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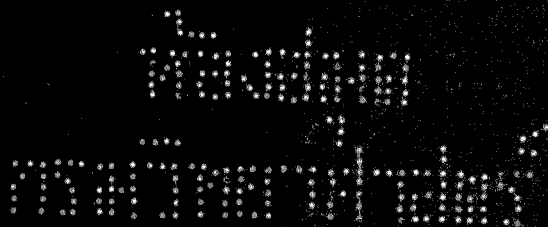
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1. Pecherer, B., Gambrell, C. M., and Wilcox, G. W., *Anal. Chem.*, 1950, **22(2)**, 311
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1. MacIntyre, I., and Ralston, M., *Biochem. J.*, 1954, **56**, xliii

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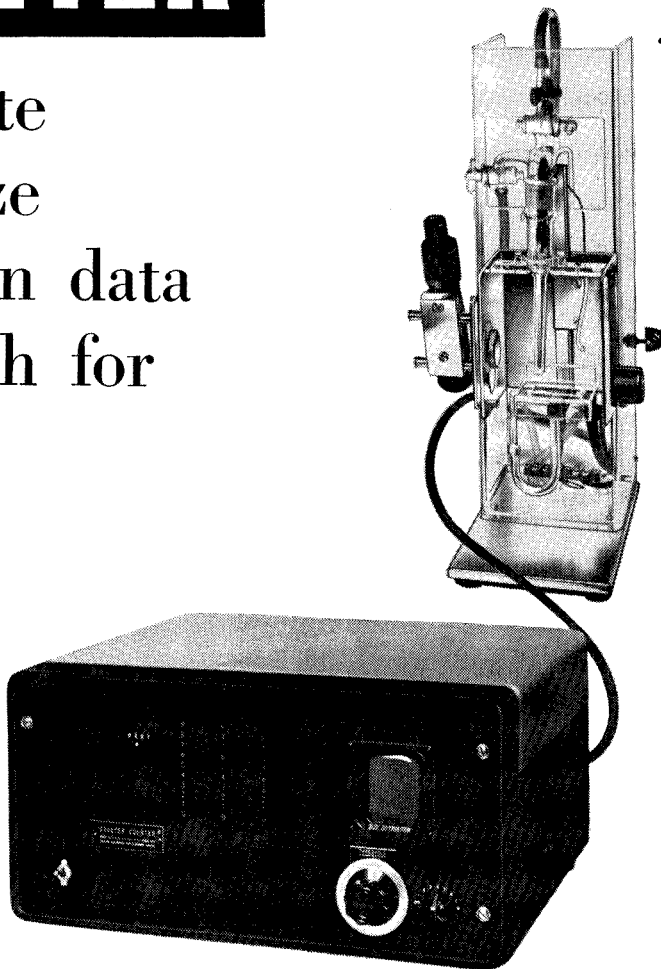
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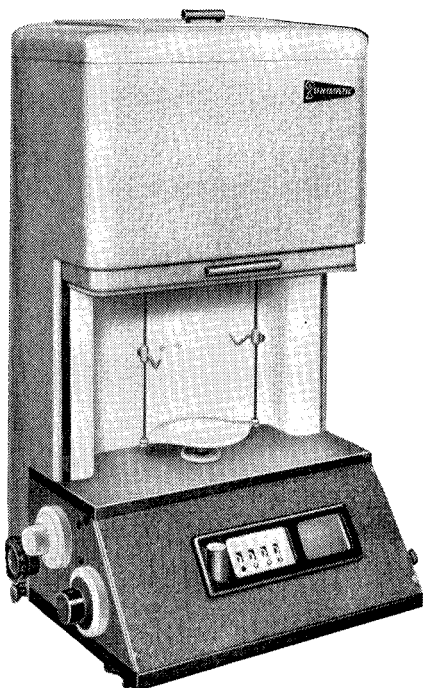
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<sup>1</sup> J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

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

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<sup>4</sup> W. Jones, *Brit. Pat.* 654321, 1959.

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## APPLICATIONS DE LA CHELATOMETRIE—XV\*

### DOSAGE VOLUMETRIQUE DU 6-PURINETHIOL

CLAUDE HENNART

Seraincourt, Seine et Oise, France

**Résumé**—La 6-Mercaptopurine ou 6-purinethiol, peut être dosée par chélatométrie après une précipitation au moyen du nitrate d'argent; l'excès de celui-ci est dosé, après filtration, par l'acide éthylène-diamino-tétracétique en présence de tétracyanonickelate de potassium et de murexide.

(Received 16 June 1961. Accepted 28 June 1961)

#### INTRODUCTION

DANS un travail en collaboration avec E. Merlin<sup>1</sup> sur la synthèse de la dichloro 4-6 pyrimidine, nous indiquions l'importance prise par les dérivés de la pyrimidine dans la recherche des produits à activité antitumorale, ceci en raison, sans doute, de la préférence marquée par les tissus cancéreux pour l'uracile dans la synthèse de leurs acides nucléiques.<sup>2,3</sup> Une substance particulièrement intéressante pour le traitement des leucémies aigües est certainement la 6-mercaptopurine ou 6-purinethiol<sup>4-15</sup> facilement obtenue à partir de la 6-hydroxypurine.<sup>16</sup>

La 6-mercaptopurine est capable de fixer, par substitution, deux atomes d'argent, l'un sur la partie iminazolique de sa molécule et l'autre sur sa fonction thiol; Blazek et Stejskal<sup>17</sup> en ont déduit, en 1956, un procédé de dosage argentométrique: après une précipitation en milieu ammoniacal par une solution décimale de nitrate d'argent suivie d'une filtration, l'argent en excès dans le filtrat est titré par la méthode courante au thycyanate d'ammonium en présence d'ions ferriques. Nous nous sommes inspirés de ce procédé pour établir une méthode chélatométrique basée sur le dosage de l'argent selon Flaschka et Huditz,<sup>18,19</sup> nous avons déjà utilisé avec satisfaction ce mode de dosage dans le cas des halogènes organiques,<sup>20,21</sup> et de diverses sulfamides:<sup>22</sup> en présence de tétracyanonickelate de potassium, l'argent prend, dans ce complexe, la place du nickel et on dose celui-ci, en milieu ammoniacal, par l'acide éthylène diamino-tétracétique en présence de murexide comme indicateur.

