiwertige. Hysterese effekte wurden nur beim Übergang von alkalischen zu sauren Lösungen gefunden, in der umgekehrten Richtung nicht.

**Résumé**—On a obtenu les erreurs alcalines d'électrodes de verre en isopropanol à partir d'une comparaison avec l'électrode à hydrogène. Les électrodes de verre qui montrent de faibles erreurs alcalines dans l'eau sont aussi plus idéales en isopropanol. Les ions métalliques monovalents provoquent des déviations plus grandes que les divalents. On a trouvé des effets d'hystérésis en passant de solutions alcalines en solutions acides mais non dans le sens inverse.

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# SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH 8-QUINOLINOL

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**Summary**—A spectrophotometric method is described for the determination of 2–80 μg of ruthenium. The method involves oxidation of ruthenium to ruthenate, addition of 8-quinolinol, adjustment of the pH to 4–6.5, digestion of the complex formed at 85° for 30 min, extraction with chloroform, and measurement of absorbance at 430 nm. Almost all other metals and excess of reagent are removed by washing the extract. About 98% of $^{106}$Ru tracer was recovered.

VERY little information is available in the literature concerning the behaviour of ruthenium with 8-quinolinol (oxine). Sandell[1] has mentioned that in acetate medium oxine forms a green complex with ruthenium(III) which is extractable with chloroform, but no experimental details are given. No optimum extraction conditions for quantitative recovery of ruthenium were obtained by the authors using ruthenium trichloride solution.

Jasim and co-workers[2] have developed a spectrophotometric method using oxine for determining ruthenium. To extract insoluble dark green particles which were thought to be the hydrated oxine complex, they used butylcellosolve in conjunction with chloroform. However, this method is time-consuming and not very sensitive.

Kato[3] has investigated the extraction behaviour of the ruthenium–oxine complex, using the tracer $^{106}$Ru, and established a method for the separation of $^{106}$Ru from uranium fission products.[4] He claimed the reactive and extractable oxidation state is ruthenium(IV), and that the ruthenium should be adjusted to this oxidation state *via* ruthenate before treatment with oxine. However, the overall recovery of the nuclide was only 70% in this method.

We have found conditions for quantitative extraction of the ruthenium–oxine complex by modifying Kato's procedure. On treatment of ruthenate with oxine, ruthenium in a lower oxidation state [presumably (III) and/or (IV)] forms the oxine complex. The reaction is slow at room temperature but sufficiently rapid at elevated temperatures to be useful for the spectrophotometric determination of ruthenium in the range 2–80 μg. The method has been successfully used for the separation of $^{106}$Ru from fuel reprocessing solutions containing uranium and fission products.[5]

## EXPERIMENTAL

### *Reagents*

*Standard ruthenium solution.* A stock solution was prepared by dissolving analytical grade ruthenium chloride in water. The solution was standardized gravimetrically by precipitating ruthenium with thionalide, igniting in air and then in hydrogen to the metal. More dilute solutions were prepared as needed.

*Oxine solution, 2%.* Prepared by dissolving 2 g of analytical grade oxine with 5 ml of hot glacial acetic acid and diluting to 100 ml with water.

*Potassium persulphate solution*, 2%.
*Sodium hydroxide solution*, 6*M*.
*Sulphuric acid*, 9*M*.
*Chloroform*.

*Ruthenium-106* (*carrier-free*). Separated from a fission product mixture (obtained from ORNL, U.S.A.) by the proposed extraction method. The separated $^{106}$Ru was dissolved in 9*M* sulphuric acid after the chloroform had been evaporated off and organic materials decomposed with nitric acid. The radiochemical purity of the $^{106}$Ru was confirmed from the $\gamma$-ray spectrum and the $\beta$-ray energy.

### *Procedure*

A solution containing 2–80 $\mu$g of ruthenium is treated with sodium hydroxide solution to give a hydroxide concentration of 2*M* or greater. Then 2 ml of potassium persulphate solution are added and the solution is boiled for 20 min to form ruthenate and to decompose the excess of persulphate. The solution is then diluted to 60 ml with water and 3 ml of oxine solution are added, the pH is adjusted to 4–6·5, and the resulting solution is heated to 85 ± 5° for 30 min to form the ruthenium complex. After cooling to room temperature, the solution is transferred to a separatory funnel and shaken with exactly 10 ml of chloroform for 1 min. Then dilute sulphuric acid is added till its concentration in the solution is 2*M*, the aqueous phase is diluted to 100 ml with water, and the mixture is shaken again for 1 min to remove other metals. The organic phase is then transferred into a small bottle containing 1 g of anhydrous sodium sulphate and its absorbance is measured at 430 nm against a blank.

## RESULTS AND DISCUSSION

### *Absorption spectrum*

Ruthenium oxine complex extracted into chloroform is greenish yellow in colour and has absorption maxima at 430 and 710 nm as shown in Fig. 1. The absorbance at 430 nm is about 6 times that at 710 nm. The molar absorptivity at 430 nm is $12{\cdot}0 \times 10^3$ l.mole$^{-1}$.cm$^{-1}$.

### *Extraction conditions*

Jasim *et al.*[2] did not specify the ruthenium solution used or mention the effect of common ions such as chloride, nitrate and sulphate. They directly extracted ruthenium without oxidation to ruthenate. Their method involves shaking the ruthenium solution (4–5 ml) with 5 ml of 10% oxine solution in chloroform for 3 min before and after adjustment of the pH of the aqueous solution to 6·4, then with a further 5 ml of the reagent, with a 3-ml portion of butylcellosolve to extract hydrated dark green particles and with three 5-ml portions of chloroform. All the extracts are collected and diluted to 50 ml with chloroform. Although conformity to Beer's law in the range of 12·5–150 $\mu$g of ruthenium at 420 nm was reported, the absorbance measured seems to be too low for accurate and precise results.

In Kato's procedure,[4] ruthenium was oxidized with persulphate in an alkaline solution to form ruthenate and then treated with hydrochloric acid (2*M*)–hydrogen peroxide (1%) solution to adjust the oxidation state to 4, before formation of the complex. The complex formed at pH 4 by heating at 60° for 30 min was extracted with 6 ml of benzene, and the extract was washed with 0·1*M* oxalic acid and with 0·1*M* hydrochloric acid to eliminate other radionuclides and the excess of oxine. Kato reported that in this method 8–9% of the ruthenium remained in the aqueous solution as $RuO_4^{2-}$ and $RuO_2{\cdot}xH_2O$, and 20% of the ruthenium extracted into benzene as $RuO_4$ was back-extracted in washing the extract. The recovery of ruthenium extracted as oxine complex was about 70%.

In the initial stages of the present work, we tried to determine ruthenium in ruthenium trichloride solution, which is reported[6] to contain an appreciable amount of

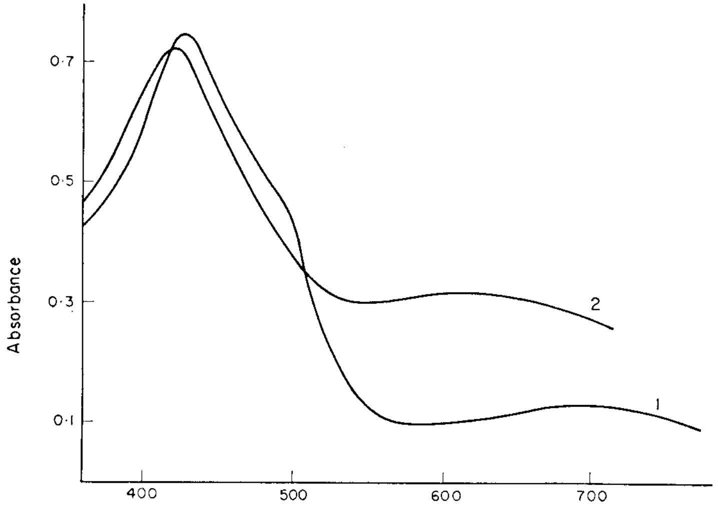

FIG. 1.—Absorption spectra of ruthenium oxine complex in $CHCl_3$.
1. Ru 6 μg/ml. With oxidation to $RuO_4^{2-}$ (proposed method).
2. Ru 12 μg/ml. Without oxidation to $RuO_4^{2-}$.

ruthenium(IV), without oxidation to ruthenate. The extract was green and showed absorption maxima at 420 and 610 nm as shown in Fig. 1. The absorption spectrum seems to be in accordance with that described by Sandell[1] and Jasim *et al.*[2] but not with that obtained by our proposed method. Reproducible absorbances, however, could not be obtained in this way, as seen in Table I. The poor reproducibility may be caused by the complicated oxidation states and complex formation of ruthenium. To eliminate such effects, ruthenium in these solutions was oxidized to ruthenate by Kato's procedure, but reduction of ruthenate with hydrochloric acid-hydrogen peroxide was omitted because ruthenate was considered to be reduced to a lower oxidation state by the oxine, and formed the complex during the digestion. Satisfactory values were obtained (Table I). The value of this method of complex formation was confirmed with another ruthenium solution prepared by dissolving the metal with hydrochloric acid–perchloric acid in a sealed tube at 300°. Thus, the oxidation

TABLE I.—EXTRACTION OF RUTHENIUM IN ACID SOLUTIONS AS OXINE COMPLEX

| Medium* | Absorbance of extract | |
|---|---|---|
| | Without oxidation to $RuO_4^{2-}$ | Oxidation to $RuO_4^{2-}$ |
| 0·05*M* $HNO_3$ | 0·255 | 0·614 |
| | 0·270 | 0·610 |
| 0·05*M* $H_2SO_4$ | 0·402 | 0·628 |
| | 0·365 | 0·629 |
| 0·05*M* HCl | 0·415 | 0·625 |
| | 0·375 | 0·627 |

* $RuCl_3$ dissolved in water was diluted with the appropriate acid. Each solution contains 50 μg of Ru.

step is a necessary condition for the quantitative extraction of ruthenium, and ruthenate seems to be the most favourable chemical form in order to eliminate the troublesome properties of ruthenium such as the variable oxidation state and the complex formation. Potassium persulphate is a favourable oxidizing agent because its excess can easily be decomposed by boiling.

In this method the complex formed is readily dissolved in chloroform, and appears to be different from that obtained by Jasim *et al.*,[2] because of the difference in the absorption spectrum and the molar absorptivity.

*Effect of pH.* The procedure was followed with variation of the pH of the solution before digestion. As shown in Fig. 2, a constant absorbance was obtained at pH 4–6·5 and this pH range was used in all subsequent work.

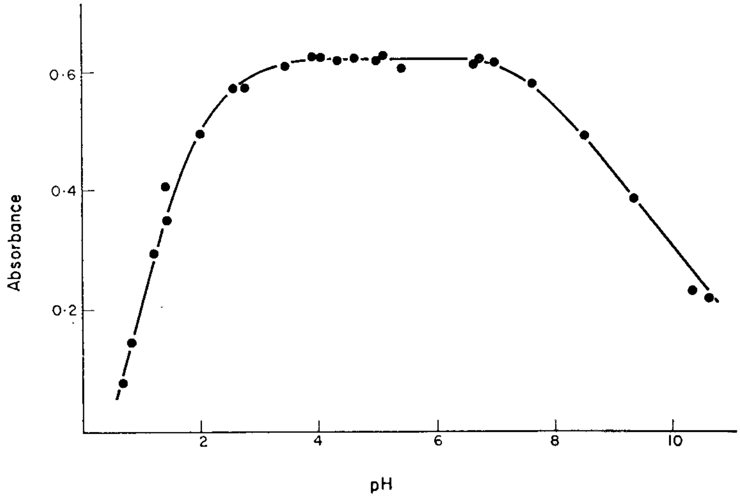

Fig. 2.—Effect of pH on extraction of 50 μg of Ru.

*Effect of digestion.* As seen in Fig. 3, the solution must be heated at 80° or higher for at least 30 min to form the complex and extract it quantitatively.

*Washing the extract.* Although the formation of the complex necessitates the digestion, the complex once formed is very stable. When 10 ml of chloroform containing the ruthenium complex were shaken with 50 ml each of solutions of sulphuric acid, hydrochloric acid, oxalic acid and sodium hydroxide, the following concentrations of the aqueous solutions were found to have no effect on the absorbance of the extract: $H_2SO_4 < 2{\cdot}5M$, $HCl < 4M$, $H_2C_2O_4 < 0{\cdot}5M$, $NaOH < 4M$. This property is specific and is useful for removing other metals. In the washing of the extract, the excess of oxine is also completely eliminated. Regardless of the washing, the absorbance of the extract does not change for at least 1 week.

*Effect of other substances.* Most metals extracted as oxine complexes were removed by the sulphuric acid (2*M*) treatment as reported in the previous paper[7] on palladium and rhodium. The complexes of cobalt, chromium, molybdenum, palladium and rhodium, extracted into chloroform, are very stable, and microgram amounts of these metals interfere seriously in this method (Table II). The absorbance due to 1 μg each of these metals corresponds to the following amounts of ruthenium: cobalt 0·2 μg, chromium 0·4 μg, molybdenum 0·11 μg, palladium 1 μg, rhodium

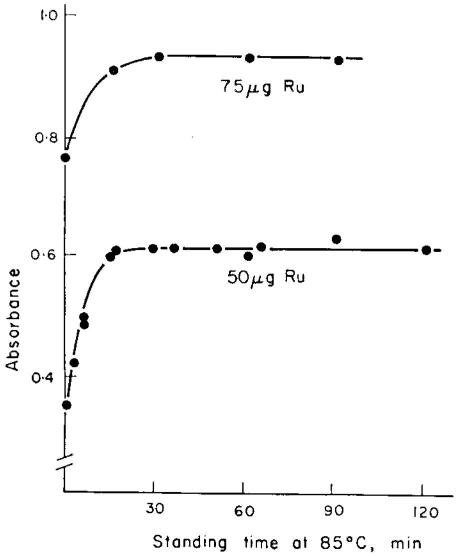

FIG. 3.—Effect of digestion of complex.

TABLE II.—EFFECT OF FOREIGN METALS ON DETERMINATION OF RUTHENIUM

| Metal | Added as | Absorbance measured | |
|---|---|---|---|
| | | Without Ru | In the presence of Ru |
| — | | — | 0·615 |
| Al | $Al_2(SO_4)_3$ | 0·001 | 0·613 |
| Au | $(HNO_3)$ | 0·008 | 0·617 |
| Cd | $CdSO_4$ | 0·001 | 0·620 |
| Co | $CoSO_4$ | 0·510 | 1·080 |
| Cr | $KCr(SO_4)_2$ | 0·488 | 1·050 |
| Cu | $Cu(NO_3)_2$ | 0·005 | 0·612 |
| Fe | $Fe_2(SO_4)_3$ | 0·000 | 0·626 |
| Ga | $Ga_2(SO_4)_3$ | 0·004 | 0·617 |
| In | $In_2(SO_4)_3$ | 0·004 | 0·614 |
| Mg | $MgSO_4$ | 0·005 | 0·614 |
| Mn | $Mn(NO_3)_2$ | 0·000 | 0·619 |
| Mo | $Na_2MoO_4$ | 1·035 | 1·60 |
| Nb | $Nb_2(SO_4)_5$ | 0·000 | 0·620 |
| Ni | $NiSO_4$ | 0·001 | 0·615 |
| Pb | $Pb(NO_3)_2$ | 0·002 | 0·622 |
| Pd | $PdSO_4$ | 0·130 | 0·788 |
| Pt | $(H_2SO_4)$ | 0·060 | 0·713 |
| Rh | $Rh_2(SO_4)_3$ | 0·610 | 1·280 |
| Sn | $Sn(SO_4)_2$ | 0·004 | 0·623 |
| Ti | $Ti(SO_4)_2$ | 0·008 | 0·622 |
| U | $UO_2(NO_3)_2$ | 0·003 | 0·628 |
| V | $VOSO_4$ | 0·003 | 0·613 |
| W | $Na_2WO_4$ | 0·030 | 0·653 |
| Zn | $ZnSO_4$ | 0·004 | 0·618 |
| Zr | $Zr(SO_4)_2$ | 0·003 | 0·612 |

Ru: 50 µg. Other metals: 1 mg (except for Co 0·2, Cr 0·1, Pd 0·01, Pt 0·3, Rh 0·1 mg).

0·5 μg. Molybdenum could be removed by shaking the extract with 4*M* sodium hydroxide solution and palladium almost all removed with 4*M* hydrochloric acid.

Sodium chloride, nitrate, sulphate and phosphate (3 g of each) do not interfere with the oxidation to ruthenate and the complex formation. Reducing agents and organic substances, such as sulphite, hydroxylamine, citrate, tartrate and EDTA, interfere in the complex formation.

*Composition of the complex.* A photometric determination by a slope-ratio method[7] was not successful because of the volatilization of oxine during the digestion at elevated temperature. Determination of the combined oxine and ruthenium of the complex in the extract after washing out the excess of reagent, was also difficult because the extracted complex was not dissociated even in concentrated sulphuric acid. Therefore the ruthenium and carbon were determined in a precipitate formed by the procedure used for the extraction. The precipitate was heated to constant weight at 130–140°. The absorption spectrum of its chloroform solution was the same as that of the extracted complex.

From the C/Ru ratio obtained, the oxine/Ru ratio was calculated to be 3·2 (Table III), but the results of this experiment do not justify assignment of a definite

TABLE III.—DETERMINATION OF CARBON AND RUTHENIUM IN RUTHENIUM 8-QUINOLINOLATE PRECIPITATE

| Precipitate taken, *mg* | C found, % | Precipitate taken, *mg* | Ru found, % |
|---|---|---|---|
| 10·23 | 62·4 | 190·2 | 18·1 |
| 10·68 | 60·8 | 322·2 | 17·7 |
| 10·16 | 61·0 | 213·3 | 17·4 |
| 8·33 | 61·1 | 210·5 | 17·7 |
| 7·35 | 59·4 | | Ave. 17·7 |
| | Ave. 60·9 | | |
| C/Ru(Mole ratio) = 28·9 | | | |

TABLE IV.—RECOVERY TEST FOR $^{106}$Ru*

| Ru present, μg | Recovery, % |
|---|---|
| 5 | 98·3 95·0 |
| 25 | 97·5 99·8 |
| 45 | 99·3, 96·3 |
| | Ave. 97·7 |

* γ-Activity: 8·42 × $10^4$ cpm.

TABLE V.—DETERMINATION OF RUTHENIUM IN THE PRESENCE OF URANIUM AND IRON

| Ru taken, μg | Added, *mg* U | Fe | Ru found, μg | Standard deviation,* μg |
|---|---|---|---|---|
| 30 | 3 | 0·1 | 30·2 | 1·5 |
| 60 | 3 | 0·1 | 60·7 | 1·4 |

* Seven determinations.

composition to the complex extracted, which may be a mixed complex of ruthenium(III) and ruthenium(IV).

*Recovery of ruthenium-106.* A recovery test was carried out with $^{106}$Ru by measuring the $\gamma$-activity in the range of 0·4–0·7 MeV. As seen in Table IV, satisfactory results were obtained.

Finally, the result of the recovery test of the proposed spectrophotometric method is shown in Table V. In the presence of uranium and iron (simulated to reprocessing of spent nuclear fuel), ruthenium was determined with satisfactory accuracy and precision (Table V).

**Zusammenfassung**—Ein spektrophotometrisches Verfahren zur Bestimmung von 2–80 $\mu$g Ruthenium wird beschrieben. Ruthenium wird zu Ruthenat oxidiert, 8-Hydroxychinolin zugegeben, der pH auf 4–6,5 eingestellt, der gebildete Komplex 30 min bei 85° gehalten, mit Chloroform extrahiert und die Extinktion bei 430 nm gemessen. Fast alle anderen Metalle und überschüssiges Reagens werden durch Waschen des Extrakts entfernt. Etwa 98% des $^{106}$Ru-Tracers wurden wiedergefunden.

**Résumé**—On décrit une méthode spectrophotométrique pour le dosage de 2–80 $\mu$g de ruthénium. La méthode comprend l'oxydation du ruthénium en ruthénate, l'addition de 8-hydroxyquinoléine, l'adjustement du pH à 4–6,5, la digestion du complexe formé à 85° pendant 30 mn, l'extraction au chloroforme et la mesure de l'absorption à 430 nm. Presque tous les autres métaux et l'excès de réactif sont éliminés par lavage de l'extrait. On a récupéré environ 98% de $^{106}$Ru traceur.

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# A.C. POLAROGRAPHIC DETERMINATION OF UNSATURATION

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**Summary**—A wide range of olefins can be determined by a.c. polarography of their addition compounds with mercuric acetate. The first step in the reduction of these compounds is a reversible, one-electron process to form the organo-mercury radical and gives a well defined a.c. peak. The optimum conditions for the determination of a representative selection of olefins has been established.

THERE are four main groups of method commonly employed for the determination of olefinic unsaturation.[1,2] These involve bromination, including the various inter-halogen reagents,[3] addition of iodine monochloride (Wij's method[4] for the determination of iodine number), catalytic hydrogenation and the addition of mercury(II) salts. Bromine and the more reactive bromine monochloride provide rapid straight forward reactions but careful control of experimental conditions is necessary to prevent unwanted side-reactions. The use of iodine monohalides offers an alternative for the more reactive olefins. Catalytic hydrogenation, although specific for C—C double and triple bonds is time consuming and difficult.

Titrimetric methods based on the reaction of double bonds with mercury(II) acetate have been widely exploited.[5–8] These methods are particularly useful for small quantities of olefins.

Direct polarographic determination of double bonds is difficult as large negative potentials are required unless the double bond is activated in some way by another group. Indirect polarographic methods involving bromination have been described but are prone to interference.[9] A polarographic method involving the addition of nitrous acid has also been described.[10,11]

The organo-mercury addition compounds formed between olefins and mercuric salts have been shown to be polarographically reducible. The first paper describing the polarography of this class of compound is by Sullam,[12] in which he examined ethylene mercurials. Usami[13] has described the determination of vinyl acetate and allyl alcohol *via* their mercury complexes. Similar methods have been described[14,15] for the determination of *N*-vinyl-2-pyrrolidone, α-methylstyrene and styrene.

The polarographic behaviour of this class of organo-mercury addition compounds has been described in detail elsewhere.[16] Direct current polarograms show two waves corresponding to the electrode reactions:

(1) $R—Hg^+ + e = R—Hg'$ (this step is often split into two waves, owing to adsorption effects.)

(2) $R—Hg' + e + H^+ \rightarrow R—H + Hg$

The first step has been shown to be reversible, by cyclic voltammetry.

Other workers[13,14,15] used classical d.c. polarography and were forced to keep the excess of mercury(II) acetate to a minimum. Only the first wave was of real analytical use owing to a large maximum on the second wave. The use of a fast sweep technique[15] is one solution to the large prewave problem. The reversibility of the first reduction step suggested the possibility of developing an a.c. polarographic method.

## EXPERIMENTAL

### *Materials*

The mercury(II) acetate, sodium nitrate (A.R.), lithium chloride, buffer materials, allyl alcohol, allyl acetate, α-methylstyrene, styrene, vinyl acetate and cyclohexene were from British Drug Houses Ltd. The rest of the olefinic compounds were obtained from Koch-Light Ltd. All except the 2,5-dimethyl-1,5-hexadiene were used without further purification. The 2,5-dimethyl-1,5-hexadiene was redistilled before use.

### *Buffers*

Sodium acetate/acetic acid, phosphate, borate and sodium hydroxide buffers were used; in all cases the final concentration was $0{\cdot}1M$.

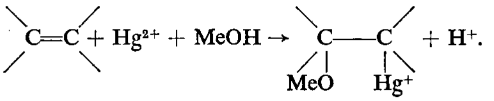
### *Equipment*

A Cambridge Univector a.c. polarograph attachment in conjunction with the Cambridge manual polarograph was used throughout. A polarograph type OH 102 (Metrimpex, Hungary) was used for the recorder, and the sensitivity and damping controls of this polarograph rather than of the Cambridge instrument were used. Unless otherwise stated, a Heyrovský type cell was used; the capillary constants were $m = 1{\cdot}88$ mg/sec and $t = 4{\cdot}41$ sec.

## RESULTS AND DISCUSSION

The a.c. polarogram peak height is very sensitive to reversibility and adsorption effects. This will be influenced by the solvent medium and supporting electrolyte used. Thus initially it was necessary to carry out an investigation to find the optimum conditions for these organo-mercury compounds.