#### PARTIE EXPERIMENTALE

##### Réactifs utilisés

*Ammoniaque*: 10%

*Nitrate d'argent*: 0,05M

*Tétracyanonickelate de potassium*: 0,025M: on dissout 6,25 g d'acétate de nickel,  $(\text{CH}_3\text{COO})_2\text{Ni}$ ,  $4\text{H}_2\text{O}$ , dans 300 ml d'eau distillée, puis ajoute 100 ml d'ammoniaque et 10 mg de murexide; à cette solution, on ajoute, jusqu'à virage précis au violet, une solution contenant 6,2 g de cyanure de potassium dans 500 ml d'eau distillée (on procède d'abord par approximation sur les 9/10ème de la solution nickélique et termine à la burette après avoir ajouté le dernier dixième de cette solution); on complète le tout à un litre au moyen d'eau distillée.

*Chélate*: 0,01M: nous avons appelé ainsi une solution préparée par dissolution de 3,7 g d'éthylène-diaminotétracetate disodique dans un litre d'eau fraîchement bouillie et distillée; on détermine

\* Articles précédents: XIII—*Chim. Analyt.*, 1961, (sous presse); XIV—*Analyt. Chim. Acta*, 1961, 25, 21.

la molarité de cette solution à partir d'un poids connu de magnésium ou de zinc métalliques chimiquement purs en utilisant le noir-ériochrome T comme indicateur ou à partir d'une solution titrée de nitrate d'argent en présence du réactif ci-dessus et de murexide.

*Murexide*: 1%: on pèse 0,1 g de murexide, ajoute 10 g de chlorure d'ammonium bien sec et broye le tout intimement.

#### Mode opératoire

On pèse un poids  $p$  supposé contenir 50 mg qu'on dissout dans 10 ml d'eau et 3 ml d'ammoniaque 10%; on ajoute 25 ml de nitrate d'argent 0,05M, agite pendant quelques minutes et complète à 100 ml au moyen d'eau distillée; on agite et filtre; on prélève 25 ml du filtrat auxquels on ajoute 25 ml de tétracyanonickelate de potassium 0,025M, 25 ml d'ammoniaque 10% et quelques décigrammes de murexide 1%; on verse le chélate 0,01M au moyen d'une burette de 10 ml jusqu'au virage au violet.

Le titre % calculé en Purinethiol anhydre est donné par la formule:

$$T_{D,p} = \frac{V \times 7,609}{P}$$

où  $V = (25 \times N'_A) - (8 \times N'_C \times V')$

$V'$  = nombre de ml de chélate utilisé

$N'_C$  = molarité de ce réactif

$N'_A$  = molarité du nitrate d'argent

$p$  est exprimé en grammes

Le titre % calculé en monohydrate peut être obtenu en remplaçant le nombre 7,609 par le nombre 8,51 dans la formule précédente.

#### RESULTATS OBTENUS

$p$ en mg (produit anhydre)	titre trouvé, %	déviaton, %
47,2	99,2	-0,8
46,4	100,3	+0,3
49,3	99,5	-0,5
53,2	99,1	-0,9
51,7	100,5	+0,5
48,8	99,4	-0,6

**Summary**—6-Mercaptopurin, or 6-purinethiol, can be precipitated by means of standard silver nitrate solution, the excess of which is determined, in the filtrate, chelatometrically.

**Zusammenfassung**—6-Mercaptopurin, oder 6-purinethiol, werden dann mit Silbernitratlösung bekannter Normalität gefällt, deren Überschuss im Filtrat chelatometrisch bestimmt wird.

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## PHOTOMETRIC DETERMINATION OF SCANDIUM WITH $\alpha$ -(2,4-DIHYDROXYPHENYL-AZO)-PYRIDINE\*

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**Summary**—Under certain conditions the scandium ion gives a characteristic coloration with  $\alpha$ -(2,4-dihydroxyphenylazo)-pyridine on interaction with it in the molar ratio 1:1. A photometric method has been worked out for the determination of 0.05–2  $\mu$ g of Sc/ml using this reagent. Be, Mo, Ca, Mg do not interfere with the determination, but Zn, Co, Ni, Cd, Cu, Tl, In, Ga, Zr, Th, U and Fe do.

FEW colour reactions and photometric methods are known for the determination of scandium.<sup>1–5</sup> This study was aimed at an examination of the possibility of carrying out the photometric determination of scandium by means of  $\alpha$ -(2,4-dihydroxyphenylazo)-pyridine (DPP), which has in recent years been introduced widely in analytical chemistry as a complexometric indicator.

### EXPERIMENTAL

#### Reagents

**Standard scandium solution:** Prepared by dissolving an accurately weighed amount of spectrally pure scandium oxide in hydrochloric acid. Its concentration was equal to  $1.589 \times 10^{-3}M$ .

**$\alpha$ -(2,4-Dihydroxyphenylazo)-pyridine (DPP) solution:** Prepared by dissolving a pure preparation of the base (m.p. 185–6°) in a dilute solution of caustic soda and diluting with water. To the solution obtained hydrochloric acid was added until the reaction was neutral to universal indicator paper. A DPP solution having a concentration of  $1.589 \times 10^{-3}M$  used for titrations was prepared by accurate weighing. To attain the desired pH a 20% aqueous solution of ammonium acetate was used.

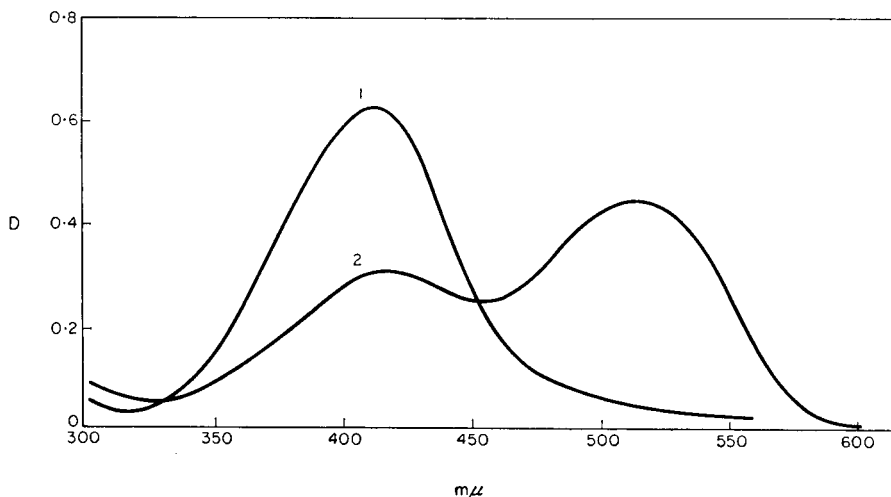


Fig. 1—Absorption curves (spectrophotometer SF-4; 1-cm cell; optical density referred to water):

1—Solution of DPP at pH 6.22; 2—Complex of scandium with DPP at pH 6.12.

\* Translated from the Russian: *Vestnik Mosk. Univ., Ser. Khim.* 1960, No. 6, 46.

*Complex of scandium with  $\alpha$ -(2,4-dihydroxyphenylazo)-pyridine*

The scandium ion reacts with DPP forming a soluble compound having an intensely red colour. At relatively high concentrations of the scandium salt a flocculent precipitate separates out. The colour is stable with time, the optical density of the solutions undergoing no decrease on standing. The absorption curve of the solution of the compound formed was obtained in the presence of an excess of scandium. The solution contained  $1.27 \times 10^{-4}M$  scandium and  $1.66 \times 10^{-5}M$  DPP, the pH of the solution being adjusted to a value of 6.12 by a pH meter with a glass electrode. The optical density was measured on a spectrophotometer (CF-4) using a 1-cm cell, with reference to water. The absorption curve (Fig. 1) exhibits two maxima, at 420  $m\mu$  and at 515  $m\mu$ . The absorption curve of the reagent at the same concentration and pH 6.22 has one maximum at 410  $m\mu$ . The reagent solution absorbs only very slightly at 515  $m\mu$ . In the photometric determination of scandium the optical density at this wavelength must be measured with reference to a blank solution prepared by the same method but without the addition of scandium.

The molar ratio in the reaction of the scandium ion and DPP was determined by the isomolar series method. The constant overall concentration of scandium and the reagent was  $6.36 \times 10^{-5}M$ ; the concentration of scandium varied within the limits of  $6.36 \times 10^{-6}$  to  $5.72 \times 10^{-5}M$  and that of the reagent from  $5.72 \times 10^{-5}$  to  $6.36 \times 10^{-6}M$ . The optical density of the solutions was determined at 515 and 550  $m\mu$  with reference to water. For the optical density at 515  $m\mu$ , a correction was introduced for the absorption by the reagent itself (curve 3, Fig. 2).

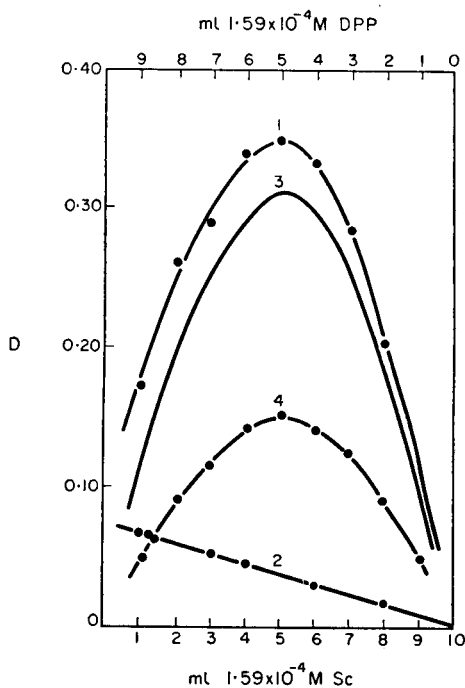


Fig. 2—Molar absorption in the interaction of the scandium ion with DPP by the method of isomolar media:

1-Measured values of the optical density at 515  $m\mu$  referred to water; 2-Optical density of the corresponding solutions of DPP at 515  $m\mu$  referred to water; 3-Difference between curves 1 and 2; 4-Measured values of the optical density of isomolar solutions of a scandium salt and DPP at 550  $m\mu$ , referred to water.

The remaining conditions were identical with those employed in deriving the calibration curve (*cf.* below). On the curves (Fig. 2), the optical density maximum appears at a molar ratio of scandium to the reagent equal to 1:1. The position of the maximum reflects a fairly strong dissociation of the compound formed under the conditions of the experiment.