The reaction between olefins and mercury(II) acetate depends on the solvent medium in two ways. First, the solvent can alter the rate of reaction, and secondly it can take part in the reaction. The reaction occurs most rapidly in a methanol medium, the rate decreasing with higher alcohols.[17] Thus the solvent medium more or less needs to be methanol for the initial chemical step



$$\rangle C{=}C\langle + Hg^{2+} + MeOH \rightarrow \rangle \underset{MeO}{C} - \underset{Hg^{+}}{C} \langle + H^{+}.$$

For the purposes of recording the a.c. polarogram a supporting electrolyte must be added; this may be an aqueous or methanolic solution.

The sodium nitrate–methanol medium used by Usami was first investigated. In practice, owing to strong adsorption of the R—Hg′ species the first reduction step gives two peaks; this interferes considerably with the form of the peaks, making it impossible to draw a usable base-line from which to make measurements (Fig. 1.). Evidence for the strong adsorption of R—Hg′ comes from the d.c. polarograms recorded in this medium and also from electrocapillary measurements. A methanol–water–sodium nitrate medium gives a single peak, with a sloping base-line. Lithium chloride–methanol solution similarly gives a single peak of rather poor reproducibility.

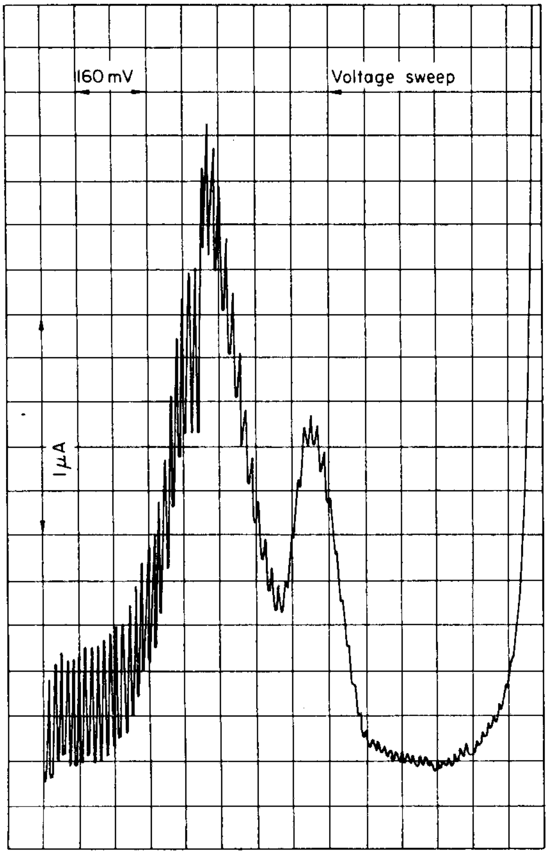


FIG. 1.—a.c. polarogram of mercury(II) acetate complex of allyl alcohol ($1 \times 10^{-4}M$) in methanol/0·1$M$ sodium nitrate medium.

The effect of methanol–water ratio at various pH values was investigated for a number of compounds. The compounds investigated for this purpose included allyl alcohol and α-methylstyrene, which from their d.c. polarograms would be expected to give respectively the best and one of the poorest resolved peaks for the compounds under investigation. In the pH region 5–7 the resolution of the peak from that due to the excess of mercury(II) acetate or anodic discharge was very poor, giving a sloping base-line. Increasing the methanol content caused a small improvement in peak form. The higher the pH for a given methanol–water ratio the better resolved was the peak (Fig. 2.), the peak height reaching a maximum at about pH 9·5. Increasing the methanol content also caused some improvement in peak resolution and in particular a great enhancement in peak height (Fig. 3.). This increase in peak height is almost certainly due to the increase in adsorption effects. Addition of buffer to the methanolic solution of organo-mercury and excess of mercury(II) acetate causes the precipitation of yellow mercury(II) oxide in the case of borate or sodium hydroxide supporting electrolytes, or a pale yellow precipitate of mercury(II) phosphate in the case of phosphate buffers when the free mercury(II) acetate concentration is above approximately $3 \times 10^{-4}M$. The presence of a precipitate causes a time-dependence of the a.c. peak height. With a phosphate buffer there is a considerable decrease in

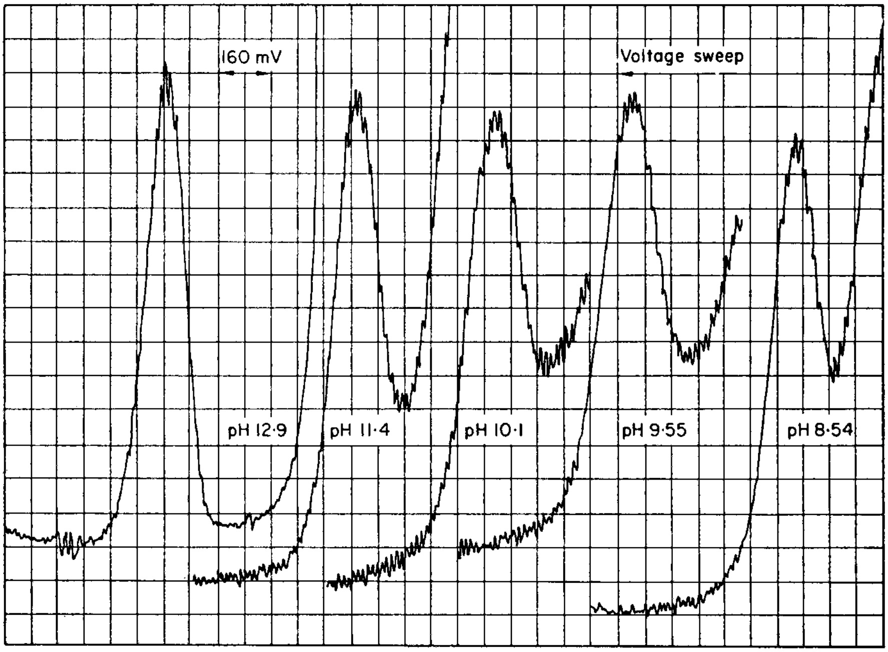


FIG. 2.—pH-dependence of a.c. polarographic wave for mercury(II) acetate addition compound of allyl alcohol ($2 \times 10^{-4}M$) in 50% methanol.
Peak heights ($\mu$A) pH 12·9, 1·85; pH 11·4, 2·52; pH 10·1, 3·25; pH 9·55, 3·29; and pH 8·54, 2·78. Note: the polarograms shown are not all recorded at the same sensitivity.

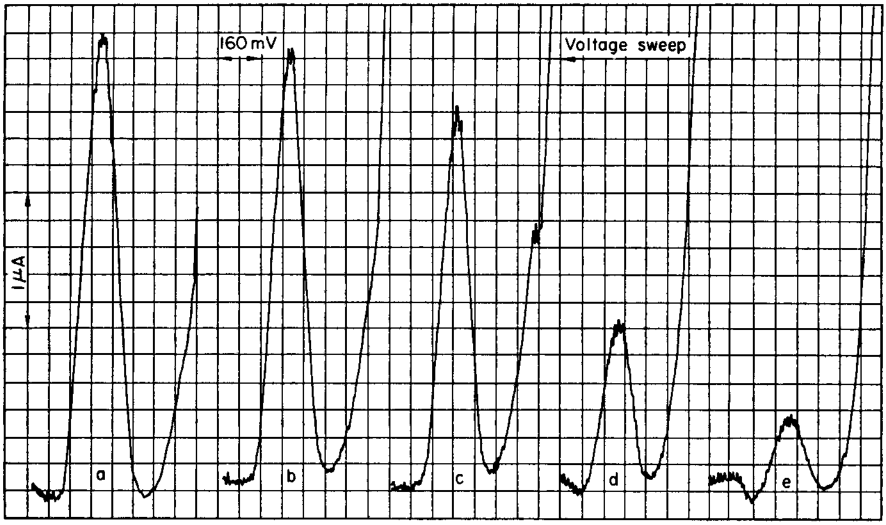


FIG. 3.—Effect of solvent composition on a.c. polarographic wave for mercury(II) acetate addition compound of α-methylstyrene ($2 \times 10^{-4}M$) at pH 12·9.
Water–methanol medium. Methanol content (*a*) 100%; (*b*) 90%; (*c*) 75%; (*d*) 50%; (*e*) 25%.

peak height over a period of 40 min. The presence of mercury(II) oxide caused a small increase in height with time. In the absence of a precipitate a stable system is obtained. The slow seepage of chloride ions from a reference electrode appears to alter the peak height so measurements should preferably be made in a Heyrovský type cell. Any precipitate present in the solution is caused to dissolve slowly by the seepage of chloride ions, again adding to poor reproducibility (Fig. 4.). Using a Heyrovský cell and keeping the free mercury(II) acetate to approximately 2–3 × $10^{-4}M$ or below gives a stable system. From the investigations above a 90–100% methanolic 0·1$M$ sodium hydroxide medium would appear best.

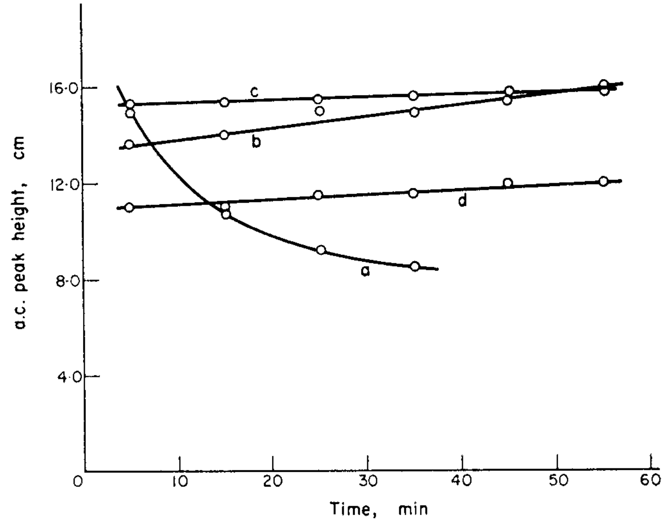


Fig. 4.—Stability with respect to time for the mercury(II) acetate compound of allyl alcohol from the time dependence of the a.c. polarographic wave.
(*a*) pH 12·25, phosphate buffer, 50% methanol, 25-fold excess of mercury(II) acetate, Kalousek cell; (*b*) pH 10·1, borate buffer, 75% methanol, 25-fold excess of mercury(II) acetate, Kalousek cell; (*c*) pH 12·9 (0·1$M$ sodium hydroxide), 90% methanol, 1-fold excess of mercury(II) acetate, Heyrovský cell; (*d*) pH 12·9 (0·1$M$ sodium hydroxide), 90% methanol, 5-fold excess of mercury acetate, Heyrovský cell.

A number of the papers describing the titrimetric procedure give reaction times necessary for the various olefinic compounds; however, the various values given are not consistent with one another and so the reaction times were redetermined for the specific conditions used here. Solutions of olefin and mercury(II) acetate were mixed and after a suitable time interval the buffer was added and a polarogram recorded. This was repeated for a number of different reaction times and for all the compounds, see Table I and Fig. 5. The presence of sodium nitrate catalyses the reaction[18] and its addition was found necessary for a number of the compounds investigated, so as to reduce the reaction time to an acceptable value. The increase in reaction rate is about threefold. Heating also increases the rate of reaction.

The titrimetric methods, when applied to vinyl ethers in particular, require the whole procedure to be carried out at a reduced temperature (0 to −10°). In the polarographic method developed here these compounds can be determined at room temperature. They are in fact the most readily determined compounds by this method,

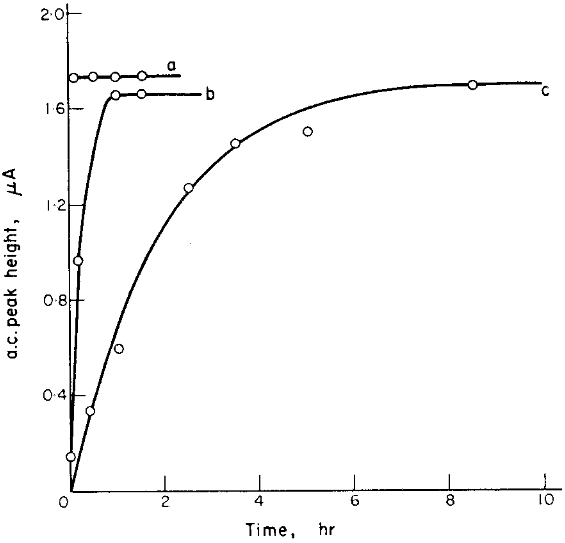


FIG. 5.—Time of formation of mercuric acetate addition compounds.
(*a*) vinyl n-butyl ether; (*b*) 4-methyl-1-pentene; (*c*) crotyl alcohol (with sodium nitrate as catalyst). All with $2 \times 10^{-4}M$ mercury(II) acetate and approx. $1 \times 10^{-4}M$ with respect to compound, 90% methanol, pH 12·9.

TABLE I.—ALTERNATING CURRENT POLAROGRAPHIC DATA FOR A SELECTED RANGE OF OLEFINS

| Compound | $E_s$, *V* | $i_p/c$. | Half-peak width, *mV*. | Time of formation (room temperature) *min* |
|---|---|---|---|---|
| 4-methyl-1-pentene | −0·51 | 1·84 | 125 | 60 |
| cyclohexene | −0·46 | 2·13 | 137 | 90* |
| 2,5-dimethyl-1,5-hexadiene | −0·44 | 12·3 | 80 | 60 |
| styrene | −0·47 | 1·85 | 121 | 60* |
| α-methylstyrene | −0·45 | 2·03 | 121† | 40 |
| allyl alcohol | −0·57 | 2·09 | 129 | 60* |
| allyl acetate | −0·55 | 2·05 | 125 | 720* |
| allylacetone | −0·51 | 1·94 | 113 | 2 |
| vinyl acetate | −0·55 | 2·29 | 121 | 2 |
| *N*-vinyl-2-pyrrolidone | −0·49 | 2·03 | 165‡ | 7 |
| *N*-vinyl carbazole | −0·41 | 4·54 | 80 | 2 |
| vinyl n-butyl ether | −0·51 | 1·85 | 129 | 2 |
| vinyl isobutyl ether | −0·51 | 1·81 | 121 | 2 |
| vinyl 2-chloroethyl ether | −0·51 | 2·11 | 121 | 2 |
| crotyl alcohol | −0·51 | 1·80 | 177§ | 720* |

$E_s$ = summit potential w.r.t. S.C.E.

$i_p/c$ = current in μA for a $1 \times 10^{-4}M$ solution. Taken from slope of concentration plot.

Instrument sensitivity: a deflection of 2·36 μA was observed for the "calibration" setting of the Univector.

* 2 ml of 0·2*M* sodium nitrate solution 10 ml added as catalyst.

† Decreases to 109 mV at $1 \times 10^{-4}M$.

‡ Decreases to 121 mV at $1 \times 10^{-4}M$

§ Decreases to 129 mV at $1 \times 10^{-4}M$.

owing to their short reaction times. It can be seen from Table I that compounds with the C—C double bond conjugated to an unsaturated grouping react most rapidly.

### *Recommended procedure*

The sample of olefin (0·1–2 meq) dissolved in methanol is placed in a 10–ml volumetric flask. An excess of methanolic mercury(II) acetate solution (stabilized with 0·1 ml of glacial acetic acid 100 ml of 0·1*M* solution) is added so that the final concentration will be approximately 2–3 × $10^{-4}M$. After a suitable time has elapsed for the formation of the organo-mercury compound (see Table I) 1 ml of 1*M* aqueous sodium hydroxide is added as supporting electrolyte, and methanol to give the final volume of 10 ml. For those compounds requiring a catalyst, 2 ml of 0·2*M* sodium nitrate (methanolic solution) were added at the same time as the mercury(II) acetate. The solution is de-aerated by passage of nitrogen for 5 min and the a.c. polarogram recorded. It is very important that the 10–ml volumetric flask or other vessels used must be free from traces of water, or precipitation of mercury(II) oxide will occur. As soon as the supporting electrolyte is added the reaction between olefin and mercury(II) acetate stops.[17] By recording the polarogram after a fixed time it is possible to work with a precipitate of mercury(II) oxide present.

The results obtained for a representative range of olefins, together with the relevant polarographic data, are shown in Table I. With the procedure outlined above the reproducibility of the method was examined for allyl alcohol and α-methylstyrene. The results are summarized in Table II.

TABLE II.—REPRODUCIBILITY OF A.C. PEAK HEIGHT FOR THE REDUCTION OF MERCURY ADDITION COMPOUNDS OF OLEFINS

| Compound | Peak height, μA | Average, μA | Standard deviation, μA |
|---|---|---|---|
| allyl alcohol | 1.92, 1·91<br>1·88, 1·91$_5$<br>1·96 | 1·91$_5$ | 0·027 |
| α-methylstyrene | 1·49, 1·52$_5$<br>1·52$_5$, 1·50<br>1·55, 1·50$_5$ | 1·51$_5$ | 0·022 |

Figure 6*a* shows a typical concentration plot over the range 1 to 20 × $10^{-5}M$. In all cases the calibration curve is a straight line with the exception of *N*-vinyl carbazole (Fig. 6*b*) which shows considerable curvature at high concentrations. Theory predicts that a calibration curve in the form of a Langmuir isotherm should be obtained.[19] The calibration curves do not pass through the origin but cut the concentration axis at approximately 1 × $10^{-5}M$. This could be due to the effect of adsorption of R—Hg′ which causes a change in the double-layer capacity so that the a.c. base-line will be different in the presence of R—Hg′.

From Table I it will be noted that in the case of *N*-vinyl carbazole and 2,5-dimethyl-1,5-hexadiene the $i_p/c$ values are considerably greater than for any of the other compounds. This is almost certainly due to adsorption effects. The surface concentration of the electroactive species will be higher, explaining the large $i_p/c$ values. The effect of adsorption on the double-layer capacity will cause a nonfaradaic alternating current to flow which may be larger than the a.c. base-current in the absence of R—Hg′, thus causing an enhancement in peak height.[19] Whether or not this effect applies here cannot be stated conclusively as the phase sensitive nature of the Univector system eliminates capacitative currents. However, considering the fact that many tensammetric currents have highly distorted waveforms owing to the presence of harmonics then some enhancement in peak height could be gained from this effect.[20]

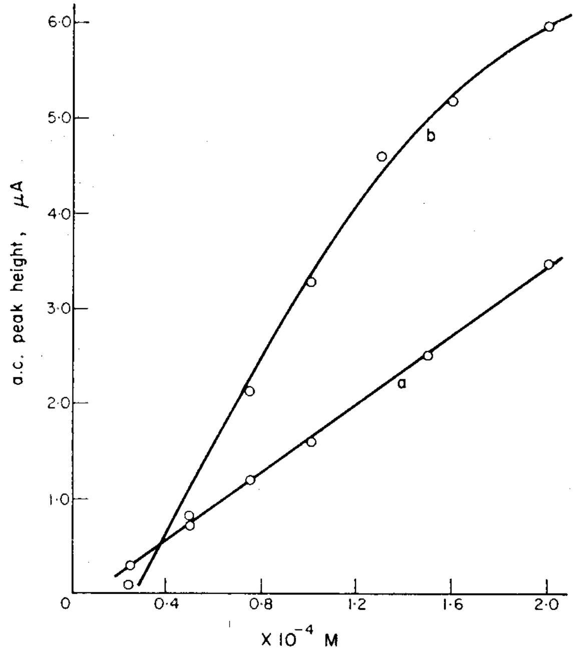


FIG. 6.—Dependence of a.c. peak height on concentration. pH 12·9, 90% methanol. (*a*) vinyl isobutyl ether; (*b*) *N*-vinyl carbazole.

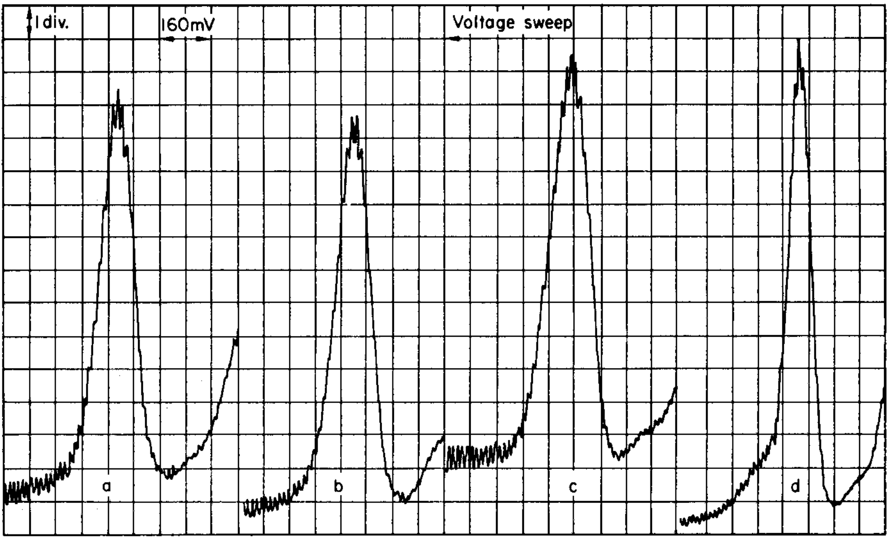


FIG. 7.—a.c. polarograms for a representative selection of olefins, pH 12·9, 90% methanol.
(*a*) 4-methyl-1-pentene; (*b*) vinyl n-butyl ether; (*c*) crotyl alcohol; (*d*) *N*-vinyl carbazole. Sensitivity (*a*)–(*c*) 0·15 μA/div; (*d*) 0·3 μA/div.

The a.c. peaks are nearly all symmetrical in shape and with a half-peak width somewhat larger than the theoretical value of $90 \cdot 4/n$.[19] It is of interest that the two compounds which show abnormalities give very sharp peaks with a half-width of only 80 mV. In the case of *N*-vinyl carbazole the peak shape is also somewhat distorted as can be seen in Fig. 7.

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**Zusammenfassung**—Eine Vielzahl von Olefinen kann durch Wechselstrompolarographie ihrer Additionsprodukte mit Quecksilber(II)-acetat bestimmt werden. Die erste Stufe bei der Reduktion dieser Verbindungen ist ein reversibler Einelektronenprozeß, der zum Organoquecksilberradikal führt und einen wohldefinierten Wechselstrompeak liefert. Die optimalen Bedingungen zur Bestimmung einer repräsentativen Auswahl von Olefinen wurden ermittelt.

**Résumé**—On peut doser une large gamme d'oléfines par polarographie en courant alternatif de leurs composés d'addition avec l'acétate mercurique. Le premier stade de la réduction de ces composés est un processus réversible à un électron formant le radical organo-mercure, et il donne un pic de courant alternatif bien défini. On a établi les conditions optimales pour la détermination d'une sélection représentative d'oléfines.

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# CHITIN AND CHITOSAN AS CHROMATOGRAPHIC SUPPORTS AND ADSORBENTS FOR COLLECTION OF METAL IONS FROM ORGANIC AND AQUEOUS SOLUTIONS AND SEA-WATER*

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**Summary**—The rates of adsorption of several metal ions on chitin and chitosan in water and sea-water have been measured; chitin and chitosan are proposed as chromatographic chelating supports. These natural polymers are also suitable for recovery of trace metals from sea-water.

AMINOETHYLCELLULOSE, diethylaminoethylcellulose, epichlorhydrinethanolaminecellulose and *p*-aminobenzylcellulose are complexing agents for transition metals and are suitable for analytical and technological applications.[1,2] These substituted polyanhydroglucosides contain relatively few amino groups and the elemental analysis indicates 0·5–1·5% nitrogen, corresponding to a low degree of substitution.

Therefore, a completely substituted polysaccharide, carrying one amine or amide group on each glucose ring should have a much higher capacity than substituted celluloses for adsorbing metal ions. Recent researches show that it is not possible to introduce more than 1·5% nitrogen into the cellulosic chain.[3,4]

Chitin, a naturally occurring polymer, contains 9% nitrogen. The name chitin indicates polymers containing both glucosamine and *N*-acetylglucosamine monomers. Poly-*N*-acetylglucosamine is called chitan and is $\beta$-(1 → 4)2-acetamido-a-deoxy-D-glucan: chitosan is completely deacetylated chitan or chitin.

Among these natural polymers, chitin is the most abundant in vegetables and animals[5] and its degradation leads to *N*-acetylglucosamine and chitobiose. Elemental analysis of chitins from various sources gives constant values, indicating that there is one nitrogen atom on each ring.[6] Chitin has also been studied by chemical and enzymatic hydrolysis,[5,7–10] by deuterium exchange, infrared spectrometry, differential thermal analysis,[8–10] nuclear magnetic resonance, X-ray diffraction,[9,11–12] and electron microscopy.[13] Data on chitan[9,14] and on chitosan[15] have also been published. Nevertheless no information is available concerning the interactions of metal ions with these polymers, in spite of their interesting characteristics mentioned above.