To verify the molar ratio found, the influence exerted by an excess of each of the components on the displacement of the equilibrium was studied. The formation of a compound with molar ratio 1:1 may be represented by the following reaction scheme:



where  $\text{HP} = \text{DPP}$ . In this case an excess of scandium and an excess of the reagent must displace the equilibrium to an identical extent for a constant hydrogen ion concentration. If scandium does not react with the reagent in a molar ratio of 1:1 but 1:2 or any other ratio, equal excesses of either components will not exert the same influence on the displacement of the equilibrium. When the ratio of scandium:reagent is equal to 1:2, a change in the excess concentration of scandium by a factor of 10 must change the ratio  $(\text{ScOP}):(\text{ScO}^+)$  by  $\sqrt{10}$ , *i.e.* by 3.1 times, while a change in the excess concentration of the reagent by a factor of 10 must change the ratio in question by a factor of  $10^2$ , *i.e.* 100. Two series of solutions were prepared as when deriving the calibration curve, one series of solutions containing 0.2 ml of a  $1.59 \times 10^{-3}M$  solution of scandium and 0.2, 0.4, 0.7, 1.6 and 3.0 ml of a  $1.59 \times 10^{-3}M$  solution of the reagent, and the other series containing 0.2 ml of a  $1.59 \times 10^{-3}M$  solution of the reagent and 0.2, 0.4, 0.8, 1.6 and 3.0 ml of a  $1.59 \times 10^{-3}M$  solution of scandium.

The right branch of the curve shown in Fig. 3 illustrates the change in the optical density of the solutions of the first series and the left branch refers to the solution of the second series.

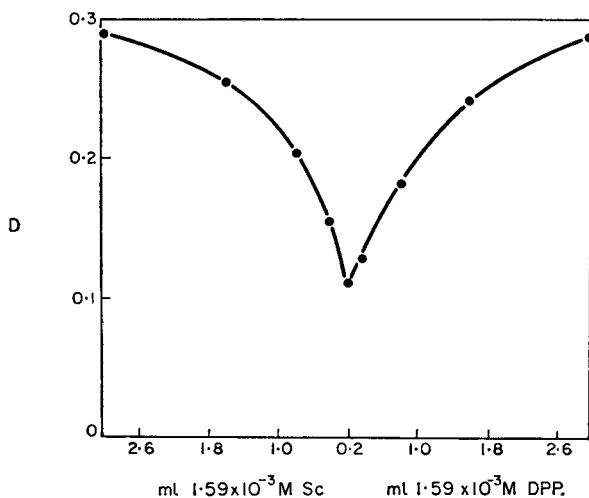


Fig. 3—The influence of an excess of scandium salt or of DPP on the optical density of solutions of the compound formed.

The figure clearly shows that an excess of either component influences the displacement of the equilibrium to an equal extent so that they evidently react in a molar ratio of 1:1.

The molar absorption coefficient of the solutions of the scandium compound formed was determined at  $515 m\mu$ . The solutions were prepared as for the derivation of the calibration curve, they contained acetate ions. The concentration of scandium was constant ( $2.54 \times 10^{-3}M$ ). The solutions contained different amounts of excess DPP (15 ml, 13 ml and 10 ml of a 0.01% solution of the reagent). The molar absorption coefficients calculated for each solution were, respectively, equal to  $2.26 \times 10^4$ ,  $2.26 \times 10^4$ ,  $2.3 \times 10^4$  and  $2.14 \times 10^4$ , giving an average value of  $2.21 \times 10^4$ .

The results of the calculations relating to the equilibrium constants of reaction (1) are shown in Table 1.

The concentration of the complex was calculated from the equation

$$C_{\text{comp}} = D/l\Sigma,$$

where  $\Sigma$  is the molar absorption coefficient of the complex,  $l$  the thickness of the solution layer and  $D$  the measured optical density.



TABLE I—EQUILIBRIUM CONSTANT OF REACTION (1) AT 19° AND pH 5.95.

Total concentration $C_{\text{tot}} \text{ mol/l} \times 10^{-5}$		Molar ratio of Sc : DPP	$D^{515}$ ( $l = 1 \text{ cm}$ )	Concn. of the complex $C_{\text{comp}} \times 10^{-5}$	Concn. of the free components $C_f \times 10^{-5}$		Equilibrium constant,* $K \times 10^{-2}$
Scandium	DPP				Scandium	DPP	
1.27	1.27	1:1	0.110	0.50	0.77	0.77	9.4
3.18	3.18	1:1	0.350	1.60	1.58	1.58	7.2
2.54	2.54	1:1	0.230	1.05	1.49	1.49	5.3
1.27	1.27	1:1	0.110	0.50	0.77	0.77	9.4
2.54	1.27	2:1	0.155	0.71	1.83	0.56	7.7
5.08	1.27	4:1	0.206	0.94	4.14	0.33	7.7
1.27	5.08	1:4	0.200	0.91	0.36	4.17	6.8

\* Average  $7.6 \times 10^{-2}$

The concentrations of free scandium and reagent were found from the difference between the total concentrations and those parts of them which are bound in the complex. The apparent equilibrium constant of the reaction at pH 5.95 is equal to  $7.6 \times 10^{-2}$  (mean value of 8 results). It shows that the complex formed between scandium and the reagent under the conditions of the experiment is not very stable.

The apparent constant makes it possible to calculate the excess of reagent necessary for the spectrophotometric determination of scandium. It was found that more than a six-fold molar excess of the reagent must be present in the solution to ensure that 90% of the scandium is bound in the red coloured complex, and to raise this level to 99%, a sixty-fold molar excess of the reagent is required. Thus, in the photometric determination of scandium large amounts of the reagent must be employed. This result finds experimental confirmation.

Fig. 4 shows that the maximum development of the colour of the complex is only observed when the solution contains a greater than six-fold molar excess of the reagent with respect to the scandium.

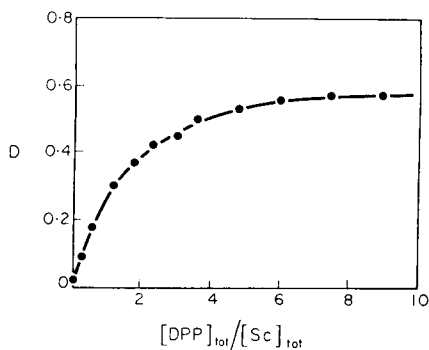


Fig. 4—Influence of an excess of DPP on the optical density of solutions of the scandium compound.

To carry out these experiments 0.4 ml of a  $1.59 \times 10^{-3} M$  solution of scandium and different volumes of a 0.01% solution of the reagent were used (the remaining conditions were as in the derivation of the calibration curve).

In clarifying the optimum pH values of the solution in the photometric determination of scandium, the experiments were carried out in the following manner: 2.0 ml of a  $1.59 \times 10^{-4} M$  solution of scandium and 1.0 ml of an 0.05% and the reagent are introduced into a 50-ml volumetric as flask, 30–40 ml of water are added solution of pH of the solution is adjusted to the desired value determined by means of universal indicator paper, by the addition of sodium hydroxide or hydrochloric acid. The solution is then made up to the volume with water, and its pH is checked by means

of a glass electrode. The optical density of the solutions obtained is determined at 515 m $\mu$  with respect to water (Fig. 5). In the same manner a solution of DPP of identical concentration (without scandium) is prepared and its optical density is determined with respect to water (curve 2, Fig. 5).

These experiments showed that the optimum pH value of the solution for the photometric determination of scandium lies within the pH range 6 to 7.3. The optical density is thereby independent of the pH of the solution. To obtain the required medium it is recommended that a 20% solution of ammonium acetate be added. The best results are obtained by the addition of 2.5 ml of 20% ammonium acetate solution per 25 ml of the final solution.

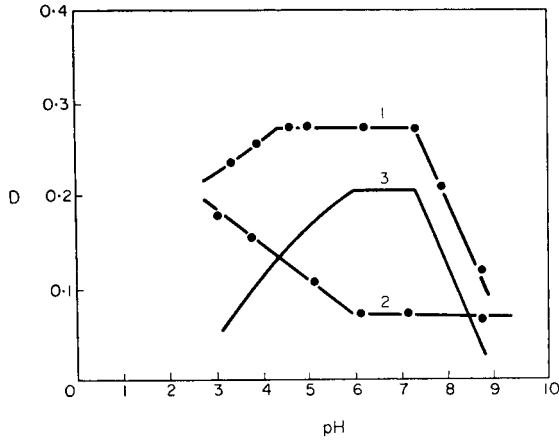


Fig. 5—Optimum pH value of the solution in the spectrophotometric determination of scandium by means of DPP:

1-Scandium compound in the presence of an excess of the reagent; 2-Reagent; 3-Difference between the curves 1 and 2.

*Calibration curve*

Twelve ml of neutral standard solution of scandium salt, of a concentration such that the final solution (after dilution to 25 ml) contains 0.05–2.0  $\mu$ g of scandium/ml, is placed in a 25-ml volumetric flask. 2.5 ml of 20% ammonium acetate solution is added, followed by 2.0 ml of a 0.05% solution of the reagent. The solution is made up to the mark with water, well mixed and the optical density is measured at 515 m $\mu$  on a spectrophotometer using a 1-cm cell with reference to a solution prepared in the same way but without the addition of scandium. The solutions follow Beer's law within the limits of 0.05–2.0  $\mu$ g of scandium/ml.

*Interferences*

Zinc, cobalt, nickel, cadmium, copper, thallium, indium, gallium, zirconium, thorium, uranium, iron and aluminium interfere with the determination of scandium either by forming coloured solutions or a coloured precipitate when the reagent is added. Beryllium, molybdenum, calcium and magnesium do not interfere (Table II). Thus, DPP is not a selective reagent for scandium.

TABLE II—DETERMINATION OF SCANDIUM IN THE PRESENCE OF OTHER ELEMENTS (29  $\mu$ g OF SCANDIUM PRESENT)

Foreign ion, $\mu$ g	Be 50	Mo 50	Ca 50	Ca 25	Mg 50	Mg 26
Sc found, $\mu$ g	28	29	29	28	28	30
Error, $\mu$ g	-1	0	0	-1	-1	+1

CONCLUSIONS

The scandium ion gives a characteristic coloration with  $\alpha$ -(2,4-dihydroxyphenylazo)-pyridine under determined conditions and thereby interacts with the reagent in a molar ratio of 1:1. A photometric method for the determination of 0.05–2  $\mu$ g of scandium/ml

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by means of  $\alpha$ -(2,4-dihydroxyphenylazo)-pyridine is worked out. Be, Mo, Ca and Mg do not interfere with the determination, but Zn, Co, Ni, Cd, Cu, Tl, In, Ga, Zr, Th, U and Fe do.

**Zusammenfassung**—Unter bestimmten Bedingungen gibt Scandium einen charakteristisch gefärbten 1:1 Komplex mit  $\alpha$ -(2,4-dioxyphenylazo)-pyridin. Eine photometrische Methode wurde entwickelt zur Bestimmung von 0.05–2  $\mu\text{gSc/ml}$ . Be, Mo, Ca, Mg stören nicht. Störung verursachen: Zn, Co, Ni, Cd, Tl, In, Ga, Th, Zr, U und Fe.