In fact chitin and chitosan appear attractive as chelating chromatographic supports. They are unaffected by temperature variations. Chitin does not putrefy, as it is not attacked by bacteria, and it is indifferent to pH. Chitosan is slightly soluble in mineral acids at pH below 5·8; it is soluble in some organic acids.

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Chromatographic applications of chitin are sparse and fundamental studies are lacking. The separation of carboxylic acids has been reported[16] and so has the behaviour of lisozima;[17] in the inorganic field there is only one attempt to separate calcium, magnesium and iron in 0·005$M$ hydrochloric acid[18] but it should be remarked that the ion concentrations were too high for a first approach to the study of the adsorption capacity of the polymer, and that the acidity was too low because chitin has a tendency to neutralize acidic solutions; moreover the retention mechanism was not discussed.

No studies or applications of chitosan in inorganic chromatography are known.

The present article describes a fundamental study of the adsorption capacity of chitin and chitosan.

## EXPERIMENTAL

Radiochemical techniques, which enable the adsorptions at very low concentration levels to be followed, were used wherever possible: they have been previously described.[2] Standard colorimetric techniques were used for a few elements.

Chitin flakes were obtained from crab shells. They were ground and the 100–200 mesh fraction was used. Chitosan was obtained by deacetylation of chitin as has been reported.[15] Columns 150 × 10 mm prepared.

Test solutions were $4{\cdot}42 \times 10^{-4}M$ in metal ion. Sea-water was collected near Rimini, Italy, and used at once with no treatment other than the introduction of radioisotopes. The radioactive solutions contained ($\mu$g of metal in 50 ml): Hg 0·040, Co 0·0104, Ag 0·38, Mo 0·02, Ir 2·6, Cs 0·004, Zn 0·02, Fe, Au, Sb and Cr not specified.

## RESULTS AND DISCUSSION

The adsorption rates of twelve transition and post-transition metal ions, caesium, antimony and sulphite, have been measured. To make possible a comparison of chitin and chitosan with the substituted celluloses, the adsorption rates of a few elements have been measured in ethyl ether. At the previously mentioned concentrations,[2] the adsorption was instantaneous and total. This confirms that chitin has higher capacity than substituted celluloses.

In aqueous solutions, where celluloses are generally unsuitable for the collection of metals, chitin and chitosan present selectivity and preferential adsorption for certain ions. Generally speaking, adsorption depends on time of contact, temperature, pH, concentration of the ion under examination and concentration of the other ions present. Figure 1 shows the adsorption of mercury on chitin from solutions at various concentrations of mercury(II) chloride, at 20° after 2-hr contact.

In Table I are listed the adsorption data for chitin from a reference concentration of $4{\cdot}42 \times 10^{-4}M$. Chitin is particularly effective in collecting gold, iron, antimony, iridium, copper, palladium, molybdate and chromate from distilled water solutions. No large differences were found for potable water solutions. Generally at pH 6 the values are higher than at pH 2·5 but for cobalt and caesium are too low to be measurable. For molybdenum, the values are higher at low pH; at pH 1 a gram of chitin adsorbs more than 1 mmole. Data for chromate are in Table II; the adsorption capacity is maximal at a pH between 3 and 4 and chitosan is more effective than chitin. These results indicate that chromate ion is adsorbed on chitin in preference to chromium(III). This is in agreement with Table I, where sea-water values for chromium are higher than the corresponding values for distilled water media. Previous work has shown that in sea-water chromium exists as chromate.[19]

In neutral sea-water, the values are in any case very high for all the ions studied,

TABLE I.—ADSORPTION OF METAL IONS ON 200 mg OF CHITIN, 100–200 MESH, FROM 50 ml OF WATER CONTAINING 22·1 $\mu$mole OF METAL, AT 20°C.

| Ion | Time, *hr* | Degree of adsorption, % | | |
|---|---|---|---|---|
| | | pH 2·5 | pH 6 | pH 7 |
| | | distilled water | | sea-water |
| Hg$^{2+}$ | 1 | | 42 | |
| | 2 | 7 | 51 | |
| | 4 | 7 | 62 | 7 |
| | 7 | | | 7 |
| | 24 | | 55 | 10 |
| Co$^{2+}$ | 2 | N.M. | N.M. | N.M. |
| | 6 | N.M. | N.M. | 5 |
| | 24 | N.M. | N.M. | 8 |
| Au$^{3+}$ | 1 | | 100 | 80 |
| | 2 | 71 | 100 | 85 |
| | 5 | 66 | 100 | 90 |
| Sb$^{3+}$* | 1 | 40 | | 42 |
| | 16 | 30 | | 42 |
| | 18 | 44 | | 42 |
| | 24 | 30 | | 42 |
| Ag$^{+}$† | 1 | | 38 | |
| | 2 | | 56 | |
| | 3 | | 62 | |
| | 4 | | 70 | |
| | 8 | | 70 | |
| Cr$^{3+}$ | 1 | 10 | 25 | 35 |
| | 2 | 15 | 20 | 46 |
| | 17 | | 30 | |
| | 24 | | 25 | 55 |
| Fe$^{2+}$ | 1 | 40 | | 100 |
| | 2 | 40 | | 100 |
| | 16 | 55 | | |
| | 24 | 50 | | |
| Zn$^{2+}$ | 1 | 0 | 45 | 30 |
| | 2 | 0 | 35 | 29 |
| | 5 | 0 | 22 | 38 |
| | 8 | 0 | 20 | 36 |
| Ir$^{3+}$* | 1 | 30 | | 18 |
| | 5 | 30 | | 30 |
| | 8 | 32 | | 43 |
| | 24 | 36 | | 46 |
| Pd$^{2+}$ | 1 | 30 | 80 | 40 |
| | 2 | 60 | 100 | 50 |
| Cu$^{2+}$ | 1 | 80 | 100 | 80 |
| MoO$_4^{2-}$ | 1 | 20 | 5 | 5 |
| | 2 | 25 | 6 | 8 |
| SO$_3^{2-}$ | 1 | adsorbed 1·07 mg from 3·17 mg/50 ml distilled water. | | |

* pH 1·5
† pH adjusted with nitric acid
N.M. = not measurable, below detection limits.

with the exception of mercury, cobalt, caesium and molybdenum. Antimony measurements were done at pH 1·5 to avoid precipitation of oxychloride; gold and iron may be partially in a colloidal state.[20,21]

At a lower concentration level, close to the natural concentration in sea-water, the ions examined are equally adsorbed, particularly gold, antimony and zinc (Table III). Some of the ions were determined by emission spectrography. Spectrographic

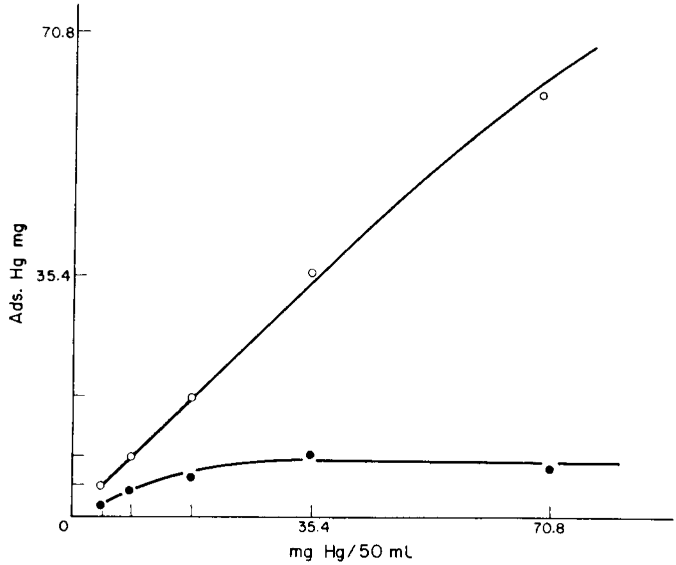

FIG. 1.—Adsorption of mercury on 200 mg of (*a*), ○ chitin and (*b*), ● chitosan, 100–200 mesh, from aqueous solutions of different concentrations of mercury(II) chloride, at 20°C, after 2-hr shaking.

analysis of chitin as supplied showed the presence of Si, P, Mg, and traces of Mn, Al, Ca and Fe. After treatment with sea-water (400 mg of chitin stirred for 12 hr in 4 l. of filtered sea-water) the chitin was found to contain Cr, Al, Cu, B, Si, Mg, Mn, Mo, V, Ag, Zn, Ti, Ni and Fe, but no Co; Na was remarkably low; Cr, Al and Cu were higher than the other metals but in accordance with their concentrations in sea-water. Gold was not detected as it is present at too low a concentration.[22]

These data are of value because, among other facts, they show that adsorption equilibria take place even at these very low concentrations, in the presence of the relatively enormous amounts of sodium, potassium and magnesium salts present in sea-water.

Adsorption capacity and adsorption rates on chitosan are much higher than those for chitin as can be seen in Table IV, certainly because there are more available

TABLE II.—DEGREE OF ADSORPTION OF CHROMATE ON CHITIN AND CHITOSAN (200 mg/50 ml OF SOLUTION).

| Amount of Cr, *mg* | pH | Adsorption, % | |
|---|---|---|---|
| | | Chitin | Chitosan |
| 1·00 | 3 | 75 | |
| | 4 | 90 | |
| | 5 | 50 | |
| 0·50 | 3 | 50 | |
| | 4 | 40 | |
| | 5 | 40 | |
| 0·25 | 3 | 80 | |
| | 4 | 60 | |
| | 5 | 25 | 80–84 |

TABLE III.—ADSORPTION OF TRACES OF METAL IONS (SEE LIST UNDER EXPERIMENTAL) ON 200 mg OF CHITIN, 100–200 MESH, FROM 50 ml OF WATER AT 20°C AND pH 7

| | | Degree of adsorption, % | | | | Degree of adsorption, % | |
|---|---|---|---|---|---|---|---|
| Ion | Time, *hr* | distilled water | sea-water | Ion | Time, *hr* | distilled water | sea-water |
| Hg$^{2+}$ | 1 | 46 | 32 | Ag$^{+}$ | 1 | 41 | 18 |
| | 2 | 40 | 32 | | 5 | 73 | 39 |
| | 6 | | 36 | | 8 | 60 | 65 |
| | 24 | | 60 | | 24 | 74 | 52 |
| Co$^{2+}$ | 1 | 75 | 41 | Ir$^{3+}$ | 1 | 13 | 7 |
| | 2 | 70 | 48 | | 15 | 23 | 14 |
| | 4 | 78 | 50 | | 18 | 25 | 14 |
| | 24 | 80 | 50 | | 24 | 28 | 13 |
| Au$^{3+}$ | 1 | 79 | 29 | Cs$^{+}$ | 1 | 57 | 3 |
| | 3 | 79 | 44 | | 2 | 65 | 5 |
| | 6 | 82 | 40 | | 8 | 65 | 4 |
| | 8 | 86 | 36 | | 24 | 62 | 5 |
| Sb$^{3+}$ | 1 | 46* | 40* | Zn$^{2+}$ | 1 | 100 | 70 |
| | 5 | 46 | 46 | | 2 | 100 | 80 |
| | 7 | 54 | 52 | | 5 | 100 | 80 |
| | 24 | 52 | 42 | | | | |

* pH 2·2.

TABLE IV.—ADSORPTION (%) OF METAL IONS ON 200 mg OF CHITOSAN, 100–200 MESH FROM 50 ml OF WATER (CONCENTRATIONS UNDER EXPERIMENTAL) AT 20°C AND pH 7, AFTER ONE HOUR SHAKING.

| | With carrier added | | Without carrier | |
|---|---|---|---|---|
| | dist. | sea | dist. | sea |
| Hg$^{2+}$ | 90 | 92 | 100 | 100 |
| Co$^{2+}$ | 40 | 65 | 100 | 100 |
| Au$^{3+}$ | 100 | 100 | 55 | 63 |
| Sb$^{3+}$ | — | — | 32 | 37 |
| Ag$^{+}$ | 100 | — | 90 | |
| Zn$^{2+}$ | 70 | 100 | 55 | 100 |
| Ir$^{3+}$ | 15 | 14 | 44 | 11 |
| Cs$^{+}$ | — | — | 100 | 5 |
| Cu$^{2+}$ | 100 | 100 | 100 | 100 |
| Pd$^{2+}$ | 100 | 100 | 100 | 100 |
| MoO$_4^{2-}$ | 25 | 9 | 20 | 8 |
| UO$_2^{2+}$ | 100 | 100 | 100 | 100 |

Values are average of five measurements.

electrons on the nitrogen atom. As a point of difference, chitosan can collect cobalt, and adsorption on chitosan is often accompanied by appearance of colour, for instance, deep blue with copper and green with iridium.

Several chromatographic separations and preconcentrations were carried out.

When 180 mg of tetrachloroauric acid were dissolved in 600 ml of distilled water, and the pH was adjusted to 1 and the solution passed through a column of chitin, no gold leakage was detected even after washing with 100 ml of water. Gold was completely recovered by elution with 100 ml of 1*N* hydrochloric acid. Gold was separated from iridium on a chitosan column by eluting iridium with 0·01*M* hydrochloric acid.

When 3 l. of sea-water with 6·5 μg of radioactive mercury added were passed through a chitin column at a flow-rate of 500 ml/hr, 68% of the mercury was retained and could be completely eluted with 1*M* ammonium thiocyanate.

Under the same conditions, 1 μg of radioactive iron was completely collected from 6 l. of sea-water, but only 30% of 0·010 μg of radioactive cobalt was recovered.

Chromate (5 mg) in 5 l. of potable water was collected on a chitin column and then recovered by washing with 100 ml of 0·1*M* disodium phosphate or sodium sulphite.

Chitosan columns are very effective in collecting iron and copper. Experiments with 1 litre of solution at a flow-rate of 10 l./hr showed that adsorption was complete for both in the upper part of the column. Copper was then eluted by passage of 5 ml of 0·1*M* EDTA, and so quantitatively separated from iron.

## CONCLUSIONS

Chitin and chitosan are proposed as chromatographic supports and as adsorbents for collection of metal ions from organic and aqueous solutions and from industrial and sea waters. They compare favourably with chelating resins now being developed;[23,24] chitin shows considerable resistance to hydrolysis.[25] The cost of chitin is competitive with that of chelating resins or resins in general. Chitosan is not on the market (though listed in one catalogue) but could become readily available, should the demand justify its production.[26] Chitin has a capacity at least as high as that of resins, and different stirring arrangement, *i.e.*, ultrasonic, might increase it. Chitin columns can be easily regenerated.

We believe that interest will mainly centre on recovery of trace metals: for instance, in the field of recovery of trace metals from waste, sea and source waters existing methods need to be improved, particularly for uranium,[26–29] and chitosan should prove useful. Chelating polymers are applied in oceanography.[30]

Chitin and chitosan should also find wide applications in the final stage of treatment of waste waters, following co-precipitation or other purification processes.

Analytically, these polymers are of value for trace metal preconcentration in laboratory or field procedures for colorimetric analysis. Problems existing in this field have already been pointed out,[31–34] other applications include water pollution surveys,[35] studies on corrosion and radiochemical separations.

As far as separations are concerned, we must stress the ability of chitin and chitosan to separate large amounts of Group IA and IIA ions from trace amounts of other metal ions. The large amounts of sodium, potassium and magnesium salts present in sea-water are not detrimental to the adsorption of transition metals on these polymers.

Crustacean chitin is presumably responsible for the adsorption of metal ions on organic residues which fall to the bottom of the sea.[36,37] Therefore studies on the interaction of ions with chitin are of importance in ecology not only in connection with water pollution but also with ionic equilibria in uncontaminated natural waters.

The nature of the chemical bonds between chitin and metal ions will be discussed in due course.[38]

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**Zusammenfassung**—Es wurden die Adsorptionsgeschwindigkeiten einiger Metallionen auf Chitin und Chitosan in Wasser und Meerwasser gemessen. Chitin und Chitosan werden als Adsorptionmittel in der Chromatographie vorgeschlagen. Diese Naturpolymere sind zur Gewinnung von Metallspuren aus dem Meerwasser geeignet.

**Résumé**—On a mesuré les vitesses d'adsorption de plusieurs ions métalliques sur la chitine et le chitosane dans l'eau et l'eau de mer; on propose la chitine et le chitosane comme supports chélatants chromatographiques. Ces polymères naturels sont aussi convenables pour la récupération de métaux à l'état de traces dans l'eau de mer.

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# SHORT COMMUNICATIONS

## Cloud-point analysis of microlitre samples—determination of water in six common solvents

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BECAUSE of the versatility of cloud-point analysis we have attempted a more systematic and general study than those in the literature, and have modified the method for analysis of microlitre samples. Because observation of the cloud-point is no more difficult with 0·5 ml of solution than 10 ml, the method is ideally suited to small samples. We have accurately determined the water content of 10–50 $\mu$l samples of several common laboratory solvents by observing their effect on the cloud-point of 0·5 ml of a test solution of methanol in n-hexane.

The cloud-point of a two-component system is strongly dependent on the presence of traces of any other component, for example, water. A knowledge of the functional relationship between the amount of contaminant and the cloud-point temperature makes it possible to assay unknown samples by measuring their cloud-points.

The early literature on cloud-point analysis was summarized in a previous paper.[1] Robertson[2] used a cloud-point technique, similar to those described here, to determine the amount of water in ethanol. The work described here does not differ in principle from Robertson's; we hope it is a wider and more systematic study of his method.

## EXPERIMENTAL

### *Reagents*

Methanol, acetone and ethyl methyl ketone of reagent grade, gas-chromatographic grade 2-propanol and spectrographic quality dioxan were obtained from J. T. Baker Co. Chromatographic grade n-hexane was obtained from City Chemical Corp. and absolute ethanol from National Distillers Corp., U.S.A.

### *Apparatus*

A test-tube or centrifuge-tube was half submerged in a water-bath fitted with a magnetic stirrer and an accurate thermometer. A wire, connected to an electrical buzzer, intruded to the bottom of the tube. The buzzer was operated intermittently, causing the wire to oscillate rapidly and agitate any liquid in the tube.

### *Procedure*

A test solution of dry methanol in n-hexane was prepared, the mole fraction of methanol being 0·550. The test solution was warmed above its critical point to make it homogeneous and 500 $\mu$l were placed in the test-tube. The unknown was added to the test solution in quantities of 10, 25, or 50 $\mu$ml and the temperature of the water-bath raised until the new solution was homogeneous and clear when stirred with the vibrating wire. As the water-bath and sample slowly cooled, thermal equilibrium was maintained between the bath and the contents of the test-tube by vigorously stirring both. At a well defined temperature, a distinct turbidity appeared. Typical standard deviations for measurement of the cloud-point in 50-$\mu$l aliquots range from 0·1° to 0·20. The amount of water in the unknown was read from a graph like those in Figs. 2–4.

## RESULTS AND DISCUSSION

The lower curve in Fig. 1 is a typical phase diagram for two partially miscible liquids. The critical solution temperature, CST, can be determined accurately for a truly binary solution (no trace contaminants), but the critical solution *composition* is usually uncertain because the solubility curve is normally flat around the CST; solutions of different mole fractions near the critical solution composition show turbidity at essentially the same temperature. The term "cloud-point" is more general than "critical solution temperature"; it simply means the temperature at which turbidity appears, without reference to composition.

We selected a 0·550 mole fraction solution of methanol in n-hexane as the test solution because that is a convenient concentration on the flat part of the solubility curve near, but not necessarily at, the critical solution composition. When samples of 10, 25, or 50 μl of dry methanol are added to the test solution, the composition changes, but not enough to cause a change in the cloud-point, which is the same as the CST under these conditions. This behaviour can be seen in Fig. 2.

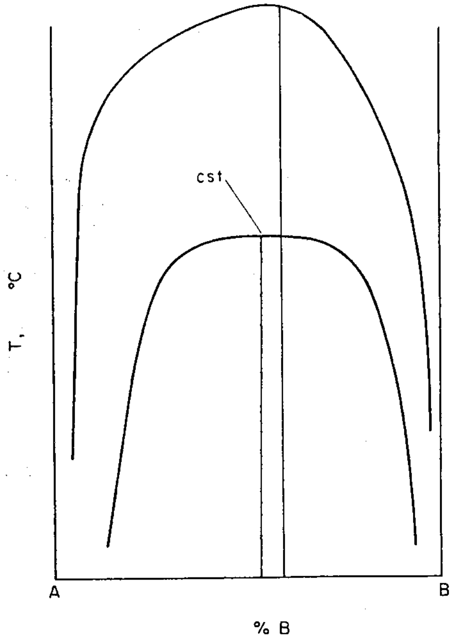

Fig. 1.—Displacement of the solubility curve in a two-component system by the introduction of a small amount of a third component. Depending on the nature of the third component, displacement can also be downward.

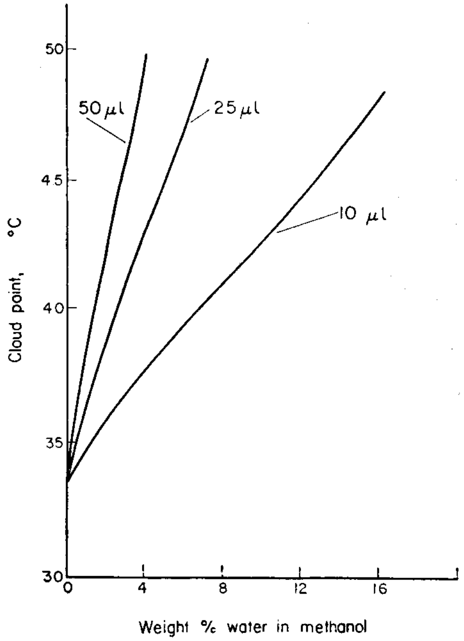

Fig. 2.—Displacement of the cloud-point of a 0·550 mole fraction solution of methanol in n-hexane. Displacement is caused by 10, 25 and 50-μl additions of methanol contaminated with water.

### *The CST of methanol in n-hexane*

The critical solution temperature of methanol and n-hexane has an interesting seventy-year history. Early results are high,[3] probably owing to difficulties in drying methanol. More recent results[4] are too low because, the methanol problem having been solved, the n-hexane could not be completely rid of structural isomers which lower the entire solubility curve, though their effect is quantitatively smaller than that of water.

We have used the purest reagents we could obtain, have calibrated our thermometers, and are convinced, like a dozen of our predecessors, that our value is the correct one: 34·4 ± 0·2°.

For the analyst, however, the point is academic. The calibration curve is constructed with the reagents to hand and the procedure applied. The calibration curve will be displaced but the method is the same.

### *Pseudo-binary solutions*

Small amounts of a third component have a profound effect on the entire solubility curve. If the new component is extremely insoluble in one of the original components, as water is in n-hexane, the solubility curve is displaced upward. Other third components may displace the solubility curve downward, for example, methyl pentane contaminating the n-hexane–methanol system. We shall refer to binary solutions contaminated with a trace of other components as pseudo-binary solutions.

As Fig. 1 shows, the shape of the pseudo-binary curve may be changed. There is no reason to suppose that the maximum in the pseudo-binary solution curve will come at the same mole fraction of major components as it did for the true binary solution.

Figure 2 shows the cloud-point as a function of the amount of water in methanol sample solutions added to the test solution of dry methanol in n-hexane. The extreme sensitivity of cloud-point methods is evident. The addition of 50-µl samples produces a calibration curve with a slightly varying slope of about 0·28% water (w/w) per degree. Assuming the cloud-point can be observed to within 0·2°, variation in water content of less than 0·06% w/w should be detectable. Similarly, the sensitivity is about 0·13% for 25-µl samples and 0·20% for 10-µl samples.

The calibration curve is not linear, but reverses curvature, as is most clearly seen in the 10-µl curve of Fig. 2, at about 10% water. Judging from Figs. 3 and 4, the positive curvature is probably spurious. Water is more dense than methanol and addition of a constant volume of sample, of increasing water content means that an increasing weight of sample is being added at higher water concentrations. Positive curvature is not observed in any of the other five systems studied.

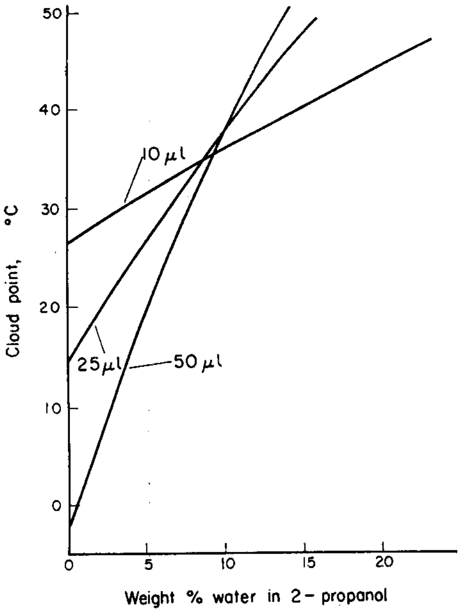

FIG. 3.—Displacement of the cloud-point of a 0·550 mole fraction solution of methanol in n-hexane. Displacement is caused by 10, 25 and 50-µl additions of 2-propanol contaminated with water.