**Résumé**—L'ion scandium donne, dans certaines conditions, une coloration caractéristique avec l' $\alpha$ -(2,4-dihydroxyphénylazo)-pyridine par réaction dans le rapport molaire 1/1. Une méthode photométrique a été réalisée pour le dosage de 0,05–2  $\gamma\text{Sc/ml}$  en utilisant ce réactif. Be, Mo, Ca, Mg ne gênent pas le dosage au contraire de Zn, Co, Ni, Cd, Cu, Tl, In, Ga, Zr, Th, U et Fe.

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## PHOTOMETRIC DETERMINATION OF MOLYBDENUM IN THE QUINQUEVALENT STATE BY MEANS OF 8-HYDROXYQUINOLINE-5-SULPHONIC ACID\*

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**Summary**—A new photometric method has been worked out for the determination of small quantities of molybdenum (after its reduction to the quinquevalent state with hydrazine hydrochloride) using 8-hydroxyquinoline-5-sulphonic acid. From 3 to 20 mg of molybdenum can be determined by the method. Large quantities of tungsten, as well as magnesium, calcium, barium, nickel, cadmium, aluminium, thorium, bivalent manganese, trivalent chromium and small quantities of bismuth, copper and uranium do not interfere with the determination of molybdenum.

THE literature<sup>1</sup> contains references to the fact that the addition of 8-hydroxyquinoline-5-sulphonic acid to a solution of a salt of quinquevalent molybdenum followed by heating leads to the appearance of an intensely red coloration. In the cold, the reagent gives a soluble yellow compound with quinquevalent molybdenum, which is evidently not of great interest to analytical chemistry. Sexavalent molybdenum (at a concentration of 0.005 M/l.) is not precipitated by 8-hydroxyquinoline-5-sulphonic acid at a pH of 4–8† and does not form any coloured compounds with it. Most ions of other metals are thereby also not precipitated and do not form any soluble compounds having a characteristic colour.

The aim of this study was the clarification of the possibility of utilising 8-hydroxyquinoline-5-sulphonic acid for the photometric determination of molybdenum in the presence of other elements.

### EXPERIMENTAL

#### Reagents

**10<sup>-2</sup>M solution of quinquevalent molybdenum:** Two-five ml of a solution of hydrazine hydrochloride (concentration: 0.01 g/ml) and 1–3 ml of conc. hydrochloric acid are placed in a 100-ml beaker, and the volume is then made up to 20 ml with water. The solution is heated to boiling and 9.44 ml of a 0.05136M solution of sodium molybdate is added dropwise. Boiling is continued for a further few min, then the solution is transferred to a 50-ml calibrated flask, cooled and the volume made up to the mark with water.<sup>2</sup>

**0.1M solution of 8-hydroxyquinoline-5-sulphonic acid:** Prepared by dissolving 2.3 g of crystalline reagent‡ in 100 ml of water followed by the addition of a small amount of 1M sodium hydroxide solution. The suspension obtained is filtered, the solution is neutralised by the addition of hydrochloric acid until neutral or slightly acid to a universal indicator paper.<sup>3</sup>

The concentration of the aqueous solution of sodium molybdate is determined by the oxine method.<sup>4</sup>

**Solution of the reducing agent:** Twenty g of hydrazine hydrochloride is dissolved in a small amount of distilled water and the solution is neutralised with alkali until neutral to universal indicator paper. The volume is then made up to 100 ml with water.

**Acetate buffer solution (pH 3.6):** One hundred ml of 1M sodium acetate is mixed with 90 ml of 1M hydrochloric acid and the volume is made up to 250 ml with water.

\* Translated from the Russian: *Vestnik. Mosk. Univ., Ser. II, Khim.* 1961, No. 2, 36.

† One product is precipitated at a pH of 2–3.

‡ 8-Hydroxyquinoline-5-sulphonic acid was synthesised by the usual method.<sup>3</sup>

*Conditions for the formation of a compound between quinquevalent molybdenum and 8-hydroxyquinoline-5-sulphonic acid*

Molybdenum<sup>V</sup> forms two soluble complex compounds with 8-hydroxyquinoline-5-sulphonic acid. At room temperature a yellow compound is formed which slowly changes to a red one on prolonged standing. On heating an intensely red compound is formed almost immediately. The formation of two different compounds was established earlier on. Molybdenum<sup>V</sup> does not give a precipitate with 8-hydroxyquinoline-5-sulphonic acid at pH values of 3–10. The explanation for this lies in the presence of the sulphonic-group in the reagent.

The red coloured compound of molybdenum<sup>V</sup> with 8-hydroxyquinoline-5-sulphonic acid is very stable, which is confirmed by the fact that it does not undergo hydrolysis even in a strongly alkaline medium in the presence of an excess of 8-hydroxyquinoline-5-sulphonic acid; it should be noted that a solution of  $(\text{NH}_4)_2\text{MoOCl}_5$  is readily hydrolysed.

Solutions of the red compound of molybdenum<sup>V</sup> used to derive the absorption curve were prepared in the following manner: an excess (10 ml) of a 0.1M solution of 8-hydroxyquinoline-5-sulphonic acid was added to 20 ml of a hot solution containing 0.5 ml of a  $10^{-2}M$  solution of molybdenum<sup>V</sup>, the pH of the solution was adjusted to a value of 4.01 by means of a glass electrode and the mixture was heated on a boiling water bath for 20 min; the solution obtained was cooled, diluted to the mark with water in a 50-ml calibrated flask and the optical density was measured at different wavelengths on an SF-4 spectrophotometer, with reference to a blank solution prepared in an identical manner but without the addition of molybdenum (Fig. 1, curve 1). The absorption curve of a  $10^{-2}M$  solution of 8-hydroxyquinoline-5-sulphonic acid at a pH of 4.77 is also shown in Fig. 1 (curve 2).