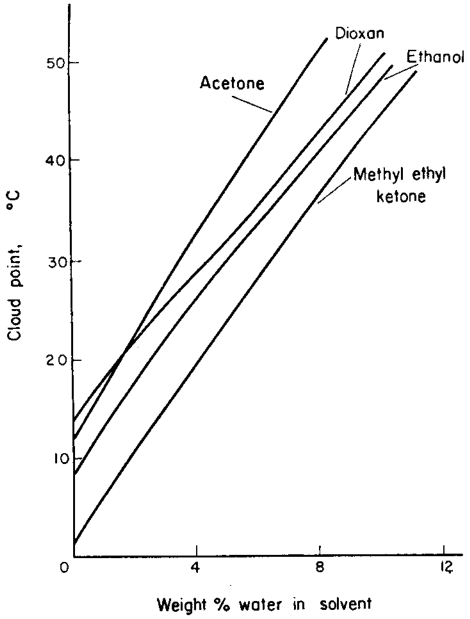

FIG. 4.—Displacement of the cloud-point of a 0·550 mole fraction solution of methanol in n-hexane. Displacement is caused by 50-µl additions of acetone, dioxan, ethanol and ethyl methyl ketone contaminated with water.

Figure 3 shows the effect of adding a sample of 2-propanol, containing water, to the test solution. The pseudo-binary solutions are now actually quaternary. The new factor is the depression of the cloud-point by propanol, counteracted by the water in the propanol. Larger samples, introducing more propanol, depress the intercept of the calibration curve more than smaller ones.

Figure 4 shows analogous curves for acetone, dioxan, ethanol and 2-butanone. The slopes are similar to the corresponding plots for methanol and 2-propanol, except that no reversal of curvature is observed and dioxan has a greater negative curvature than the other solvents. Since dioxan has a slightly greater density than water, we expect the density effect just mentioned to be reversed and to contribute to the normal negative curvature.

## CONCLUSION

We believe the sensitivity, convenience and generality of the cloud-point method make it compare favourably with other physical criteria for determination of the composition of binary solutions, particulary of pure solvents contaminated by an unknown amount of water. Routine analysis of many samples can be achieved simultaneously. A constant-temperature bath is set at the CST corresponding to the maximum tolerable water contamination and any number of samples are immersed and agitated in the bath. After temperature equilibrium has been attained, those which are turbid contain more than the tolerable amount of water; those which are not turbid pass specification.

The primary disadvantage is that of other physical methods. The number, amount and identity of components must be known for a calibration curve to be constructed. Any component not accounted for invalidates quantitative results.

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**Summary**—The classical cloud-point technique for determination of small amounts of water in organic solvents has been systematically investigated. The extreme sensitivity of the critical solution temperature of binary liquid mixtures to traces of impurity in one of the components makes the cloud-point method capable of high accuracy and sensitivity for routine determination of solvent contamination by water, and is admirably suited to analysis of small samples. Typically, the absolute error for water as contaminant is about 0·2% for 10-μl samples and 0·06% for 50-μl samples. The critical solution temperature used was that of the n-hexane–methanol system. Its value is in dispute and considerable care was taken to obtain what is believed to be the correct value of 34·4 ± 0·2°. Small amounts of water in methanol, ethanol, 2-propanol, acetone, ethyl methyl ketone and dioxan were determined.

**Zusammenfassung**—Das klassische Trübungspunkt-Verfahren zur Bestimmung kleiner Wassermengen in organischen Lösungsmitteln wurde einer systematischen Prüfung unterzogen. Die extreme Empfindlichkeit der kritischen Lösungstemperatur binärer flüssiger Mischungen gegen Spuren von Verunreinigung in einer der Komponenten bewirken hohe Genauigkeit und Empfindlichkeit des Trübungspunkt-Verfahrens bei der Routinebestimmung von Wasser in Lösungsmitteln; außerdem ist es zur Analyse kleiner Proben hervorragend geeignet. Der absolute Fehler für Wasser als Beimischung beträgt im typischen Fall etwa 0,2% bei 10 μl-Proben und 0,06% bei 50 μl-Proben. Als kritische Lösungstemperatur wurde die im System n-HexanMethanol verwendet. Ihr Wert ist umstritten; mit beträchtlicher Sorgfalt wurde als wahrscheinlich richtiger Wert 34,4 ± 0,2° ermittelt. Kleine Wassermengen in Methanol, Äthanol, 2:Propanol, Aceton Äthylmethylketon und Dioxan wurden bestimmt.

**Résumé**—On a systématiqement étudié la technique classique du point de trouble pour la détermination de petites quantités d'eau dans les solvants organiques. L'extrême sensibilité de la température critique de solution de mélanges liquides binaires à des traces d'impuretés dans l'un des constituants rend la méthode du point de trouble capable de hautes précision et sensibilité pour la détermination de routine de la contamination d'un solvant par l'eau, et convient admirablement à l'analyse de petits échantillons. Ainsi, l'erreur absolue pour l'eau en tant que contaminat est d'environ 0,2% pour des échantillons de 10 μl et de 0,06% pour des échantillons de 50 μl. La température critique de solution utilisée a été celle du système *n*-hexane-méthanol. Sa valeur est en discussion et l'on a pris un soin considerable pour obtenir ce qu'on croit être la valeur correcte de 34,4 ± 0,2°. On a déterminé de petites quantités d'eau en méthanol, éthanol, 2-propanol, acétone, méthyléthylcétone et dioxane.

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# Emission spectral analysis using photographic plates treated with a phenidone developer

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PHENIDONE (1-phenyl-3-pyrazolidone) is a relatively new agent for photographic plates.[1–5] Developers containing phenidone are notable for their high activity and storage stability, but have seldom been used for processing spectrographic plates. Because of this, we undertook a more detailed investigation of this type of developer with a view to its application in spectrographic analysis. Certain sensitivity characteristics of spectral photographic plates, treated with phenidone developers, were investigated. Comparisons were made under standard conditions, with the same types of spectral photographic plates treated with the standard developers recommended by the manufacturers. The characteristics were also investigated after subsidiary treatment of the plates with a chromium intensifier.[6] The combination of these two methods makes it possible to obtain a double intensification of the blackening of the spectral lines and in this way, for the weaker lines, up to 6-fold intensification could be obtained.

## EXPERIMENTAL

The ISP-28 (USSR) and Q-24 (Carl-Zeiss, Jena) spectrographs were used; the former had a nine-step filter, and the latter a six-step filter, the transmission of both filters being calibrated in the laboratory. Blau Hart WU-2 and Ultraviolett UV-1 (ORWO) spectral photographic plates were used. The results are generally analogous for other types of plate, with some exceptions. On each plate the emission from standards was photographed several times, while simultaneously the spectrum of certain standards was photographed several times through the appropriate step-filter. The blackening-curve for a given spectral line in a particular wavelength region is obtained by use of the step-filters, whilst the concentration-calibration curves are prepared by the three-standard method, employing very homogeneous low-alloy steel standard samples. The excitation used throughout was a spark source, with previously chosen electrical parameters.

The phenidone-hydroquinone developer had the following composition.

| | |
|---|---|
| Water (35–40°) | 600 ml |
| Sodium sulphite | 100 g |
| Hydroquinone | 6 g |
| Borax | 5 g |
| Boric acid | 4 g |
| Phenidone | 0·2 g |
| Potassium bromide | 1 g |
| Water | to 1000 ml |

We later substituted 2 mg of benzotriazole for potassium bromide as antifogging agent, obtaining much less fogging of the plates. The chemical components are given in order of dissolution. The borax, boric acid, bromide and phenidone are dissolved separately in water at 50–60° and added to the bulk solution.

The optimum development time varies between 12 and 16 min at 22°, depending on the type of plate. For the Blau Hart plates it is 15 min. If the developer is diluted with an equal volume of water the optimum development time of the Blau Hart plates is 25 min.

The plates were developed under strictly similar conditions, those of a given series being done at one time in a special container holding up to 10 plates. The blackness of the spectral lines was measured with a Zeiss high-speed microphotometer.

The results were compared with those obtained by developing absolutely similar plates in a conventional Rodinal R-09 developer (recommended by the firm ORWO), diluted 1:20, for 6 min at 20°.

## RESULTS AND DISCUSSION

Figure 1 shows typical blackening curves (at 337·0 nm) for the Blau Hart plates treated in the proposed phenidone–hydroquinone developer (curve 2) and, for comparison, in the R-09 developer (curve 1). The contrast is 0·96 with the R-09 developer, 1·18 with the concentrated phenidone developer, and 1·26 for the phenidone developer diluted 1:1. Figure 2 shows similar curves for the Ultraviolett plates (at 228·0 nm). With the R-09 developer the contrast is 0·36, and for the concentrated phenidone developer is 0·68, 0·74 and 0·90 for 8, 10 and 14 min development respectively.

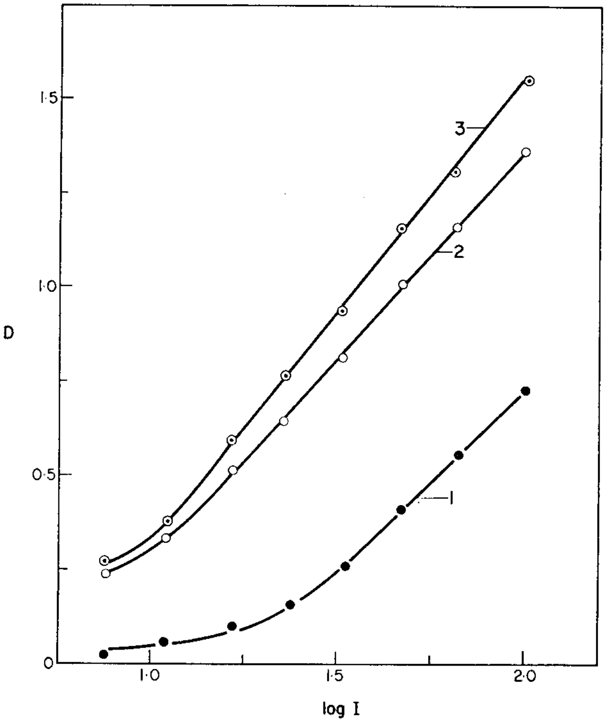

FIG. 1.—Blackening curves of Blau Hart (ORWO) photographic plates for the zone around 337·0 nm.
*1*—R-09 developer; *2*—concentrated phenidone developer; *3*—diluted phenidone developer.

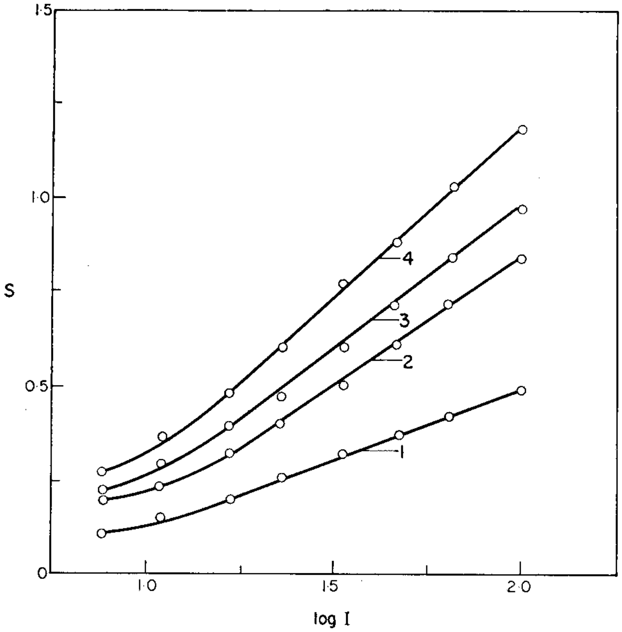

FIG. 2.—Blackening curves of Ultraviolett (ORWO) photographic plates for the zone around 228·0 nm for different development times at constant exposures.
*1*—R-09 developer; *2*,*3*,*4*—concentrated phenidone developer for 8, 10 and 14 min respectively.

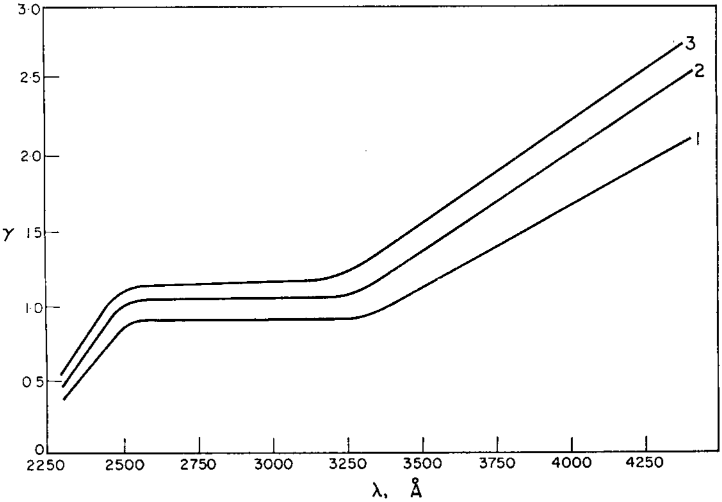

FIG. 3.—Change in contrast as a function of wavelength with Blau Hart (ORWO) photographic plates.
*1*—R-09 developer; *2*—concentrated phenidone developer; *3*—diluted phenidone developer.

The dependence of the contrast on wavelength in our three cases is shown in Fig. 3. Use of the diluted phenidone developer does not substantially increase the graininess of the plates.

The increase in the contrast increases the concentration-sensitivity of spectral analysis, because the slope of the concentration calibration curves becomes steeper. We have utilized the developer in the spectrographic determination of certain alloying elements in low-alloy steel. For example, for determination of 1·0–2·9% silicon by means of the homologous line pair Si I (251·6 nm) and Fe (251·8 nm) the slope of the calibration curve is much greater when the phenidone developers are used; both give practically the same slope but the diluted developer gives slightly higher sensitivity.

Simultaneously with the increase in contrast and in the slope of the concentration-calibration curves, a 2–3-fold increase in the density of the spectral lines is given by the phenidone developers.

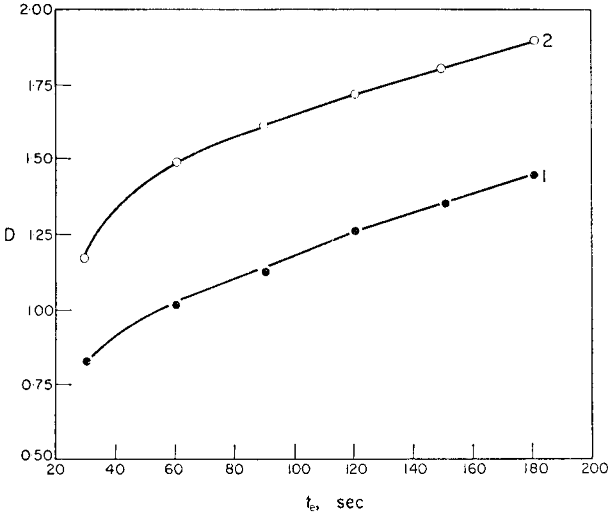

FIG. 4.—Dependence of density (*D*) on exposure time, for Blau Hart (ORWO) photographic plates.
*1*—R-09 developer; *2*—concentrated phenidone developer.

This increased density is much more important for the fainter lines than for the denser ones. Furthermore, when phenidone developers are used a number of new spectral lines appear which are not found when the conventional developers are used. This makes it possible (*a*) to lower the limits of detection and determination, (*b*) for higher contents, to reduce the exposure time. The second possibility is illustrated in Fig. 4, which shows the change in density with exposure time. To obtain a density of 1·20 an exposure of 100 sec is needed with the conventional R-09 developer, but only 30 sec with a phenidone developer. Use of a phenidone developer can reduce exposure time by a factor of 2–4.

Earlier[6] we examined the use of a chromium intensifier in subsidiary treatment of spectral photographic plates. The plate is developed and fixed and then bleached in a solution compounded as follows.

| | |
|---|---|
| Potassium dichromate (10% solution) | 15 ml |
| Hydrochloric acid (10% solution) | 5 ml |
| Distilled water | 100 ml |

The bleaching is continued until the spectral lines have practically completely disappeared, the plate is washed in running water until its yellowish tint disappears, and is then developed, fixed, and washed. The whole operation is done in diffuse daylight or strong artificial light and can be repeated; it results in an increased density and contrast. The density of the fainter lines may be increased by a factor of up to 6. The slope of concentration-calibration curves is also increased.

The effect of this double intensification is clearly seen in Table I. For comparison of the results to be more thorough, the spectra were photographed through a nine-step filter. In this way the sensitivity towards weaker lines can be assessed. The results for the 216·2 nm line are particularly significant, since the phenidone developer/chromium intensifier treatment permits greater attenuation, thus establishing the possibility of lowering the limits of detection and determination.

TABLE I.—DENSITY OF THE SPECTRAL LINES AND THE FOGGING

| Step no. | Density of the spectral lines (corrected for fogging) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fe II, 216·20 *nm* | | | Fe I, 227·99 *nm* | | | Fe I, 293·69 *nm* | | |
| | A | B | C | A | B | C | A | B | C |
| I | 0·055 | 0·108 | 0·194 | 0·28 | 0·51 | 0·75 | 0·66 | 1·22 | 1·80 |
| II | 0·041 | 0·096 | 0·150 | 0·24 | 0·46 | 0·66 | 0·52 | 1·01 | 1·55 |
| III | 0·034 | 0·075 | 0·112 | 0·19 | 0·38 | 0·56 | 0·44 | 0·86 | 1·30 |
| IV | 0·024 | 0·061 | 0·095 | 0·14 | 0·32 | 0·46 | 0·33 | 0·68 | 1·06 |
| V | — | 0·042 | 0·082 | 0·10 | 0·25 | 0·35 | 0·23 | 0·53 | 0·87 |
| VI | — | 0·032 | 0·056 | 0·07 | 0·19 | 0·28 | 0·17 | 0·37 | 0·66 |
| VII | — | 0·025 | 0·031 | 0·04 | 0·13 | 0·22 | 0·10 | 0·24 | 0·47 |
| VIII | — | — | 0·021 | 0·20 | 0·07 | 0·13 | 0·05 | 0·12 | 0·27 |
| IX | 0·054 | 0·106 | 0·194 | 0·25 | 0·48 | 0·74 | 0·60 | 1·18 | 1·76 |
| fog | 0·08 | 0·18 | 0·25 | 0·08 | 0·18 | 0·25 | 0·08 | 0·18 | 0·25 |

A—R-09 developer.
B—Phenidone developer.
C—Phenidone developer and repeated intensification.

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**Summary**—When spectral photographic plates are not treated in the conventional metol–hydroquinone developer, but in a phenidone developer, a strong increase in the sensitivity and a certain increase in the contrast are observed. With phenidone development, weak lines are intensified, permitting the lowering of the limits of detection and determination. The increase in the contrast increases the slope of the concentration-calibration curves and hence the concentrational sensitivity of the spectral analyses. This is illustrated in the curves for the determination of Si and Mn in low-alloy steels. Further sensitivity can be obtained by following the phenidone development by a chromium intensifying process.

**Zusammenfassung**—Wenn photographische Spektralplatten nicht im gebräuchlichen Metall-Hydrochinon-Entwickler, sondern in einem Phenidon-Entwickler behandelt werden, beobachtet man ein starkes Anwachsen der Empfindlichkeit und einen etwas besseren Kontrast. Bei Phenidon-Entwicklung werden schwache Linien intensiver, was ein Absinken der Grenzen für Nachweis und Bestimmung bedingt. Der bessere Kontrast erhöht die Steigung der Konzentrations-Eichkurven und damit die Konzentrations-Empfindlichkeit der Spektralanalyse. Dies wird an den Kurven für die Bestimmung von Si und Mn in niedrig legierten Stählen gezeigt. Weitere Empfindlichkeit kann gewonnen werden, wenn man an die Phenidon-Entwicklung eine Chrom-Verstärkung anschließt.

**Résumé**—Lorsque les plaques photographiques spectrales ne sont pas traitées dans le révélateur ordinaire au métol-hydroquinone, mais dans un révélateur à la phénidone, on observe un fort accroissement dans la sensibilité et un certain accroissement dans le contraste. Avec le développement à la phénidone les raies faibles sont intensifiées, permettant l'abaissement des limites de détection et de détermination. L'accroissement dans le contraste accroît la pente des courbes d'étalonnage de concentration et de là la sensibilité au point de vue concentration de l'analyse spectrale. Ceci est illustré par les courbes pour la détermination de Si et Mn dans les aciers à bas alliage. On peut obtenir davantage de sensibilité en faisant suivre le développement à la phénidone par un procédé d'intensification au chrome.

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# Determination of the ratio of copper(I) to copper(II) present as traces in ionic crystals

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It has been shown by polarographic analysis that copper added to sodium chloride melts from which crystals are grown by pulling from the melt, is present in the crystals always in the univalent state, irrespective of the oxidation state in which it was added.[1] Some physical measurements have more recently shown[2] that in some cases at least part of the copper may be present in the bivalent state, and an analytical method was therefore required to substantiate this evidence. Such a method is described in this paper.

In aqueous solutions, copper(II) may be titrated complexometrically, Chromazurol S or Murexide being used as indicator. For the determination of copper in both oxidation states a method has been described[3] in which one sample is titrated under an inert atmosphere for copper(II) only, and a second sample is oxidized by nitric acid and the total copper content titrated. This method has been applied with success for the determination of copper contents around $10^{-2}$ mole %, more than 1 g of sample being used. The need has arisen recently for analyses of smaller samples (about 0·2 g) which have been used for physical measurement, and which contain much lower copper contents. The complexometric method is not sufficiently sensitive, and a polarographic method has been developed, using a recording polarograph.

Copper(II) in solutions containing chloride ions is reduced polarographically in two steps: $Cu^{2+} \rightarrow Cu^{+}$ and $Cu^{+} \rightarrow Cu^{0}$, the second step gives rise to a well defined wave which may be used for the determination of copper. There is no wave corresponding to the first step, but a diffusion current is measurable, as can be seen in curve *b* in Fig. 1. Curve *a* is the polarogram recorded in the absence of copper. Though the diffusion current for the reduction of copper(II) cannot be measured relative to the "galvanometer zero", it can be measured relative to the blank value for the supporting electrolyte.

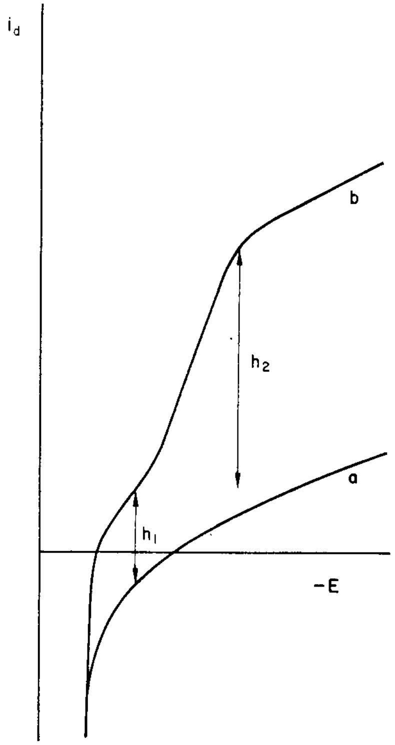

FIG. 1.—Polarograms of (*a*) 0·2 g of sodium chloride in 5 ml of 0·1*M* hydrochloric acid, (*b*) the same solution with traces of CuCl and $CuCl_2$.

The total copper content may be determined by the method of standard addition.[1] The fraction which is present as copper(II) is given by the ratio of the height of the first wave to the height of the second wave:

$$[Cu^{2+}]/([Cu^{2+}] + [Cu^{+}]) = h_1/h_2.$$

This method cannot be used for samples which contain, in addition to copper, other substances with a half-wave potential more positive than that of copper (*e.g.*, silver). In such cases it is not possible to distinguish between the diffusion current for copper(II) and that of the other component, and a complexometric method must again be used.

## EXPERIMENTAL

Nitrogen gas was purified by bubbling through a solution of alkaline pyrogallol, and no effects attributable to traces of remaining oxygen were observed. Hydrochloric acid (0·1*M*) was used for dissolving the samples, and was thoroughly de-oxygenated before use, by bubbling out with nitrogen.

### *Procedure*

Dissolve the sample in de-oxygenated hydrochloric acid, and record the polarogram (Fig. 2, curve *a*). Bubble oxygen through the solution for about 15 min to oxidize the copper(I), remove the excess of oxygen by further bubbling with nitrogen, and record the polarogram (Fig. 2 curve *b*).

The height of the more negative wave should not change, but for the other one, three possibilities exist:

(a) it does not change—all copper was originally in the bivalent state in the sample,

(b) it increases by an amount equal to the height of the second wave—all copper was originally in the univalent state,

(c) it increases to a lesser extent, in which case the proportions of the two oxidations states may be estimated as described.

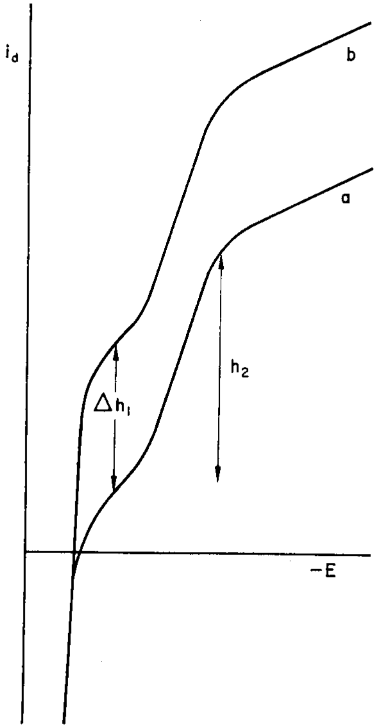

FIG. 2. —Polarograms of a solution of 0·2 g of sodium chloride containing traces of AgCl, CuCl and $CuCl_2$, (*a*) after dissolution, (*b*) after oxidation.

The method described permits the determination of as little as $10^{-4}$ mole % copper in samples of about 0·2 g of sodium chloride, and also of the ratio of copper(II) to copper(I) up to about 20:1. The method is clearly much more sensitive than the complexometric one. As an example, a sample prepared with $5 \times 10^{-3}$ mole % CuO was found to contain $2{\cdot}6 \times 10^{-4}$ moles % of copper(II), which was in good agreement with the value estimated from physical measurements.[13]

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**Summary**—A polarographic method is described for the determination of traces of copper in ionic crystals, which also allows the determination of the ratio of the concentrations of copper(II) and copper(I).

**Zusammenfassung**—Ein polarographisches Verfahren zur Bestimmung von Kupferspuren in Ionenkristallen wird beschrieben, das auch die Ermittlung des Konzentrationsverhältnisses von Kupfer(II) und Kupfer(I) gestattet.

**Résumé**—On décrit une méthode polarographique pour la détermination de traces de cuivre dans des cristaux ioniques, qui permet aussi la détermination du rapport des concentrations du cuivre(II) et du cuivre(I).

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# Extraction and determination of molybdenum with tributyl phosphate Application to analysis of copper–molybdenum ores

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THE YELLOW peroxymolybdate complex formed in aqueous solution has been used by several authors[1-3] for the determination of molybdenum. More recently, Bacon and Milner[4] have developed a differential spectrophotometric method for molybdenum determination in uranium alloys, using the same peroxymolybdate complex in aqueous solution.

In this paper the extractive properties of tributyl phosphate (TBP) for peroxymolybdate complex formed in sulphuric acid medium are reported. A reliable and precise method for molybdenum determination by means of differential spectrophotometry of the organic phase has been developed, and successfully applied to ore analysis.

## EXPERIMENTAL

Standard solutions of molybdenum were prepared from anhydrous molybdic acid, previously dried at 105°. Tributyl phosphate was purified by the Peppard procedure.[5] All reagents used were analytical grade.

The α-benzoinoxime method[6] was used for comparison in testing the application of the proposed method to analysis of copper/molybdenum ores from Sociedad Minera El Teniente, Rancagua, Chile.

### *Procedure*

Place a neutral aliquot, containing 0·3–4·5 mg of molybdenum, in a 250-ml separatory funnel, add 25 ml of 7*M* sulphuric acid and 2 ml of 6% w/w hydrogen peroxide solution and dilute to 50 ml with distilled water. Add exactly 20 ml of TBP to the mixture and shake it gently for 1 min. Separate the aqueous phase, put the TBP phase into a dried cell and read its absorbance at 340 nm against a reference TBP solution subjected to the same procedure. The relative absorbance of the sample should not be higher than 0·5.

## RESULTS AND DISCUSSION

### *Spectral characteristics*

The absorption spectrum of the peroxymolybdate complex in TBP has an absorption maximum between 325 and 350 nm (Fig. 1). This wide absorption maximum permits the application of differential spectrophotometry, because the incidence of non-monochromatic radiations that will appear on account of the greater slitwidth used, will not produce a significant error in the absorbance measurements.

### *Study of the complex extraction*

The absorbance of the extract became constant after 30 sec of shaking. Even after 48 hr the absorbance remained unchanged. Variation of temperature between 17 and 30° did not affect the quantity of peroxymolybdate complex extracted.

Maximal extraction of the complex is obtained with a molar ratio $H_2O_2/MoO_4^{2-} > 1$ in the

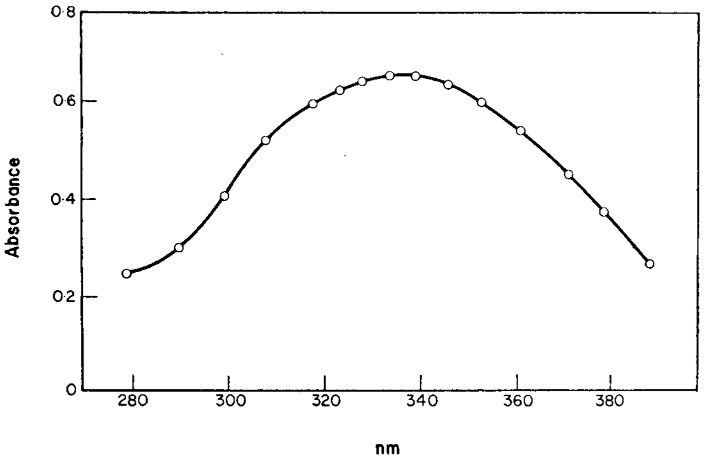

FIG. 1.—The absorption spectrum of the peroxymolybdate complex in TBP.

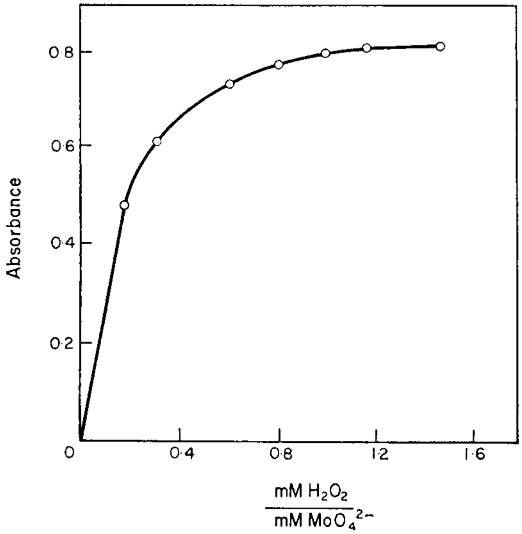

FIG. 2.—The effect of $H_2O_2$ concentration on the extraction of peroxymolybdate complex by TBP.

aqueous phase (Fig. 2). At high sulphuric acid concentration the extraction of the complex diminishes linearly according to the expression:

$$y = -0{\cdot}09x + 0{\cdot}95$$

where $x$ = molarity of sulphuric acid in the aqueous phase, $y$ = absorbance of the complex in the TBP after extraction. This can be explained by using the following equations reported by Csanyi:[7]

$$n\mathrm{MoO_4}^{2-} + n\mathrm{H}^+ \rightleftharpoons \underset{\text{polymolybdate ion}}{(\mathrm{MoO_3})_n\mathrm{O}^{2-}} + n/2\mathrm{H_2O} \qquad (1)$$

$$(\mathrm{MoO_3})_n\mathrm{O}^{2-} + 2n\mathrm{H_2O_2} \rightleftharpoons \underset{\text{peroxymolybdate ion}}{n\mathrm{HMoO_6}^-} + (n-2)\mathrm{H}^+ + (n+1)\mathrm{H_2O} \qquad (2)$$

In reaction (2), when TBP is added, a competition is established for the peroxymolybdate ion, between the protons of the aqueous phase to form polymolybdate and the organic solvent to extract the peroxy complex. This equilibrium will be shifted towards formation of non-extractable polymolybdate if the hydrogen ion concentration is increased.

A variation of ±0·1*M* in the acid concentration will produce an error of ±1% in the absorbance readings. Because of this the acid concentration must be carefully controlled. In order to avoid emulsification of TBP it is best to use 3·5*M* sulphuric acid, this being the minimum concentration to give a good phase separation.

### *Recovery of the organic solvent*

The peroxymolybdate complex is re-extracted from TBP with 1*M* sodium hydroxide. In the alkaline aqueous phase the complex is probably decomposed to yield molybdate and peroxide. Two extractions with alkali, one extraction with 3·5*M* sulphuric acid and washing twice with distilled water will allow complete elimination of the peroxymolybdate complex from the organic phase. Each washing, *etc*, is done with volumes equal to that of the TBP.

### *Calibration curve*

The calibration curves obtained at 340 nm and with various slitwidths, were straight lines with the same slope, demonstrating that Beer's law was obeyed over a large concentration range. These curves were obtained by differential spectrophotometry, with various concentrations of molybdenum in the reference solutions. The slitwidths used were 0·30, 0·50, 0·50, 0·80, 0·80 mm respectively for reference amounts of 0·30, 1·20, 2·10, 3·00, 3·90 mg of molybdenum. The limits of optimum amounts of molybdenum were determined from a series of absorbance measurements of standard solution and calculation of the error of these measurements, and were found to be 0·3–4·5 mg. The error in the absorbance values is about 1% and the standard deviation is of the order of 0·001 absorbance units.

The molar absorptivity for the complex in TBP appears to be 98 $\text{l.mole}^{-1}.\text{mm}^{-1}$, a suitable value for precision differential spectrophotometry.

### *Effect of foreign ions*

The behaviour of some cations was studied under the experimental conditions previously established. Cu(II), Cr(VI), Al, Mn(II), Zr and $UO_2$(VI) show no extraction and as such do not interfere. Fe(III), $WO_4^{2-}$, $VO_3^-$, Ti and Nb(V) are partly extracted and also impart colour to the TBP phase. In this case, the minimum permissible concentration was determined, and is given in Table I.

TABLE I.—INTERFERENCE OF SOME FOREIGN IONS IN DETERMINATION OF 0·90 mg OF Mo

| Ion | Amount added, *mg* | Mo found, *mg* | Error, % |
|---|---|---|---|
| Fe(III) | 90 | 1·23 | 36 |
| | 2·1 | 0·92 | 2 |
| | 1·05 | 0·90 | 0 |
| $WO_4^{2-}$ | 90 | 2·08 | 130 |
| | 2 | 0·94 | 5 |
| | 1 | 0·90 | 0 |
| Ti | 2 | 0·94 | 5 |
| | 1 | 0·93 | 4 |
| $VO_3^-$ | 90 | 0·99 | 10 |
| | 2 | 0·90 | 0 |
| Nb(V) | 5 | 1·08 | 20 |
| | 1·7 | 0·90 | 0 |

For the study of $WO_4^{2-}$, Ti, $VO_3^-$, and Cr(VI) it was necessary to add an additional amount of hydrogen peroxide because these ions consume it. For the first three, 1 ml of 20-volume peroxide was added, and 4 ml for Cr(VI).

*Application to ore analysis*

Many methods are described in the literature for the determination of molybdenum in ores. The gravimetric methods are very slow, and the colorimetric methods in aqueous solution suffer from many interferences.

In Table II are shown the results obtained with the proposed method and the commonly used α-benzoinoxime method.[6] An acid dissolution procedure was used.[6] The interference of iron in the TBP method was avoided by adding ammonia to the sample solution till the pH reached 8, and then filtering. In the filtrate molybdenum was determined by the procedure described.

TABLE II.—DETERMINATIONS OF Mo IN ORES

| Sample | Molybdenum, % | |
|---|---|---|
| | α-Benzoinoxime method* | TBP method* |
| 302–1 | 1·12 | 1·16 |
| 567–3 | 1·74 | 1·71 |
| 84–7 | 0·19 | 0·18 |
| 82–9 | 3·04 | 3·05 |

* Average of three determinations.

The good results obtained and the simplicity of the method enables us to present this method as very promising for the routine analysis of molybdenum ores, especially in laboratories where expensive apparatus is not available.

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**Summary**—A differential spectrophotometric method is described for the determination of molybdenum by means of solvent extraction with tributylphosphate of the peroxymolybdate complex formed with $H_2O_2$ in 3·5*M* $H_2SO_4$. The extraction parameters are studied, and the behaviour of some other ions is reported. The method is used for ore analysis.

**Zusammenfassung**—Eine spektrophotometrische Differenzmethode zur Bestimmung von Molybdän wird beschrieben. Dabei wird der mit $H_2O_2$ in 3,5*M* $H_2SO_4$ gebildete Peroxymolybdatkomplex mit Tributylphosphat extrahiert. Die Extraktionsparameter werden studiert und es wird über das Verhalten einiger anderer Ionen berichtet. Das Verfahren wird zur Erzanalyse verwendet.

**Résumé**—On décrit une méthode spectrophotométrique différentielle pour le dosage du molybdène au moyen d'extraction par solvant avec le tributylphosphate du complexe peroxymolybdate formé avec $H_2O_2$ en $H_2SO_4$ 3,5*M*. On étudie les paramètres d'extraction, et rapporte le comportement de quelques autres ions. La méthode est utilisée pour l'analyse de minerais.

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# Oxidimetric determination of triphenylphosphine

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TRIPHENYLPHOSPHINE (TPP) is widely used in co-ordination chemistry and extensive studies have been made with regard to its donor properties. However, there is a lack of suitable analytical methods for its rapid and accurate determination. Oxidation of TPP with dimethylsulphoxide to its oxide which is then gravimetrically determined as its boron trifluoride adduct,[1] oxidation with concentrated sulphuric acid and potassium persulphate at 330° to phosphorus pentoxide which can be determined by conventional methods,[2] and a mercurimetric method[3] based on the formation of difficultly soluble crystals of $(Ph_3P)_2 . HgCl_2$ have been proposed. All these methods are indirect, tedious and time-consuming, the second has to be carried out in the absence of moisture and the third is subject to many interferences. Investigation of the behaviour of TPP towards various oxidants showed that iodine and chloramine-T, in acidic medium in the presence of organic solvents such as benzene and carbon tetrachloride, readily oxidize TPP to phosphine oxide. These oxidations form the basis of a procedure for the rapid and accurate determination of TPP.

## EXPERIMENTAL

### *Reagents*

*Chloramine-T*, 0·1*N*. Approximately 0·1*N* aqueous chloramine-T solution was prepared and standardized iodometrically by the procedure of Bishop and Jennings.[4]

*Iodine*, 0·1*N*. Approximately 0·1*N* aqueous iodine solution was prepared and standardized with thiosulphate *via* dichromate.

*Triphenylphosphine*. B.D.H. "O.A.S." grade was used in the experiments.

### *Procedures*

*Determination of optimum conditions*. Known amounts of TPP were weighed into an iodine-flask, and after adjustment of the reaction conditions, a known excess of iodine or chloramine-T solution was added. After being allowed to stand for various intervals of time at room temperature the amount of unconsumed oxidant was determined with thiosulphate. The extent of oxidation was determined from the ratio of the number of mmole of oxidant consumed under the reaction conditions to the number of mmole of TPP taken.

*Recommended method*. To 0·3–0·5 mmole of triphenylphosphine add 10 ml of benzene or carbon tetrachloride to dissolve it. Then add 5 ml of 1*M* sulphuric acid and exactly 20 ml of ~0·1*N* iodine or chloramine-T solution. Mix well for a minute and then determine the residual iodine or chloramine-T (in this case after the addition of acidified potassium iodide) with thiosulphate. The amount of triphenylphosphine ($X$) is given by the expression:

$$X = \frac{(V_1 - V_2)Z \times 131{\cdot}1}{1000}\ \mathrm{g}$$

where $V_1$ is the volume (ml) of thiosulphate consumed in the blank experiment, $V_2$ is the volume (ml) of thiosulphate consumed by the excess of iodine or chloramine-T left after the oxidation of TPP, and $Z$ is the normality of the sodium thiosulphate solution. The values obtained are accurate to within 0·5%.

The method can be adapted for the determination of triphenylphosphine in many of its metal complexes. A known amount of the complex containing about 0·2–0·7 mmole of TPP is accurately weighed and to this are added 10 ml of benzene or carbon tetrachloride, 20 ml of 10% potassium iodide and 20 ml of 1*M* sulphuric acid. Then 20 ml of 0·1*N* iodine solution are introduced and after the contents have been well mixed for a minute, the excess of iodine is determined with thiosulphate. The amount of TPP present is then calculated as above.

## RESULTS AND DISCUSSION

A representative set of results obtained is given in Table I. It is seen that the oxidation of TPP with either chloramine-T or iodine is completed within a minute in acid medium when either benzene or carbon tetrachloride is added. The oxidation product appeared from the consumption of two equivalents of oxidant per mole of TPP to be triphenylphosphine oxide. This was confirmed from chemical and infrared examination of the product. In the absence of organic solvents, it was found

TABLE I.—OXIDATION OF TRIPHENYLPHOSPHINE (TPP) WITH IODINE AND CHLORAMINE-T

| Aqueous medium | *TPP taken, mmole* | *Standing period, min* | *Oxidant consumed, meq* | $\frac{\textit{Oxidant}}{\text{TPP}}$ |
|---|---|---|---|---|
| A 0.2*M* $H_2SO_4$ | 0·5496 | 2 | 1·094 | 1·990 |
| | 0·5183 | 5 | 1·036 | 1·999 |
| | 0·4347 | 15 | 0·865 | 1·991 |
| | 0·3961 | 30 | 0·788 | 1·990 |
| 0·2*M* HCl | 0·4946 | 2 | 0·989 | 2·000 |
| | 0·5306 | 5 | 1·056 | 1·990 |
| | 0·3432 | 30 | 0·683 | 1·991 |
| 0·2*M* $CH_3COOH$ | 0·4786 | 2 | 0·959 | 2·004 |
| (pH 2·65) | 0·4636 | 5 | 0·926 | 1·998 |
| | 0·4892 | 30 | 0·978 | 1·999 |
| B 0·2*M* $H_2SO_4$ | 0·6782 | 2 | 1·352 | 1·994 |
| | 0·5642 | 5 | 1·128 | 1·999 |
| | 0·4038 | 15 | 0·804 | 1·990 |
| | 0·5446 | 30 | 1·085 | 1·992 |
| | 0·4848* | 2 | 0·486 | 1·002 |
| | 0·4912* | 10 | 0·493 | 1·004 |

Amount of oxidant taken = 1·681 meq of chloramine-T or 1·980 meq of iodine.
Total volume = 100 ml. Organic solvent used = 10 ml of benzene or carbon tetrachloride.
A: Oxidations carried out with chloramine-T.
B: Oxidations carried out with iodine.
* Oxidations carried out without the addition of organic solvent.

that on the addition of excess of aqueous iodine solution to TPP, a brown solid appeared which presumably is a complex of the type $(PH_3P—I^+)I^-$ or $(PH_3P—I_2)$ which impedes the rapid oxidation of TPP. Complex formation of TPP with halogens under suitable conditions has been reported.[5–7] Oxidation of TPP with chloramine-T was also slow in absence of organic solvents.

In Table II are recorded typical results obtained with some metal complexes. The agreement between the expected and experimental values is within ±0·5%. The method has of course to be

TABLE II.—DETERMINATION OF TRIPHENYLPHOSPHINE (TPP) IN METAL COMPLEXES

| Compound | Weight of complex taken, *g* | TPP expected, *mmole* | TPP found, *mmole* |
|---|---|---|---|
| $(Ph_3P . HgCl_2)_2$ | 0·2122 | 0·397 | 0·396 |
| | 0·2091 | 0·391 | 0·390 |
| | 0·1292 | 0·242 | 0·241 |
| | 0·1687 | 0·316 | 0·317 |
| $(Ph_3P)_2HgCl_2$ | 0·1189 | 0·299 | 0·299 |
| | 0·2692 | 0·677 | 0·674 |
| | 0·2509 | 0·630 | 0·628 |
| | 0·2089 | 0·525 | 0·527 |
| $(Ph_3PCdCl_2)_2$ | 0·2416 | 0·542 | 0·540 |
| | 0·2586 | 0·580 | 0·578 |
| | 0·2941 | 0·660 | 0·658 |
| | 0·2018 | 0·453 | 0·454 |
| $(Ph_3P)_2CdCl_2$ | 0·2125 | 0·600 | 0·601 |
| | 0·1986 | 0·561 | 0·559 |
| | 0·2009 | 0·567 | 0·565 |
| | 0·2341 | 0·661 | 0·659 |

Amount of oxidant taken = 2·015 meq of iodine. Organic solvent used = 10 ml of benzene or carbon tetrachloride.

modified suitably for the determination of TPP in complexes featuring stabilization of unusual oxidation states of metals.

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**Summary**—A method for the determination of triphenylphosphine based on its oxidation to phosphine oxide by iodine or chloramine-T in acid medium in presence of benzene or carbon tetrachloride is described. The oxidation is completed within 2 min and the analytical values are accurate to within 0·5%. The method is applicable to determination of triphenylphosphine in its metal complexes.

**Zusammenfassung**—Ein Verfahren zur Bestimmung von Triphenylphosphin wird beschrieben, das auf seiner Oxidation zu Phosphinoxid in saurem Medium mit Jod oder Chloramin-T in Gegenwart von Benzol oder Tetrachlorkohlenstoff beruht. Die Oxidation ist in 2 min beendet und die analytischen Werte stimmen auf 0,5 %. Das Verfahren läßt sich auf die Bestimmung von Triphenylphosphin in seinen Metallkomplexen anwenden.

**Résumé**—On décrit une méthode pour le dosage de la triphénylphosphine basée sur son oxydation en oxyde de phosphine par l'iode ou la chloramine T en milieu acide en présence de benzène ou de tétrachlorure de carbone. L'oxydation est achevée en 2 mn et les valeurs analytiques sont précises à 0,5% près. La méthode est applicable à la détermination de la triphénylphosphine dans ses complexes métalliques.

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# Colorimetric determination of thorium with Methylthymol Blue

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Methylthymol Blue (MTB) is one of the most useful indicators in complexometry. The formation of intensely blue complexes has also been utilized for colorimetric determination of many metals such as zirconium,[1–6] hafnium,[6] thorium,[5,7,8] niobium,[9–13] titanium,[11,13] gallium,[5,14,15] aluminium,[16–18] iron,[11,19] mercury,[20] some rare earths,[21–26] magnesium,[27,28] and also for indirect determination of fluoride[29,30]. The selectivity of these reactions is low, except for the reactions with zirconium and hafnium which proceed in strongly acidic medium (0·2–1·0*M* hydrochloric or perchloric acid) where the other elements do not form complexes with the indicator.

Up to now, the reaction of thorium with MTB has been studied only in acidic medium, by Otomo,[7] Tikhonov,[5] and Vasilenko and Shanya.[8] According to these authors a $Th(MTB)_2$ complex is formed and has an absorption maximum at 570–595 nm. The molar absorptivity varies from $3·9 \times 10^3$ to $5·00 \times 10^3$ $l.mole^{-1}.mm^{-1}$, depending on the pH.[14] No attempts were made to eliminate the interference of elements under the same conditions.

During the systematic study of this thorium–MTB reaction, we have found that thorium forms a violet 1:2 complex with MTB in slightly alkaline medium (pH 9–10) even in the presence of EDTA and DCTA; the absorption maximum is at 535 nm. Because EDTA masks almost all other elements against this reagent, we have studied this reaction thoroughly as a new and very sensitive method for colorimetric determination of traces of thorium. In addition we have found that this 1:2 complex is extractable into trioctylmethylammonium chloride as an intensely red-orange ternary complex, which makes the reaction more selective and sensitive.

## EXPERIMENTAL

### *Reagents*

*Thorium nitrate*, 0·05*M*. Prepared by dissolution of 27·61 g of $Th(NO_3)_4 . 4H_2O$ in 1 litre of water slightly acidified with nitric acid, and standardized complexometrically. The solution was diluted 100-fold to provide a $5 \times 10^{-4}M$ thorium solution.