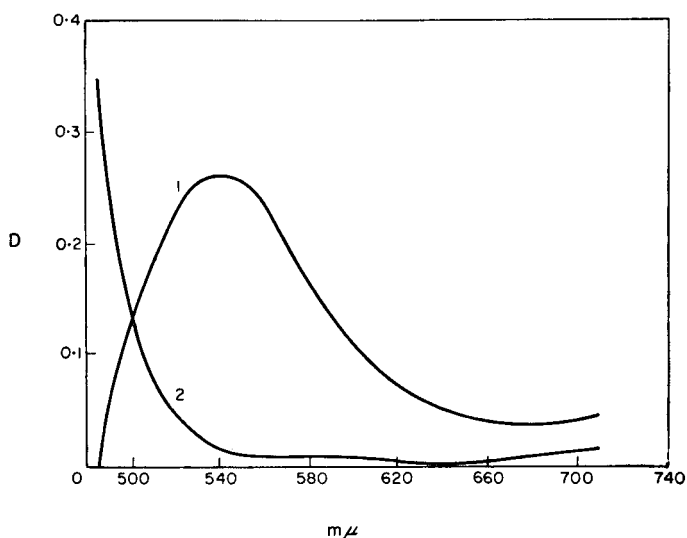


FIG. 1—Light absorption curves:

- 1-Compound formed between molybdenum<sup>V</sup> and 8-hydroxyquinoline-5-sulphonic acid. Concentration in the final solution:  $10^{-4}M$  of molybdenum<sup>V</sup> and  $10^{-2}M$  of 8-hydroxyquinoline-5-sulphonic acid; pH 4.01; after heating; optical density measured with respect to a  $10^{-2}M$  solution of 8-hydroxyquinoline-5-sulphonic acid at pH 4.77;
- 2- $10^{-2}M$  solution of 8-hydroxyquinoline-5-sulphonic acid at pH 4.77. Optical density measured with respect to water.

The absorption curve of the red coloured compound formed between molybdenum<sup>V</sup> and 8-hydroxyquinoline-5-sulphonic acid in the wavelength region of 480  $m\mu$  to 700  $m\mu$  exhibits only one maximum at 540  $m\mu$ . At 540  $m\mu$  the reagent absorbs practically no light.

The apparent molar absorption coefficient of molybdenum compound under the conditions of the spectrophotometric determination has a value of 5180.

The optimum pH value of the solution for the formation of the red compound between molybdenum<sup>V</sup> and 8-hydroxyquinoline-5-sulphonic acid lies in the interval of 3–4.5 (Fig. 2). Since the

acetate ion does not interfere, the required medium may be produced by the addition of an acetate buffer solution.

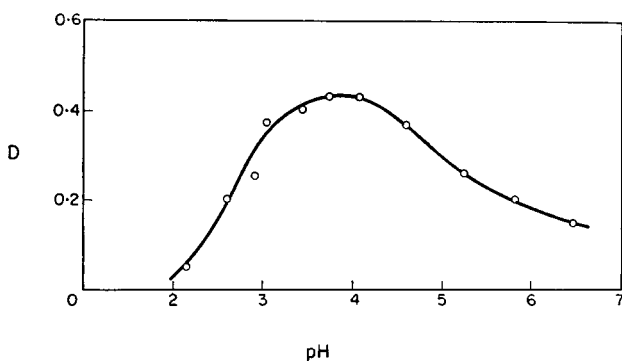


FIG. 2—Influence of pH on the magnitude of the optical density of solutions of the compound formed between molybdenum and 8-hydroxyquinoline-5-sulphonic acid.

The reduction of hexavalent molybdenum can be accomplished at a pH of 3–4.5 in the presence of large amounts of hydrazine hydrochloride if the solution contains 8-hydroxyquinoline-5-sulphonic acid which gives a very stable compound with molybdenum<sup>V</sup> as a result of which the formation of molybdenum blue is not observed. Five ml of 0.1M neutral 8-hydroxyquinoline-5-sulphonic acid solution and 5 ml of acetate buffer solution having a pH of 3.1 are added to 15 ml of a solution containing 0.5 ml of a 10<sup>-2</sup>M solution of sodium molybdate, and this is followed by the addition of 0.2, 1.0, 1.5 or 3.0 ml of a neutral or faintly acid solution of hydrazine hydrochloride (0.2 g/ml). The resultant solution is heated on a boiling water bath for a given time, cooled with water to room temperature, transferred to a 50-ml calibrated flask and the volume is made up to the mark. The optical density is then measured at 540 m $\mu$  with respect to water. The results are shown in Fig. 3.

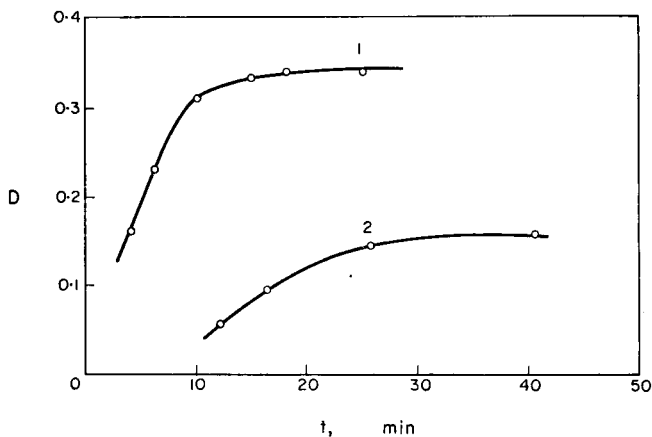


FIG. 3—Influence of the heating time on the optical density of the solution of the compound: 1- in the presence of 1.0 ml of a solution of 0.2 mg/ml of hydrazine hydrochloride in 25 ml final volume; 2- in the presence of 0.2 ml of a solution of 0.2 mg/ml of hydrazine hydrochloride in 25 ml final volume.