*Methylthymol Blue*, $5 \times 10^{-4}M$. Prepared by dissolution of 0·0383 g of the reagent in 100 ml of water acidified with formic acid. According to spectrophotometric measurements the solution is stable for two days.

### *Reaction of thorium with MTB*

*Effect of pH.* The experiments were performed as follows: to 0·5 ml of $5 \times 10^{-4}M$ thorium in 25-ml volumetric flasks were added 2 ml of $5 \times 10^{-4}M$ MTB and various amounts (0·1–15 ml) of 1*M* triethanolamine (TEA) solution, then the solutions were diluted to the mark and mixed thoroughly. One part of the solution was used for the determination of pH, the rest for obtaining the absorption spectrum in the range 400–650 nm against water as a blank (Fig. 1). The optimal pH is 9·2–10.

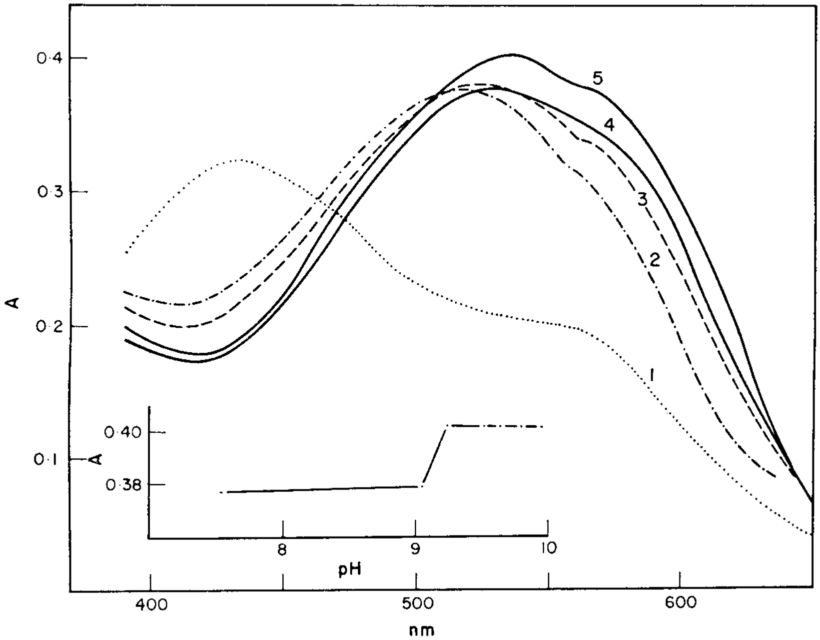

FIG. 1.—Influence of pH on absorption spectra of $Th(MTB)_2$.
2 ml of $5 \times 10^{-4}M$ MTB + 0·5 ml of $5 \times 10^{-4}M$ Th + $x$ ml of 1*M* TEA, diluted to 25 ml. Measured in 10-mm cuvette against water as a blank.
*1*—pH 2·8 (0 ml of TEA); *2*—pH 4·55 (0·1 ml of TEA);
*3*—pH 8·25 (0·5 ml of TEA); *4*—pH 9·04 (2·5 ml of TEA);
*5*—pH 9·27, 9·63, 9·80 and 9·90 (5,10,15 and 25 ml of TEA).

In this pH-range the maximum absorption is at 535 nm and is constant. For this reason further experiments were made with 15 ml of 1*M* TEA in 25 ml of final solution.

*Composition of the Th–MTB complex.* By the usual spectrophotometric methods the composition of the complex has been found to be $Th(MTB)_2$ (see Fig. 2).

*Absorption by free MTB.* MTB itself absorbs some light at 535 nm in the presence of TEA(under the same pH conditions) and has an absorption maximum at 600 nm. Because we cannot eliminate traces of calcium (or other metal impurities) in MTB itself, we compared the absorption spectra

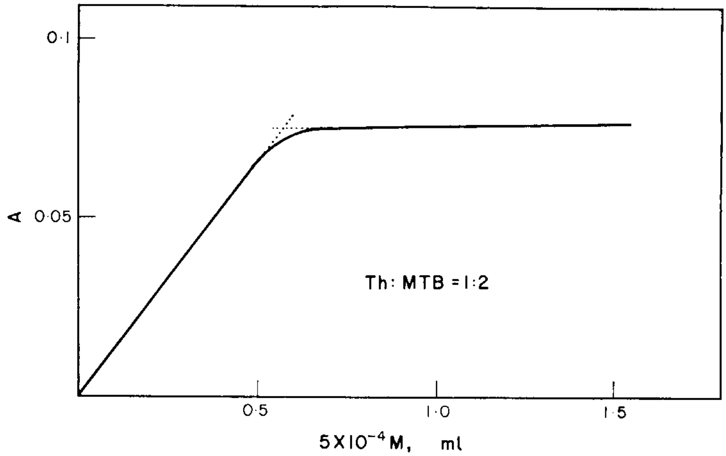

FIG. 2.—Composition of the Th–TMB complex.
0·3 ml of $5 \times 10^{-4}M$ Th + $x$ ml of $5 \times 10^{-4}M$ MTB + 15 ml of $1M$ TEA + 0·2 ml of $5 \times 10^{-2}M$ EDTA, diluted to 25 ml. Measured after 20 min against water as a blank in 10-mm cuvettes.

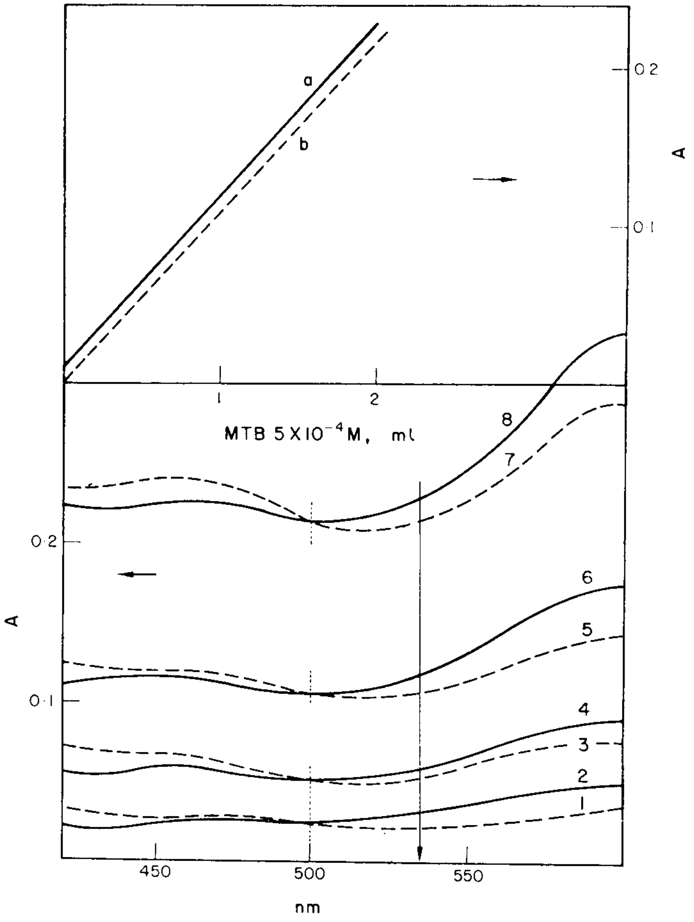

FIG. 3.—Absorption spectra of free MTB.
$x$ ml of $5 \times 10^{-4}M$ MTB + 10 ml of $1M$ TEA diluted to 25 ml
Full curves: $x = 0·2, 0·5, 1·0, 2·0$ ml
Dotted curves: the same in the presence of 0·1 ml of $5 \times 10^{-2}M$ EDTA.

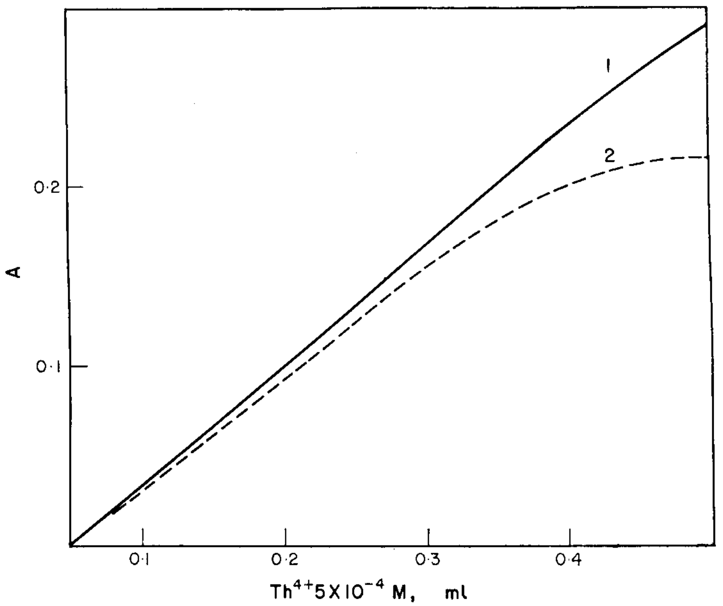

FIG. 4.—Lambert–Beer law.
Full curve: $x$ ml of $5 \times 10^{-4}M$ Th + 2 ml of $5 \times 10^{-4}M$ MTB + 15 ml of $1M$ TEA diluted to 25 ml; measured against MTB + TEA as a blank.
Dotted curve: the same with addition of 0·2 ml of $5 \times 10^{-2}M$ EDTA; measured against a blank containing the same amount of EDTA.

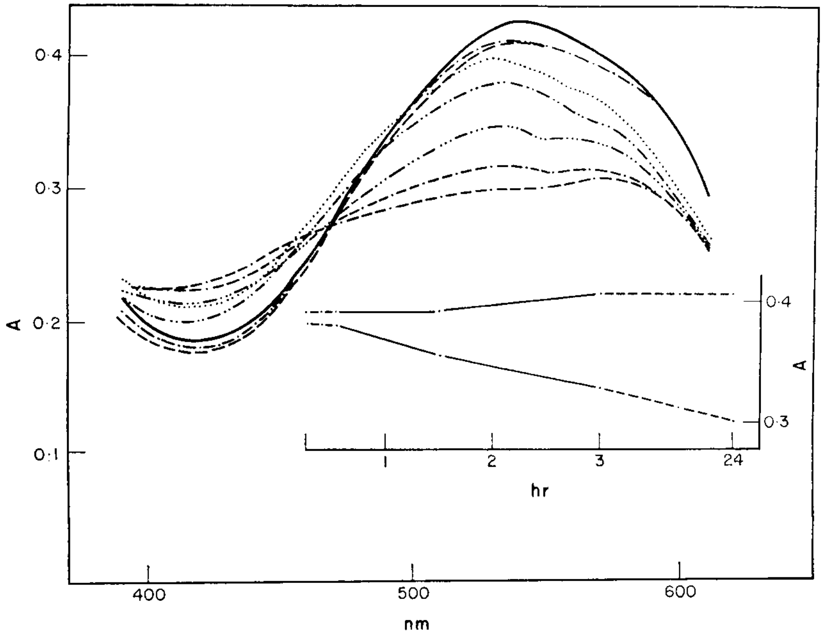

FIG. 5.—Stability with time, of Th(MTB)$_2$ complex.
0·5 ml of $5 \times 10^{-4}M$ Th + 2 ml of $5 \times 10^{-4}M$ MTB + 15 ml of $1M$ TEA; diluted to 25 ml. Measured at 535 nm in 10-mm cuvettes.
Full curve: without addition of EDTA Dotted curve: with addition of 0·5 ml of $5 \times 10^{-2}M$ EDTA.

of MTB in the presence and absence of EDTA. We found that the presence of EDTA is without effect on the absorption of MTB at 500 nm. The absorbance of the Th–MTB complex has to be measured at 535 nm, where the absorbance is a little higher in the absence of EDTA than its presence (see Fig. 4). In both cases (*i.e.*, with or without EDTA) the absorbance of an MTB solution is directly proportional to its concentration (see Fig. 3). Therefore, the reference blank should contain the same amount of EDTA as the sample solution does.

*Stability of the complex.* The concentration ratio MTB:Th must be at least 2. Figure 4 shows that the MTB:Th ratios from 4 to 20 do not alter the absorbance of the Th–MTB complex. Up to a 100-fold excess of EDTA is without effect on the colour intensity of the complex. In Fig. 4 is also shown the calibration curve of thorium in the absence of EDTA. The displacement is due to the presence of metal impurities.

The reaction between thorium and MTB proceeds instantaneously after mixing of the reagents. The absorbance does not change during the first 90 min, but then rises a little. In the presence of excess of EDTA the initial absorbance is a little lower and does not change during the first 30 min. Figure 5 illustrates the effect of EDTA over a longer period of time.

The Lambert-Beer law is obeyed for 0·5–2·8 ppm when the following procedure is used. To 5 ml of slightly acidic solution containing 2–15 $\mu$g of thorium (in a 25-ml volumetric flask) add 2 ml of $5 \times 10^{-4}M$ MTB, 15 ml of $1M$ TEA, 0·5 ml of $0{\cdot}05M$ EDTA and dilute to the mark. Mix, and measure the absorbance at 535 nm against a reagent blank.

## *Interferences*

Almost all metals are masked with EDTA, exceptions being beryllium, titanium, uranium, silver and antimony. Some bivalent metals such as copper, zinc, *etc* can also be masked with potassium cyanide. According to our preliminary experiments it is possible to eliminate the interference of uranium and other metals by the use of other masking agents. The results and practical application of the method, as well as our experiences with thorium extraction into trioctylmethylammonium chloride, will be reported elsewhere in the near future.

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**Summary**—Thorium forms with Methylthymol Blue (MTB) in alkaline medium (pH 9–10) a complex of the composition $Th(MTB)_2$, even in the presence of EDTA, which masks almost all metals against the reagent. This can be used for selective determination of traces of thorium (0.5–2.8 ppm) by measurement of the absorbance at 535 nm.

**Résumé**—Le thorium forme avec le Bleu de Méthylthymol (MTB) en milieu alcalin (pH 9–10) un complexe de composition $Th(MTB)_2$, même en la présence d'EDTA, qui dissimule presque tous les métaux vis-à-vis du réactif. Ceci peut être utilisé pour le dosage sélectif de traces de thorium (0,5–2,8 ppm) par mesure de l'absorption à 535 nm.

**Zusammenfassung**—Thorium bildet mit Methylthymolblau (MTB) in alkalischem Medium (pH 9–10) einen Komplex der Zusammensetzung $Th(MTB)_2$, auch in Gegenwart von EDTA, die fast alle Metalle gegen das Reagens maskiert. Dies kann zur selektiven Bestimmung von Thoriumspuren (0,5–2,8 ppm) durch Messung der Extinktion bei 535 nm dienen.

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# Etude potentiométrique de la réaction du tiron avec les éthylènediaminetetracétates de terres rares

(*Reçu le* 28 *janvier* 1969. *Accepté le* 23 *juin* 1969)

DEPUIS longtemps il est connu que les terres rares possèdent un nombre de coordination très élevé. Des études cristallographiques faites au moyen des rayons X ont montré que dans HLa(EDTA)$(H_2O)_4 \cdot 3H_2O$ le lanthane a un nombre de coordination égal a dix.[1]

Thompson et Loraas[2] ont étudié des complexes mixtes qui proviennent de la réaction des *N*-hydroxyéthyl éthylènediaminetriacétates de terres rares avec les coordinats suivants: glycinate, éthylènediaminediacétate, iminodiacétate et *N*-hydroxyéthyliminodiacétate. D'après ces auteurs, dans ces complexes mixtes, le nombre de coordination de l'ion central est plus grand que six.

Dans ce laboratoire nous avons étudié des complexes mixtes ayant comme ion central des métaux de transition.[3,4,5] Comme suite à ces recherches, nous avons étudié dans le présent travail la réaction des éthylènediaminetétracétates de terres rares ($MY^-$) avec le tiron ($H_2T^{2-}$). Le tiron est le nom commercial du pyrocatéchol 3,5 disulfonate de sodium. Formellement, dans les complexes mixtes contenant ces deux coordinats, le nombre de coordination du métal doit être huit.

## PARTIE EXPERIMENTALE

Pour les titrages potentiométriques, on a préparé au préalable des solutions concentrées (0,1*M*) en terres rares, dont on a déterminé la concentration par titrages complexométriques.[6] Par dilution et par addition d'acide perchlorique on a amené ces solutions, utilisées en potentiométrie, aux concentrations 0,1*M* en terre rare et en acide perchlorique.

Pour empêcher l'oxydation du tiron, on a utilisé une solution 0,1*M* de tiron contenant de l'acide perchlorique à la concentration 0,1*M*.

Tous les titrages sont effectué dans une cellule thermostatée à 25°. Pour éviter l'oxydation du tiron, on a fait barboter de l'azote dans la cellule de titrage.

Le pH est mesuré avec un pH mètre comportant une électrode de calomel reliée à la solution à titrer par un pont rempli d'une solution de nitrate de sodium 0,5*M*. Le pH mètre a été calibré avec des solutions tampons étalonnées. Etant donné que nos titrages sont effectués à une force ionique de 0,1*M* maintenue constante à l'aide de perchlorate de sodium nous avons retranché 0,096 unité du pH mesuré pour obtenir $-\log [H^+]$.[7,8]

## RESULTATS

On a titré par la soude des solutions contenant l'ion métallique, le sel disodique de l'acide éthylènediaminetétracétique ($H_2Y^{2-}$), le pyrocatéchol 3,5 disulfonate de sodium ($H_2T^{2-}$) et l'acide perchlorique dans des proportions 1:1:1:2. Sur la Figure 1, nous montrons quelques titrages de ce type. On voit qu'il y a deux points d'inflexion situés respectivement à $a = 4$ et $a = 6$, "$a$" indiquant le nombre de moles de base ajoutées pour une mole de métal.

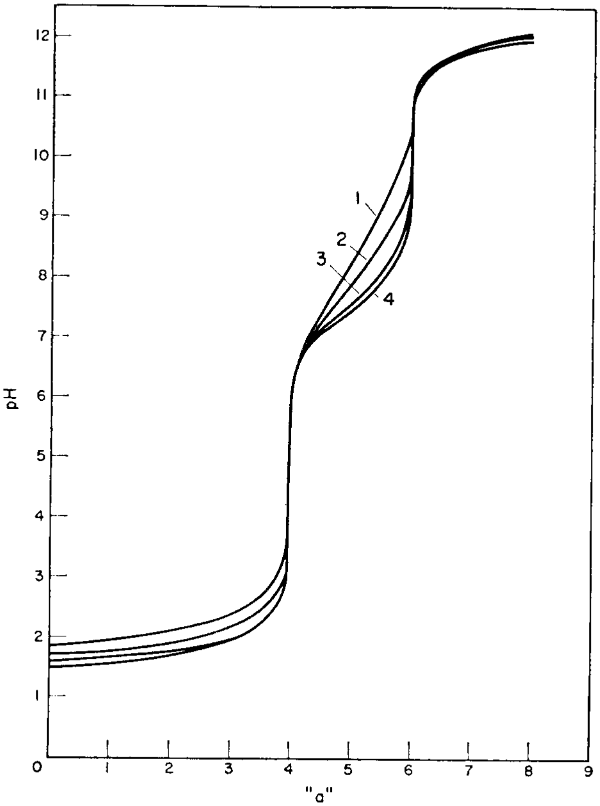

FIG. 1.—Titrage par la soude d'un mélange contenant l'ion métallique ($Me^{3+}$), le sel disodique de l'acide éthylènediamine-tétracétatique ($H_2Y^{2-}$) le pyrocatéchol 3:5 disulfonate de sodium ($H_2T^{2-}$) et l'acide perchlorique dans les proportions 1:1:1:2. La concentration du métal est 0,01*M*. La force ionique de la solution est 0,1 ($NaClO_4$) et la température est de 25°C. Le nombre de moles de base ajoutée par mole de métal est désigné par "$a$".
*1*—$La^{3+}$; *2*—$Nd^{3+}$; *3*—$Ho^{3+}$; *4*—$Yb^{3+}$

Jusqu'a $a = 4$ on titre les deux protons provenant de deux molécules d'acide perchlorique et les deux protons du sel disodique de l'acide éthylènediaminetétracétique. Dans cette région se forme aussi le complexe simple $MeY^-$.

Entre $a = 4$ et $a = 6$ on titre les deux protons du pyrocatéchol 3,5 disulfonate de sodium et en même temps on forme le complexe mixte par la réaction suivante:

$$MeY^- + H_2T^{2-} \rightleftarrows MeYT^{5-} + 2H \tag{1}$$

avec la constante d'équilibre définie par l'équation

$$K_e = \frac{[MeYT^{5-}][H^+]^2}{[MeY^-][H_2T^2]} \cdot \tag{2}$$

Ces courbes de titrages nous indiquent que les complexes mixtes contiennent le métal, l'éthylènediaminetétracétate et le tiron dans les proportions 1:1:1. Le fait que le complexe mixte soit formé dans une étape distincte de la formation du complexe simple, nous indique que les deux coordinats ont une affinité différente pour l'ion métallique.[9]

En utilisant les points expérimentaux situés entre $a = 4$ et $a = 6$, on a calculé la constante d'équilibre $K_e$ par la méthode de Schwarzenbach.[10] Dans ces conditions les équations suivantes sont variables:

$$C_{Me} = C_Y = C_T \tag{3}$$

$$C_{Me} = [MeY] + [MeYT^{5-}] \tag{4}$$

$$C_T = [H_2T^{2-}] + [HT^{3-}] + [MeYT^{5-}] \tag{5}$$

$$(a - 4)C_{Me} = [HT^{3-}] + 2[MeYT^{5-}] + [OH] - [H^+]. \tag{6}$$

Nous avons négligé dans l'équation (5) la concentration du $T^{4-}$ car pour les pH qui sont entre $a = 4$ et $a = 6$ la courbe de titrage du tiron seul montre qu'il y a seulement $HT^{2-}$ et $H_2T^{3-}$ dans la solution.

Ces équations conduisent aux expressions suivantes:

$$[H_2T^{2-}] = \frac{(6 - a)C_{Me} + [OH^-] - [H^+]}{(2 + K_1/[H^+])} \tag{7}$$

$$\frac{K_e[H_2T^{2-}]}{[H^+]^2} + 1 = \frac{C_{Me}}{[H_2T^{2-}](1 + K_1/[H^+])} = y \tag{8}$$

ou $K_1$ est la constante de dissociation de $H_2T^{2-}$.

Nous avons redéterminé $K_1$ et pour une force ionique de 0,1 on a $pK_1 = 7{,}54 \pm 0{,}01$. De l'équation (8) on voit qu'un graphique de $y$ en fonction de $[H_2T^{2-}]/[H^+]^2$ donne une droite. On obtient la même valeur de $K_e$ quand $C_{Me} = C_Y = C_T$ varie entre $0{,}01M$ et $0{,}002M$.

La constante de formation des complexes mixtes est calculée en utilisant les relations suivantes:

$$K_f = \frac{K_e}{K_1K_2}\,\frac{[MeYT^{5-}]}{[MeY^-][T^{4-}]} \tag{9}$$

Pour $K_2$ (la constante de dissociation de $HT^{3-}$) nous avons trouvé la valeur donnée dans la littérature:[11] $pK_2 = 12{,}48$.

Le Tableau I nous donne la constante de formation des complexes mixtes.

TABLEAU I.—CONSTANTES DE FORMATION $K_f$ DES COMPLEXES MIXTES

| Me | log $K_f$ | Me | log $K_f$ |
|---|---|---|---|
| La | 5,72 ± 0,03 | Tb | 7,18 ± 0,05 |
| Pr | 6,14 ± 0,06 | Y | 7,19 ± 0,05 |
| Nd | 6,45 ± 0,05 | Ho | 7,26 ± 0,03 |
| Sn | 6,69 ± 0,07 | Dy | 7,31 ± 0,04 |
| Eu | 6,90 ± 0,08 | Er | 7,45 ± 0,04 |
| Gd | 7,12 ± 0,03 | Yb | 7,45 ± 0,05 |

## DISCUSSION

Sur la Fig. 2 on indique la variation du logarithm de la constante de formation en fonction de $1/r$, $r$ étant le rayon ionique du cation. Les valeurs de $r$ sont empruntées la litérature.[12] Sur la Figure 2 on voit que le gadolinium sépare deux régions bien distinctes. Pour les éléments plus légers que le gadolinium, le logarithme de la constante de formation croît assez vite quand le rayon ionique diminue. Pour les éléments plus lourds que le gadolinium, le logarithme de la constante de formation croît un peu moins vite quand le rayon ionique diminue. Il faut noter que l'yttrium se comporte d'une façon similaire aux terres rares lourdes.

Une théorie purement électrostatique prédirait que le logarithme de la constante de formation doit augmenter d'une façon homogène quand le rayon ionique du cation diminue. Pour expliquer

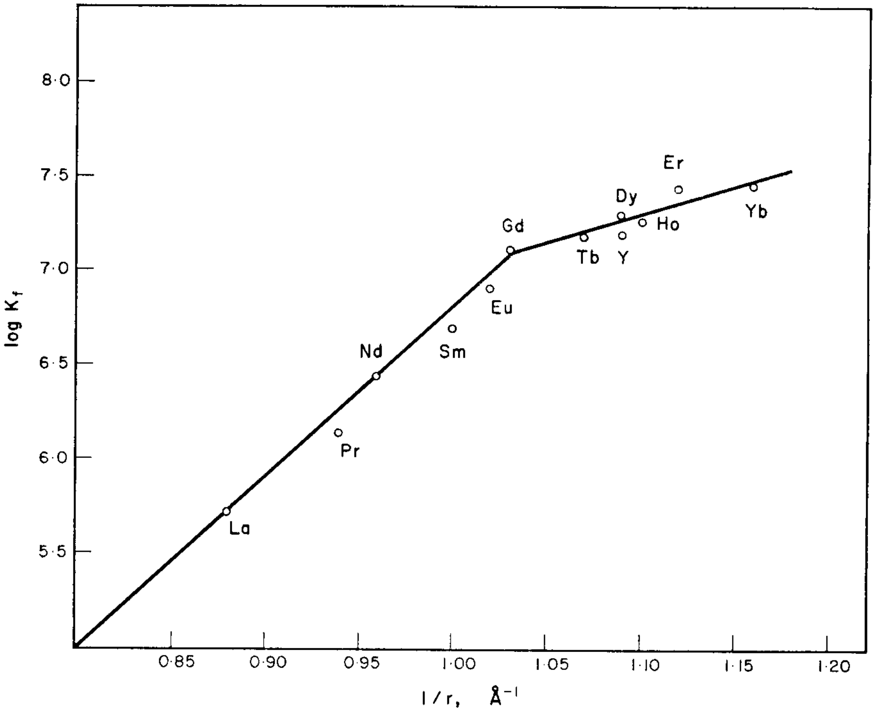

FIG. 2.—Variation du logarithme de la constante de formation des complexes mixtes en fonction de l'inverse du rayon ionique des cations.

la coupure observée au niveau du gadolinium dans d'autres réactions complexométriques des arguments stériques sont invoqués par certains auteurs.[2,13]

Les éthylènediaminetétracétates de terres rares sont beaucoup plus stables que les éthylènediaminetétracétates dérivant des métaux de transition. D'autre part les éthylènediaminetétracétates des métaux de transitions ne réagissent pas avec le tiron. Pour cette raison nous croyons que dans les complexes mixtes décrits dans ce travail le nombre de coordination des terres rares est plus grand que six.

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**Résumé**—Les éthylènediaminetétracétates de terres rares ($MeY^-$) réagissent avec le pyrocatéchol 3,5 disulfonate de sodium ($H_2T^{2-}$) et forment avec lui des complexes mixtes ($MeYT^{5-}$). On a déterminé la constante de formation des complexes mixtes, en utilisant des courbes de titrages potentiométriques. On suppose que le nombre de coordination des terres rares est plus grand que six.

**Summary**—The rare earth-EDTA complexes ($MY^-$) react with the disodium salt of catechol-3,5-disulphonic acid ($H_2T^{2-}$) and form mixed complexes ($MeYT^{5-}$). The formation constants of these mixed complexes were determined from the potentiometric titration curves. The co-ordination number of the rare earths is believed to be greater than six.

**Zusammenfassung**—Die EDTA-Komplexe der seltenen Erden ($MY^-$) reagieren mit dem Dinatriumsalz der Catechin-3,5-disulfonsäure ($H_2T^{2-}$) zu gemischten Komplexen ($MeYT^{5-}$). Die Bildungskonstanten dieser gemischten Komplexe wurden aus den potentiometrischen Titrationskurven ermittelt. Die Koordinationszahl der seltenen Erden ist vermutlich größer als sechs.

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# Determination of 2,3-dimercaptopropanol-1 (BAL) by titration with zinc, with Eriochrome Black T as indicator

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A NUMBER of analytical methods have been described for determination of thiols. Leisley[1] has proposed a coulometric procedure with electrogenerated silver ion. Zumanova and Zuman[2] used polarography and potentiometry, and Calzolari and Donda[3] used polarography and amperometry for the same purpose. Oganesyan and Zaminyon[4] applied amperometric titration with mercuric ions. Steel[5] proposed a titrimetric method with iodate-iodide as the official method of assay of thiols in pharmaceutical preparations, and recently Kemula and Brachaczek[6] used electrogenerated iodine for the same determination. It would be useful to have a method, however, which could distinguish between thiols in general, and those such as certain dithiols which are capable of chelate formation.

In the course of our investigation of the properties of Eriochrome Black T (EBT)[7] we found that EBT could be used as metallochromic indicator for the titration of 2,3-dimercaptopropanol-1 (BAL) with standard zinc solution. This method, made possible by the great difference of stability between $Zn(BAL)^{2-}$($K = 10^{23.3}$)[8] and ZnEBT($K = 10^{10}$) provides a simple, accurate, and fairly selective method capable of determining BAL in the presence of monothiols and even some (weakly) chelating thiols.

## EXPERIMENTAL

### Reagents

*Indicator solution.* EBT solution, $10^{-4}M$ was prepared by dissolving the proper amount of purified EBT[10] in methanol.

*Stock zinc solution,* $10^{-1}M$. Prepared by dissolving the proper amount of analytical grade zinc (dust) in hydrochloric acid. The reaction was accelerated by addition of bromine water. The excess of bromine was removed by boiling. The solution was diluted 10- and 100-fold to yield $10^{-2}M$ and $10^{-3}M$ solutions.

*Standard BAL solution.* Prepared by weighing out the proper amount of the BAL and dilution with distilled water.

*Buffer solution.* Carbonate-bicarbonate buffer[11], pH 10, was used for the titrations.

The interference of diverse mercapto compounds was tested with commercially available chemicals.

### *Procedure*

Take, in a conical flask, 5 ml of buffer, 10 drops of indicator, the desired amount of BAL, and dilute with water to 50 ml. Titrate with standard zinc solution. The end-point is indicated by a sharp colour change from blue to violet. For BAL amounts in the range 3–12·5 mg, the titrations were performed with $10^{-2}M$ zinc solution from a 5-ml burette. For the low range (0·3–1·2 mg), a $10^{-3}M$ solution was used.

## RESULTS AND DISCUSSION

The results for BAL alone are given in Table I. It is shown that the relative error is less than 5 and 15 ppt for the high and low ranges respectively.

TABLE I

| BAL, *mg* | | Error, *ppt* | BAL, *mg* | | Error, *ppt* |
|---|---|---|---|---|---|
| Taken* | Found† | | Taken* | Found† | |
| 3·06 | 3·05 | −3·3 | $0{\cdot}30_6$ | $0{\cdot}30_9$ | +9 |
| 6·13 | 6·10 | −4·8 | $0{\cdot}61_3$ | $0{\cdot}60_3$ | −16 |
| 9·20 | 9·20 | — | $0{\cdot}92_0$ | $0{\cdot}91_2$ | −9 |
| 12·26 | 12·27 | +0·8 | $1{\cdot}22_5$ | $1{\cdot}20_5$ | −16 |

* Calculated on basis of 98·7% purity.

† Average of 5 determinations; corrected for the blank.

The change of the colour at the equivalence point is very sharp and distinctive (blue violet). Less than half a drop of $10^{-3}M$ zinc solution was required at the end-point for a complete colour change. Blanks of 0·01 and 0·08 ml of standard zinc solution were observed for the high and low concentration ranges, respectively. These blank values are applied in the calculation of the BAL content.

The method was applied to the assay of BAL either alone or in the presence of other thiols. It may be seen from Table II that this method is more selective than those previously reported, with interference arising only from those compounds which have zinc complexes more stable than the zinc–EBT complex.

TABLE II.—INTERFERENCES OF DIVERSE MERCAPTANS IN THE TITRATION

| Compound added, *mg* | | BAL, *mg* | | Error in *ppt* |
|---|---|---|---|---|
| | | Taken | Found | |
| Mercaptoacetic acid* | 2·55 | 3·06 | 4·06 | +327 |
| | 1·02 | 3·06 | 3·56 | +163 |
| | 0·51 | 3·06 | 3·39 | +108 |
| 2-Mercaptoethanol | 3·00 | 3·06 | 3·07 | +3·2 |
| | 1·50 | 3·06 | 3·06 | — |
| | 0·75 | 3·06 | 3·04 | −6·5 |
| 6-Mercaptopurine | 4·0 | 3·06 | 3·05 | −3·2 |
| | 2·0 | 3·06 | 3·06 | — |
| | 1·0 | 3·06 | 3·07 | +3·2 |
| 3-Mercaptopropionic acid | 4·0 | 3·06 | 3·05 | −3·2 |
| | 2·0 | 3·06 | 3·06 | — |
| | 1·0 | 3·06 | 3·07 | +3·2 |
| 2-Mercapto-3-methylpyrazine | 3·0 | 3·06 | 3·08 | +6·5 |
| | 1·5 | 3·06 | 3·05 | −3·2 |
| | 0·75 | 3·06 | 3·06 | — |

* When mercaptoacetic acid is present the end-point is not sharp and after some time the colour of the solution reverts to blue, which indicates that the reaction of mercaptoacetic acid with zinc is rather slow.

From semi-quantitative observations it is concluded that the reaction would be fast enough to be used for automatic photometric titration of BAL.

*Acknowledgement*—The authors are grateful to Edgewood Arsenal for financial support for this work.

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**Summary**—A method is proposed for the titrimetric determination of BAL with zinc solution and Eriochrome Black T (EBT) as indicator. It is based on the difference of the stabilities of the $Zn(BAL)_2$ and Zn–EBT complexes. The accuracy of the method is very good and the interference of diverse mercaptans is limited to those compounds forming zinc complexes more stable than the Zn–EBT complex.

**Zusammenfassung**—Ein Verfahren zur titrimetrischen Bestimmung von BAL mit Zinklösung und Eriochromschwarz T (EBT) als Indikator wird vorgeschlagen. Es beruht auf dem Unterschied zwischen den Stabilitäten der $Zn(BAL)_2$- und Zn-EBT-Komplexe. Die Genauigkeit der Methode ist sehr gut und die Störung durch verschiedene Mercaptan beschränkt sich auf solche Verbindungen, die stabilere Zinkkomplexe als Zn-EBT geben.

**Résumé**—On propose une méthode pour la détermination titrimétrique du BAL avec une solution de zinc et le Noir Eriochrome T (EBT) comme indicateur. Elle est basée sur la différence des stabilités des complexes $Zn(BAL)_2$ et Zn-EBT. La précision de la méthode es très bonne et l'interférence de divers mercaptans est limitée à ceux de ces composés qui forment des complexes de zinc plus stables que le complexe Zn-EBT.

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# Thin-layer chromatographic separation of alkaline earth metals on diethylaminoethyl cellulose

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Some papers on the thin-layer chromatographic separation of alkaline earth metals from each other have appeared. Most such separations by thin-layer chromatography (TLC) have been performed on various supports in mixtures of hydrochloric acid and methanol,[1] ethanol,[1] isopropanol,[2] t.butanol[3] or acetone[4,5]. However, there is little information available on separation of alkaline earth metals by TLC in nitric acid or nitrate media. Zetlmeisl *et al.*[2] have measured $R_f$ values of calcium, strontium, and barium on a microcrystalline cellulose layer in collidine–0·4*M* nitric acid medium (1:1, v/v). Cozzi *et al.*[6] have summarized $R_f$ values of beryllium, magnesium, calcium, strontium and barium on an alginic acid layer in various acids including nitric acid. However, no results of the separations are given by these authors. Successful separations of calcium, strontium and barium from each other on a chelating resin layer by development with 2*M* ammonium nitrate solution have been achieved by Berger *et al.*[7]

In this work diethylaminoethyl cellulose (DEAE) has been used as a stationary phase for inorganic TLC, and it has been found that magnesium, calcium, strontium and barium can be separated simply and rapidly by development with methanol–8*M* nitric acid(20:1, v/v).

## EXPERIMENTAL

All the chemicals used were of analytical grade. Each stock solution contained 10 mg of metal ion per ml of 0·1*M* nitric acid. Before use DEAE for TLC was purified and converted into the nitrate form: 10 g of DEAE were shaken for 1 hr with 100 ml of 1*M* ammonium nitrate acidified with 1*M* nitric acid to pH 1·0. The DEAE thus treated was washed with 0·1*M* nitric acid, then three times with water, being separated each time by centrifugation. The pH of the final supernatant liquid should be about 3. The purified DEAE was slurried with water and spread 0·25 mm thick on glass plates (50 × 200 or 25 × 100 mm) with an applicator. The plates were dried in an oven at *ca.* 40° for 10 hr and then stored in a desiccator containing saturated ammonium nitrate solution until ready for use. The larger plates were used for the measurement of $R_f$ values, and the smaller ones for separations.

### *Procedure*

For the determination of $R_f$ values about 2 μl of the stock solution were applied on the larger plate 25 mm from one side with a capillary pipette and dried in air for 30 min. The plate was placed in a cylindrical glass tank (230 mm high and 70 mm in diameter) and allowed to stand for 60 min to equilibrate with the tank atmosphere. Ascending development was conducted at 25° with a solvent from those listed in Tables I and II, until the solvent front had risen 160 mm. This usually took about 80 min. For separations, about 1 μl of a sample solution was spotted on the smaller plate 15 mm from one side and development was conducted in a smaller tank (110 mm high and 50 mm in diameter) until the solvent front had travelled 75 mm (~16 min).

After development, the plate was dried under a heat lamp and the position of the metal ion was located by spraying with a 0·1% solution of thymolphthalein complexone in (1 + 1) ammonia solution or a 1% solution of alizarine in 1*M* sodium hydroxide. All the ions tested showed as blue spots on a white background or as red violet ones on a blue background, respectively.

## RESULTS AND DISCUSSION

In Table I $R_f$ values of magnesium, calcium, strontium and barium in methanol–nitric acid media (20:1, v/v) are given as a function of nitric acid concentration. $R_f$ values for calcium and strontium decrease slowly with increasing concentration of nitric acid, while those for magnesium and barium are not affected. At lower nitric acid concentrations there are sufficiently large differences in the $R_f$ values of calcium, strontium and barium to permit the resolution of the three metal ions. The separation of magnesium and calcium is somewhat difficult. The higher the concentration of nitric acid, the larger the differences in $R_f$ values of magnesium and calcium. At higher concentrations of nitric acid ($\geq 8M$), the differences in $R_f$ values are large enough to resolve magnesium, calcium, strontium and barium.

TABLE I.—VARIATION IN $R_f$ VALUES OF MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM WITH CONCENTRATION OF NITRIC ACID (VOLUME RATIO OF METHANOL TO NITRIC ACID KEPT CONSTANT AT 20:1, v/v)

| Nitric acid, *M* | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| 1·0 | 0·97 | 0·86 | 0·58 | 0·08 |
| 4·0 | 0·91 | 0·77 | 0·42 | 0·04 |
| 8·0 | 0·92 | 0·67 | 0·40 | 0·04 |
| 14 | 0·95 | 0·65 | 0·36 | 0·04 |

In Table II $R_f$ values of magnesium, calcium, strontium and barium are given as a function of volume ratios of methanol to nitric acid at a constant nitric acid concentration, 14*M*. The $R_f$ values of the four metal ions as well as differences in their $R_f$ values decrease with decreasing volume ratios of methanol to nitric acid.

A survey of the behaviour of magnesium, calcium, strontium and barium on a DEAE thin-layer in methanol–nitric acid media indicates that wide variation in volume ratios and in concentrations of nitric acid is permissible for the separation of the four metal ions from each other. Since the four

TABLE II.—VARIATION IN $R_f$ VALUES OF MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM WITH VOLUME RATIO OF METHANOL TO NITRIC ACID (CONCENTRATION OF NITRIC ACID KEPT CONSTANT AT 14*M*)

| Methanol:Nitric acid, *v/v* | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| 5·0:1 | 0·87 | 0·55 | 0·33 | 0·00 |
| 7·5:1 | 0·87 | 0·55 | 0·31 | 0·05 |
| 10 :1 | 0·86 | 0·57 | 0·30 | 0·00 |
| 20 :1 | 0·95 | 0·65 | 0·36 | 0·04 |

metal ions give well defined spots under all the experimental conditions tested, complete separation of each ion in a mixture is possible within a 75-mm development. For general purposes the development with methanol–8*M* nitric acid (20:1, v/v) is recommended.

The mobilities in all the solvent systems tested are in the order magnesium > calcium > strontium > barium and this order is consistent with that of the ionic radii of the hydrated metal ions. Similar affinity sequences have been found with silica gel,[3,5] alumina,[5] cellulose[1,2] and starch[4] for the developing systems consisting of alcohols and nitric or hydrochloric acid.

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**Summary**—Thin-layer chromatographic behaviour of magnesium, calcium, strontium and barium on diethylaminoethyl cellulose has been investigated in methanol–nitric acid mixtures. $R_f$ values are in the order magnesium > calcium > strontium > barium. The differences in $R_f$ values are large enough to allow good separations of the four metal ions from each other. The best separation is obtained by the ascending technique with methanol-8*M* nitric acid (20:1, v/v).

**Résumé**—On a étudié le comportement chromatographique sur couche mince de diéthylaminoéthylcellulose du magnésium, du calcium, du strontium et du baryum dans des mélanges méthanol–acide nitrique. Les valeurs de $R_f$ sont dans l'ordre magnésium > calcium > strontium > baryum. Les différences dans les valeurs de $R_f$ sont suffisamment grandes pour permettre de bonnes séparations des quatre ions métalliques les uns des autres. La meilleure séparation est obtenue par la technique ascendante avec le méthanol–acide nitrique 8*M* (20:1, v/v).

**Zusammenfassung**—Das dünnschichtchromatographische Verhalten von Magnesium, Calcium, Strontium und Barium an Diäthylaminoäthylcellulose wurde in Methanol-Salpetersäure-Gemischen untersucht. Die $R_f$-Werte fallen in der Reihe Magnesium > Calcium > Strontium > Barium. Die Unterschiede in den $R_f$-Werten sind groß genug, um die vier Metallionen gut voneinander trennen zu können. Die beste Trennung erreicht man aufsteigend mit Methanol-8*M* Salpetersäure 20:1 (V/V).

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# LETTER TO THE EDITOR

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## Spectrophotometric determination of small amounts of vanadium(V) with 4-(2-pyridylazo)resorcinol

SIR,

The value of the spectrophotometric determination of vanadium with PAR[1,2,3] is increased by using DCTA as a masking agent (as proposed by Budevsky and Přibil in their Xylenol Orange method[4]) to prevent the interference by the many metal ions that react with the reagent under the conditions used. Then 20 $\mu$g of vanadium(V) can be determined within 5% relative error in the presence of 1-mg amounts of Mg, Mn, Mo(VI), W(VI), Sn(II), 500-$\mu$g amounts of Al, Co, Cr, Cu(II), Fe(III) Zn, Hg(II), Pb, Ni and 200-$\mu$g amounts of Ag. The optimum pH range is 5·7–7·1, $\lambda_{max}$ is 545 nm and the conditional equilibrium constant for the reaction

$$\text{V—DCTA} + \text{PAR} = \text{V—PAR} + \text{DCTA}$$

is $10^{2.35\pm0.25}$. In other respects the reaction is as previously described.[1,2,3]

The recommended procedure is to add 4 ml of 0·01*M* DCTA and 5 ml of phosphate buffer (pH 6·5, 0·05*M*) to a solution containing 2–40 $\mu$g of vanadium(V), followed by 2 ml of 0·1% PAR solution, then to dilute to 50 ml and after 5 min measure the absorbance at 545 nm against a reagent blank.

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This volume, the first of a set of three which will cover the branches of flame spectroscopy of interest to the analyst (atomic fluorescence is also included) sets out the theoretical background to the subject. Thirteen chapters, all written by authorities in their fields, discuss History, Basic Principles, Theory of Emission, Decomposition and Atomisation, Radicals and Molecules in Flame Gases, Flames for Spectrometry, Measurement and Calculation of Flame Temperatures, Distribution of Atomic Concentration in Flames, Spectral Interferences, Physical Interferences, Chemical Interferences in Vapour Phase and in Condensed Phase, and Accuracy and Precision. The extent of overlap between the chapters is just sufficient to avoid awkward gaps in the text, without becoming repetitions; in fact it is the feeling of unity and continuity in this book which makes it both rewarding and easy to read. Though aimed at research workers and users of the techniques, individual chapters of the book could well be recommended for undergraduate study.

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# SUMMARIES FOR CARD INDEXES

**Determination of titanium in high-purity molybdenum and tungsten metals with diantipyrylmethane after separation by extraction of its cupferron complex:** ELSIE M. DONALDSON, *Talanta*, 1969, **16**, 1505. (Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, 555 Booth Street, Ottawa 4, Ontario, Canada.)

**Summary**—A method for determining 0·0005–0·10% of titanium in high-purity molybdenum and tungsten metals is described. After sample dissolution, titanium is separated from the matrix materials by chloroform extraction of its cupferronate from an alkaline (pH 8) tartrate–EDTA medium, then determined spectrophotometrically with diantipyrylmethane at 390 nm. Interference from manganese during extraction is eliminated with sodium sulphite. Iron, zirconium, thorium, tin, aluminium and antimony are partially extracted under the proposed conditions, but moderate amounts of these elements may be present in the sample solution without causing error in the results. Interference from iron(III) during colour development is eliminated with ascorbic acid. Other impurities in the two high-purity metals described do not interfere in the proposed method.

**Analysis by release of radioactivity by inorganic ion-exchange and ring oven technique—I. Determination of copper:** V. KRIVÁŇ, *Talanta*, 1969, **16**, 1513. (Chemical Laboratory of the University Freiburg i. Br., Department of Analytical Chemistry, German Federal Republic.)

**Summary**—A sparingly soluble inorganic compound, fixed as a spot on filter paper, is used as an ion-exchanger in which the exchangeable ions are labelled with a radioactive isotope. These ions are replaced by the ions of the element to be determined but not by other accompanying ions. In this exchange an equivalent amount of the radioactive labelled ions is released from the ion-exchanger and separated from the spot by the ring oven technique. The activity of the ring is measured and compared with that of a standard processed in the same way. The determination of copper in amounts greater than 25 ng in the presence of a similar amount of lead and considerably greater amounts of cobalt, nickel, zinc, manganese and thallium is described.

# ОПРЕДЕЛЕНИЕ ТИТАНА В МОЛИБДЕНЕ И ВОЛЬФРАМЕ ВЫСОКОЙ ЧИСТОТЫ ПРИ ПОМОЩИ ДИАНТИПИРИЛМЕТАНА ПОСЛЕ СЕПАРАЦИИ ЭКСТРАКЦИЕЙ КУПФЕРРОНОВОГО КОМПЛЕКСА:

Elsie M. Donaldson, *Talanta*, 1969, **16**, 1505.

**Резюме**—Описывается метод определения 0,0005–0,10 % титана в молибдене и вольфраме высокой чистоты. После растворения образцов титан отделяется от материалов матрицы экстракцией хлороформом купферрата из щелочной (pH – 8) среды тартрата и ЭДТА, после чего титан определяется спектрофотометрически диантипирилметаном при 390 нм. Воздействие марганца во время экстракции устраняется с помощью сульфита натрия. Железо, цирконий, торий, олово, алюминий и сурьма частично извлекаются при предложенном режиме, но небольшие количества этих элементов могут присутствовать в растворе образца, не вызывая ошибки в результатах. Воздействие железа (III) во время развития окраски устраняется с помощью аскорбиновой кислоты. Другие нечистоты в обоих металлах высокой чистоты не влияют на предложенный метод.

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V. Kriváň, *Talanta*, 1969, **16**, 1513.

**Резюме**—Почти нерастворимое неорганическое соединение, укрепленное в форме пятна на филтровальной бумаге служит в качестве ионообменника в котором изменимые ионы означены радиоактивным индикатором. Эти ионы замещены ионами определяемого элемента, но не другими сопровождающими ионами. В этом обмене эквивалентное количество радиоактивно индицированных ионов освобождено от ионообменника и отделено от пятна методом кольцевой печи. Активность кольца измерена и сравнена с активнстью эталона обработанного тем же образом. Описано определение больше чем 25 нг меди в присутствии подобных количеств свинца и значительно больших количеств кобальта, никеля, цинка, марганца и таллия.

**Selective titration of microgram amounts of copper with photometric end-point detection:** H. Poppe, *Talanta*, 1969, **16**, 1519. (Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam-C, Netherlands.)

**Summary**—The reaction of copper ions with pyridylazonaphthol is very suitable and sensitive for the photometric titration of copper. The titration is self-indicating, and at the 0.1-ppm level the standard deviation is 2·5%. The main interferences are caused by bismuth, iron, titanium and vanadium but can be overcome by suitable masking.

**Analytical application and spectrophotometric study of the scandium–indoferron complex:** Tsuneo Shimizu and Kazuko Ogami, *Talanta*, 1969, **16**, 1527. (Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Gunma, Japan.)

**Summary**—A new spectrophotometric method for microgram amounts of scandium with indoferron is described. The molar absorptivity is 960 l. mole$^{-1}$.mm$^{-1}$ at 600 nm. Uranium and the rare earths do not interfere, if present in amounts less than 50 $\mu$g. Scandium in silicate rocks can be determined by the procedure after separation of the scandium by a three-stage ion-exchange chromatographic technique. The acid dissociation constants of indoferron and conditional formation constants of the 1:2 complex have been determined spectrophotometrically.

**Co-precipitation of metal dimethylglyoximates generated from biacetyl monoxime or biacetyl and hydroxylamine:** S. J. Lyle and R. Maghzian, *Talanta*, 1969, **16**, 1535. (Chemistry Laboratory, University of Kent, Canterbury, Kent, England.)

**Summary**—A study has been made of some aspects of the co-precipitation of gold and platinum(II) and (IV) with palladium(II) precipitated from homogeneous solution initially containing biacetyl and hydroxylamine in 0·3$M$ hydrochloric acid. The co-precipitation of nickel(II) with palladium(II) and *vice versa* from near neutral solutions initially containing biacetyl and hydroxylamine was also explored; the solid is enriched in the minor constituent in both cases. As with biacetyl monoxime-hydroxylamine systems, both nickel(II) and palladium(II) promote formation of dimethylglyoxime from such solutions between pH 7 and 8. Factors leading to this unusual behaviour in co-precipitation are discussed and a qualitative explanation tentatively advanced. The co-precipitation of nickel and palladium(II) is different when biacetyl monoxime solutions are used; the former comes out of solution faster than the latter irrespective of their concentration ratio. This disparity in the reaction rates can be used to separate nickel directly from palladium(II) by precipitation or extraction of the dimethylglyoximate into chloroform.

## СЕЛЕКТИВНОЕ ТИТРОВАНИЕ МИРОГРАММОВЫХ КОЛИЧЕСТВ МЕДИ С ФОТОМЕТРИЧЕСКИМ ОБНАРУЖЕНИЕМ КОНЦА ТИТРОВАНИЯ:

H. Poppe, *Talanta*, 1969, **16**, 1519.

**Резюме**—Реакция ионов меди с пиридилазонафтолом очень чувствительна и применима в фотометрическом титровании меди. Титрация самопоказывающая, а стандартная ошибка при 0,1 мг/л равна 2,5%. Висмут, железо, титан и ванадий мешают определению, но их действие можно исключать маскированием.

## ПРИМЕНЕНИЕ В АНАЛИЗЕ И СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ КОМПЛЕКСА СКАНДИЯ С ИНДОФЕРРОНОМ:

Tsuneo Shimizu and Kazuko Ogami, *Talanta*, 1969, **16**, 1527.

**Резюме**—Описан новый спектрофотометрический метод определения микрограммовых количеств скандия индоферроном. Молярное светопоглощение 960 л. моль$^{-1}$. мм$^{-1}$ при 600 нм. Уран и редкоземельные элементы в количествах меньше чем 50 мкг не мешают определению. Скандий в силикатных горных породах определяют этим методом после выделения скандия трехэтапным методом ионообменной хроматографии. Кислотные константы диссоциации индоферрона и условные константы образования 1:2 комплекса определены спектрофотометрическим методом.

## СООСАЖДЕНИЕ ДИМЕТИЛГЛИОКСИМАТОВ МЕТАЛЛОВ ОБРАЗОВАННЫХ ПРИ ПОМОЩИ БИАЦЕТИЛМОНОКСИМА ИЛИ БИАЦЕТИЛА И ГИДРОКСИЛАМИНА:

S. J. Lyle and R. Maghzian, *Talanta*, 1969, **16**, 1535.

**Резюме**—Изучено соосаждение золота и платины(II) и (IV) с паддалием(II) при осаждении из гомогенного раствора, начально содержащего биацетил и гидроксиламин в 0,3*M* растворе соляной кислоты. Также исследовано соосаждение никеля(II) сапалладием(II) и наоборот из почти нейтральных растворах, начально содержащих биацетил и Гидроксиламин; в обоих случаях твердая фаза обогащена меньшим компонентом. Так как в случае систем биацетилмоноксим–гидроксиламин, никель(II) и палладий(II) способствуют образованию диметилглиоксима из таких растворов при pH 7–8. Обсуждены факторы ведущие к этому необычаому поведению при соосаждении и предложено качественное объяснение. Соосаждение никеля и палладия(II) различно в случае использования растворов биацетилмоноксима; первый элемент осаждается быстрее чем последный несмотря на отношение их концентраций. Этим неравенством между скоростями реакции можно пользоваться для прямого отделения никеля от палладия (II), осаждением или экстракцией диметилглиоксимата хлороформом.

**Alkaline errors of glass electrodes in non-aqueous solvents:** B. KARLBERG and G. JOHANSSON, *Talanta*, 1969, **16**, 1545. (Department of Analytical Chemistry, University of Umeå, 901 87 Umeå, Sweden.)

**Summary**—Alkaline errors of glass electrodes in isopropanol were obtained from a comparison with the hydrogen electrode. Electrode glasses which show low alkaline errors in water are also more ideal in isopropanol. Univalent metal ions cause larger deviations than bivalent. Hysteresis effects were found in going from alkaline to acid solutions but not for the reverse direction.

**Spectrophotometric determination of ruthenium with 8-quinolinol:** HIROSHI HASHITANI, KAZUO KATSUYAMA and KENJI MOTOJIMA, *Talanta*, 1969, **16**, 1553. (Analytical Chemistry Laboratory, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.)

**Summary**—A spectrophotometric method is described for the determination of 2–80 $\mu$g of ruthenium. The method involves oxidation of ruthenium to ruthenate, addition of 8-quinolinol, adjustment of the pH to 4–6.5, digestion of the complex formed at 85° for 30 min, extraction with chloroform, and measurement of absorbance at 430 nm. Almost all other metals and excess of reagent are removed by washing the extract. About 98% of $^{106}$Ru tracer was recovered.

**A.C. polarographic determination of unsaturation:** B. FLEET and R. D. JEE, *Talanta*, 1969, **16**, 1561. (Chemistry Department, Imperial College of Science and Technology, London, S.W.7., U.K.)

**Summary**—A wide range of olefins can be determined by a.c. polarography of their addition compounds with mercuric acetate. The first step in the reduction of these compounds is a reversible, one-electron process to form the organo-mercury radical and gives a well defined a.c. peak. The optimum conditions for the determination of a representative selection of olefins has been established.

## ЩЕЛОЧНЫЕ ОШИБКИ СТЕКЛЯННЫХ ЭЛЕКТРОДОВ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ:

B. KARLBERG and G. JOHANSSON, *Talanta*, 1969, **16**, 1545.

**Резюме**—Щелочные ошибки стеклянных электродов в изопропиловом спирте определены сравнением с водородным электродом. Электродные стекла имеющие низкие щелочные ошибки в воде оказались лучщим также в изопропиловом спирте. Одновалентные ионы металлов дали отклонения больше чем двувалентные. Эффекти гистерезиса обнаружены при переходе из щелочных в кислые растворы но не в обратном направлении.

## СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РУТЕНИЯ 8-ХИНОЛИНОЛОМ:

HIROSHI HASHITANI, KAZUO KATSUYAMA and KENJI MOTOJIMA, *Talanta*, 1969, **16**, 1553.

**Резюме**—Описан спектрофотометрический метод определения 2–80 мкг рутения. Метод основан на окислении рутения в рутенат, добавлении 8-хинолинола, приведении pH 4–6,5, дигерировании образованного комплекса при 85° в течение 30 мин, извлечении комплекса хлороформом и измерении светопоглощения при 430 нм. Промывкой экстракта удаляются почти все другие металлы и избыток реагента. Получен выход 98 % индикатора $^{106}$Ru.

## П.Т. ОПРЕДЕЛЕНИЕ НЕНАСЫЩЕННОСТИ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ:

B. FLEET and R. D. JEE, *Talanta*, 1969, **16**, 1561.

**Резюме**—Ряд олефинов может быть определен путем полярографии переменного тока их продуктов присоединения с ацетатом ртути. Первыйм этапом в восстановлении этих соединений является обратимый одноэлектронный процесс образования ртутно-органического радикала, который дает хорошо определенный переменноточный пик. Установлены оптимальные условия для определения типичной селекции олефинов.

**Chitin and chitosan as chromatographic supports and adsorbents for collection of metal ions from organic and aqueous solutions and sea-water:** Riccardo A. A. Muzzarelli and Ottavio Tubertini, *Talanta*, 1969, **16**, 1571. ("G. Ciamician" Institute of Chemistry, School of Analytical Chemistry, University of Bologna, Via Selmi 2, Bologna 40126, Italy.)

**Summary**—The rates of adsorption of several metal ions on chitin and chitosan in water and sea-water have been measured; chitin and chitosan are proposed as chromatographic chelating supports. These natural polymers are also suitable for recovery of trace metals from sea-water.

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**Cloud-point analysis of microlitre samples—determination of water in six common solvents:** D. W. Rogers and J. Scher, *Talanta*, 1969, **16**, 1579. (Chemistry Department, Connoly College, Long Island University, Brooklyn, New York 11201, U.S.A.)

**Summary**—The classical cloud-point technique for determination of small amounts of water in organic solvents has been systematically investigated. The extreme sensitivity of the critical solution temperature of binary liquid mixtures to traces of impurity in one of the components makes the cloud-point method capable of high accuracy and sensitivity for routine determination of solvent contamination by water, and is admirably suited to analysis of small samples. Typically, the absolute error for water as contaminant is about 0·2% for 10-$\mu$l samples and 0·06% for 50-$\mu$l samples. The critical solution temperature used was that of the n-hexane–methanol system. Its value is in dispute and considerable care was taken to obtain what is believed to be the correct value of 34·4 ± 0·2°. Small amounts of water in methanol, ethanol, 2-propanol, acetone, ethyl methyl ketone and dioxan were determined.

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**Emission spectral analysis using photographic plates treated with a phenidone developer:** A. Petrakiev and G. Dimitrov, *Talanta*, 1969, **16**, 1583. (Faculty of Physics, University of Sofia, Bulgaria.)

**Summary**—When spectral photographic plates are not treated in the conventional metol–hydroquinone developer, but in a phenidone developer, a strong increase in the sensitivity and a certain increase in the contrast are observed. With phenidone development, weak lines are intensified, permitting the lowering of the limits of detection and determination. The increase in the contrast increases the slope of the concentration-calibration curves and hence the concentrational sensitivity of the spectral analyses. This is illustrated in the curves for the determination of Si and Mn in low-alloy steels. Further sensitivity can be obtained by following the phenidone development by a chromium intensifying process.

## ХИТИН И ХИТОЗАН КАК ХРОМАТОГРАФИЧЕСКИЕ НОСИТЕЛИ И АДСОРБЕНТЫ ДЛЯ НАКОПЛЕНИЯ ИОНОВ МЕТАЛЛОВ ИЗ ОРГАНИЧЕСКИХ И ВОДНЫХ РАСТВОРОВ И МОРСКОЙ ВОДЫ:

A. A. Muzzarelli and Ottavio Tubertini, *Talanta*, 1969, **16**, 1571.

**Резюме**—Определена скорость адсорбции некоторых ионов металлов на хитине и хитозане в воде и морской воде. Хитин и хитозан предложены в качестве хелатообразующих хроматографических стационарных фаз. Этими натуральными полимерами также можно пользоваться для выделения примесей маталлов из морской воды.

## ОПРЕДЕЛЕНИЕ ТОЧКИ ПОМУТНЕНИЯ В МИКРОЛИТРОВЫХ КОЛИЧЕСТВАХ ПРОБЫ—ОПРЕДЕЛЕНИЕ ВОДЫ В ШЕСТЬ ОБЫКНОВЕННЫХ РАСТВОРИТЕЛЯХ:

D. W. Rogers and J. Scher, *Talanta*, 1969, **16**, 1579.

**Резюме**—Систематически изучен классический метод точки помутнения для определения небольших количеств воды в органических растворителях. Чрезвичайная чувствительность критической температуры растворения двойных смесей жидкостей для следовых количеств примесей в одном из компонентов позволяет применение метода точки помутнения с высокой точностью и чувствительностью для серийного определения следов воды в растворителях, в частности для анализа небольших проб. Примерно, абсолютная ошибка для воды составляет около 0,2 % в пробах 10 мкл, а 0,05 % в пробах 50 мкл, Использована критическая температура растворения системы н-гексан-метанол. Эта величина спорная: тщательно определена величина 34,4 + 0,2°, которая учитывается правилной. Определены небольшие количества воды в метиловом и этиловом спиртах, 2-пропаноле, ацетоне, этилметилкетоне и диоксане.

## АНАЛИЗ МЕТОДОМ ЭМИССИОНОЙ СПЕКТРОСКОПИИ С ИСПОЛЬЗОВАНИЕМ ФОТОГРАФИЧЕСКИХ ПЛАСТИНОК ОБРАБОТАННЫХ С ФЕНИДОНОВЫМ ПРОЯВИТЕЛЕМ:

A. Petrakiev and G. Dimitrov, *Talanta*, 1969, **16**, 1583.

**Резюме**—Обработка спектральных фотографических пластинок с фенидоновым проявителем вместо обыкновенным метол-гидрохиноновым проявителем производит сильно увеличение чувствительности вместе с довольным увеличением контраста. Фенидоново проявление вызивает интенсификацию слабых линий, снижая этим образом предел обнаружения и определения. Увеличение контраста увеличивает уклон калибровочных кривых концентрации и в связи с этим чувствительность спектрального анализа. В качестве примера приведены кривы определения Si и Mn в низколегированных сталях. Дальнейшее увеличение чувствительности получается интенсификацией хромом после проявления фенидоном.

**Determination of the ratio of copper(I) to copper(II) present as traces in ionic crystals:** Jaroslav Trnka and Karel Funk, *Talanta*, 1969, **16**, 1587. (Institute of Solid State Physics, Czechoslovak Academy of Sciences, Cukrovarnická 10, Prague 6–Střešovice, Czechoslovakia.)

**Summary**—A polarographic method is described for the determination of traces of copper in ionic crystals, which also allows the determination of the ratio of the concentrations of copper(II) and copper(I).

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**Extraction and determination of molybdenum with tributyl phosphate. Application to analysis of copper-molybdenum ores:** M. Caiozzi, H. Zunino and L. Sepulveda, *Talanta*, 1969, **16**, 1590. (Department of Chemistry, Faculty of Chemistry and Pharmacy, University of Chile, Santiago, Chile.)

**Summary**—A differential spectrophotometric method is described for the determination of molybdenum by means of solvent extraction with tributyl phosphate of the peroxymolybdate complex formed with $H_2O_2$ in $3{\cdot}5M$ $H_2SO_4$. The extraction parameters are studied, and the behaviour of some other ions is reported. The method is used for ore analysis.

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**Oxidimetric determination of triphenylphosphine:** V. R. S. Rao and G. Aravamudan, *Talanta*, 1969, **16**, 1594. (Department of Chemistry, Indian Institute of Technology, Madras 36, India.)

**Summary**—A method for the determination of triphenylphosphine based on its oxidation to phosphine oxide by iodine or chloramine-T in acid medium in presence of benzene or carbon tetrachloride is described. The oxidation is completed within 2 min and the analytical values are accurate to within 0·5%. The method is applicable to determination of triphenylphosphine in its metal complexes.

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**Colorimetric determination of thorium with Methylthymol Blue:** Jiři Adam and Rudolf Přibil, *Talanta*, 1969, **16**, 1596. (Analytical Laboratory, Polarographic Institute, Prague 1, Jilská 16, Czechoslovakia.)

**Summary**—Thorium forms with Methylthymol Blue (MTB) in alkaline medium (pH 9–10) a complex of the composition $Th(MTB)_2$, even in the presence of EDTA, which masks almost all metals against the reagent. This can be used for selective determination of traces of thorium (0.5–2.8 ppm) by measurement of the absorbance at 535 nm.

## ОПРЕДЕЛЕНИЕ ОТНОШЕНИЯ МЕДИ(I) И МЕДИ(II) ПРИСУТСТВУЮЩИХ В СЛЕДОВЫХ КОЛИЧЕСТВАХ В ИОННЫХ КРИСТАЛЛАХ:

JAROSLAV TRNKA and KAREL FUNK, *Talanta*, 1969, **16**, 1587.

**Резюме**—Описан полярографический метод определения следов меди в ионных кристаллах, который так же позволяет определять отношения концентраций меди(I) и меди(II).

## ИЗВЛЕЧЕНИЕ И ОПРЕДЕЛЕНИЕ МОЛИБДЕНА ТРИБУТИЛФОСФАТОМ. ПРИМЕНЕНИЕ В АНАЛИЗЕ РУД МЕДИ И МОЛИБДЕНА:

M. CAIOZZI, H. ZUNINO and L. SEPULVEDA, *Talanta*, 1969, **16**, 1590.

**Резюме**—Описан дифференциальный спектрофотометрический метод определения молибдена путем извлечения трибутилфосфатом пероксимолибдаткомплекса образованного с $H_2O_2$ в 3,5*M* $H_2SO_4$. Изучены параметры извлечения и сообщено поведение некоторых других ионов. Метод применен в анализе руд.

## ОКСИДИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТРИФЕНИЛФОСФИНА:

V. R. S. RAO and G. ARAVAMUDAN, *Talanta*, 1969, **16**, 1594.

**Резюме**—Описан метод определения трифенилфосфина основан на его окислении в окись фосфина иодом или хлорамином-Т в кислой среде в присутствии бензола или тетрахлорметана. Окисление закончено в течение 2 мин, а аналитические результаты точны в пределах 0,5 %. Метод применимый в определении трифенилфосфина в его комплексах с металлами.

## КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТОРИЯ С МЕТИЛТИМОЛОВЫМ ГОЛУБИМ:

JIŘI ADAM and RUDOLF PŘIBIL, *Talanta*, 1969, **16**, 1596.

**Резюме**—Торий образует с метилтимоловым голубим (МТГ) в щелочной среде (pH 9–10) комплекс формулы $\text{Th(МТГ)}_2$ даже в присутствии ЭДТА, который маскирует почти все металлы от этого реагента. Этот факт позволяет селективное определение следов тория (0,5 – 2,8 мкг) мл измерением светопоглощения при 535 нм.

**Etude potentiométrique de la réaction du tiron avec les éthylènediamine-tetracétates de terres rares:** B. K. AFGHAN and J. ISRAELI, *Talanta*, 1969, **16**, 1601. (Départment de Chimie, University de Montréal, P.Q., Canada.)

**Summary**—The rare earth–EDTA complexes ($MY^-$) react with the disodium salt of catechol-3,5-disulphonic acid ($H_2T^{2-}$) and form mixed complexes ($MeYT^{5-}$). The formation constants of these mixed complexes were determined from the potentiometric titration curves. The co-ordination number of the rare earths is believed to be greater than six.

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**Determination of 2,3-dimercaptopropanol-1 (BAL) by titration with zinc, with Eriochrome Black T as indicator:** G. COLOVOS and H. FREISER, *Talanta*, 1969, **16**, 1605. (Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.)

**Summary**—A method is proposed for the titrimetric determination of BAL with zinc solution and Eriochrome Black T (EBT) as indicator. It is based on the difference of the stabilities of the $Zn(BAL)_2$ and Zn–EBT complexes. The accuracy of the method is very good and the interference of diverse mercaptans is limited to those compounds forming zinc complexes more stable than the Zn–EBT complex.

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**Thin-layer chromatographic separation of alkaline earth metals on diethylaminoethyl cellulose:** KOJI ISHIDA, *Talanta*, 1969, **16**, 1607. (Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba, Japan.)

**Summary**—Thin-layer chromatographic behaviour of magnesium, calcium, strontium and barium on diethylaminoethyl cellulose has been investigated in methanol–nitric acid mixtures. $R_f$ values are in the order magnesium > calcium > strontium > barium. The differences in $R_f$ values are large enough to allow good separations of the four metal ions from each other. The best separation is obtained by the ascending technique with methanol-$8M$ nitric acid (20:1, v/v).

## ИЗУЧЕНИЕ ПОТЕНЦИОМЕТРИЧЕСКИМ МЕТОДОМ РЕАКЦИИ ТИРОНА С ЭДТА КОМПЛЕКСАМИ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ:

B. K. Afghan and J. Israeli, *Talanta*, 1969, **16**, 1601.

**Резюме**—Комплексы ЭДТА с редкоземельными элементами (МУ$^-$) реагируют с динатриевой солью катехин-3,5-дисульфоновой кислоты ($H_2T^{2-}$) и образуют смешанные комплексы (МеУТ$^{5-}$). Константы образования этих комплексов определены из кривых потенциометрического титрования. Авторы полагают что координационное число редкоземельных элементов больше чем шесть.

## ОПРЕДЕЛЕНИЕ 2,3-ДИМЕРКАПТОПРОПАНОЛА—I (ЪАЛ) ТИТРОВАНИЕМ С ЦИНКОМ, С ИСПОЛЬЗОВАНИЕМ ЭРИОХРОМ ЧЁРНОГО Т В КАЧЕСТВЕ ИНДИКАТОРА:

G. Colovos and H. Freiser, *Talanta*, 1969, **16**, 1605.

**Резюме**—Предложен метод титриметрического определения БАЛ с раствором цинка и использованием эриохром чёрного Т в качестве индикатора. Метод основан на разницы устойчивостей комплексов Zn(БАЛ)$_2$ и Zn-эриохром чёрный Т. Точность метода очень удовлетворительна, а влияние различных меркаппанов ограничено на соединения, образующая комплексы которые являются более устойчивыми чем комплекс Zn-эриохром чёрный Т.

## РАЗДЕЛЕНИЕ ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ НА ДИЭТИЛАМИНОЭТИЛЦЮЛОЗЕ МЕТОДОМ ТОНКОСЛОЙНОЙ ХРОМАТОГРАФИИ:

Koji Ishida, *Talanta*, 1969, **16**, 1607.

**Резюме**—Изучено методом тонкослойной хроматографии поведение магния, кальция, стронция и бария на слое диэтиламиноэтилцеллюлози в смесях метилового спирта и азотной кислоты. Значения R$_f$ следуют порядок магний > кальций > стронций > барий. Разницы между значениями R$_f$ позволяют получить хорошое разделение четыре ионов металлов одного от другого. Найлучшее разделение получено восходящим методом с использованием смеси метилового спирта и 8*M* азотной кислоты (20:1, по объему).

# Volume 16, 1969

## July–December, Nos. 7–12

## SUBJECT INDEX

# NOTES FOR AUTHORS

## 1. General

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

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published **in any language**, that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical.** The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists. Annotations should be critical commentaries on some aspects of analytical chemistry and may deal with topics such as sources of error, or the scope and limitations of methods and techniques.

Original papers, short communications annotations and reviews will be refereed (see *Talanta*, 1962, **9**, 89). Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

Preliminary communications will be refereed urgently and will be accorded priority in publication. Letters to the Editor will not be refereed, but will be published at the discretion of the Editor-in-Chief. If accepted, they will also be given priority.

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Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfil these conditions they will be treated as short communications.

**Scripts should be submitted in duplicate; they should be typewritten and the lines double-spaced.** Where possible, papers should follow the pattern: *Introduction, Experimental, Results, Discussions, Conclusions* (or such of these headings as apply).

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1. J. B. Austin and R. H. H. Pierce, *J. Am. Chem. Soc.*, 1955, **57**, 661.
2. S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon Press, Oxford, 1956.
3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strength of Metals.* A.E.R.E., M/R 6329, 1962.
5. W. Jones, *Brit. Pat.* 654321, 1959.

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