The optical densities of the solutions to which 1.0, 1.5 and 3.0 ml of a hydrazine hydrochloride solution containing 0.2 g/ml had been added, after which the solutions had been heated for 15 min, were practically identical (Fig. 3, curve 1). The formation of molybdenum blue was not observed at pH values of 3–4.5 or 6–7. Thus, in the photometric determination of molybdenum, molybdenum<sup>VI</sup> may be reduced to molybdenum<sup>V</sup> at a pH of 3.1, whereby the heating time on the boiling water bath amounts to 15–25 min and the necessary amount of hydrazine hydrochloride (NH<sub>2</sub>NH<sub>2</sub>·2HCl) is of

the order of 1-3 ml of a solution containing 0.2 g/ml to 25 ml of the solution to be analysed. At low concentrations of hydrazine hydrochloride (0.2 ml) the sensitivity of the reaction is lowered to a considerable extent (Fig. 3, curve 2), evidently as a result of the incomplete reduction of molybdenum<sup>VI</sup>. The optical density of the solutions obtained does not depend on the amount of hydrazine within the limits of 1-2.5 ml (heating time 20 min).

Without heating, the formation of the red molybdenum compound is also observed when a large amount of hydrazine is present and the intensity of the coloration increases with the time. But the colour has not attained its maximum value and constancy after a period of 3 hr.

For a complete development of the coloration more than 80 m mol of 8-hydroxyquinoline-5-sulphonic acid is required per m mol of molybdenum.<sup>VI</sup>

The intensity of the red colour of the solutions decreases slowly with time and after 24 hr the colour has disappeared. However, during the first 3 hr the optical density of the solutions remains practically constant.

Solutions of the compound of molybdenum<sup>V</sup> with 8-hydroxyquinoline-5-sulphonic acid obey Beer's law within the limits of 3-13  $\mu$ g/ml of molybdenum. Ten ml of a weakly acid molybdate solution containing from 0.15-0.65 mg of molybdenum, and whose concentration has been determined accurately, are placed into a 50-ml beaker. Five ml of neutral 0.1M 8-hydroxyquinoline-5-sulphonic acid solution are added, followed by 1.5 ml of neutralised hydrazine hydrochloride solution containing 0.2 g/ml and 10 ml of acetate buffer (pH 3.6). The mixture is stirred and the beaker is covered with a watch glass; it is then placed on a boiling water bath and heated for 15-25 min. The

TABLE I.—DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF TUNGSTEN AND OTHER FOREIGN IONS (0.38 MG OF MOLYBDENUM PRESENT)

Foreign ions, <i>mg</i>	Ratio of molybdenum to foreign ion	Molybdenum, <i>mg</i>	
		Found	Error
4.0 Ca	1:10	0.38	0
1.9 Mg	1:5	0.39	+0.01
54.8 Ba	1:140	0.34	-0.04
1.2 Ni	1:3	0.38	0
2.2 Cd	1:6	0.38	0
3.3 Mn	1:8	0.39	+0.01
7.0 Cu	1:18	0.41	+0.03
8.5 Cu	1:21	0.43	+0.05
1.0 Cr	1:2.5	0.38	0
3.1 Cr	1:8	0.37	-0.01
1.2 Al	1:3	0.38	0
4.2 Bi	1:11	0.35	-0.03
4.2 Bi	1:11	0.34	-0.04
1.0 Th	1:2.5	0.37	-0.01
0.24 U	1:0.6	0.37	-0.01
1.2 U	1:3	0.41	+0.03
32.5 KCN	1:80	0.37	-0.01
53.6 Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	1:134	0.38	0
60.0 C <sub>4</sub> H <sub>6</sub> O <sub>6</sub>	1:150	0.26	-0.12
72.0 Complexone III	1:180	0.11	-0.27
1.0 V	1:2.5	0.71	+0.33
5.0 W	1:13	0.39	+0.01
10.0 W	1:25	0.35	-0.03
20.0 W	1:50	0.37	-0.01
30.0 W	1:75	0.34	-0.04
40.0 W	1:100	0.37	-0.01
30.0 W	1:75	0.39	+0.01
50.0 W	1:125	0.43	+0.05

molybdenum thereby passes quantitatively into the red form. The red solution obtained is cooled with cold water to room temperature, transferred to a 50-ml calibrated flask, and the beaker washed out thoroughly with distilled water. The volume is then made up to the mark with water, the contents of the flask are mixed and the optical density of the solution is determined at 540  $m\mu$  with respect to water, at least 2 hr after cooling.

*Determination of molybdenum in the presence of tungsten and other elements*

The photometric determination of molybdenum is carried out under the same conditions as those employed in verifying the applicability of Beer's law. Sexavalent tungsten does not form any coloured compounds with 8-hydroxyquinoline-5-sulphonic acid and therefore does not in any way influence the results of the molybdenum determination. However, in the presence of large amounts of tungsten (more than 10 mg) the amount of reagent added must be increased (two to three-fold). Vanadates give a red colour with the reagent, and iron<sup>II</sup> a green colour. The last two elements interfere to a marked extent with the determination of molybdenum. Cobalt, zinc and larger amounts of copper give yellow or greenish-yellow coloured precipitates with the reagent on heating, and they also interfere with the determination. Complexone III and tartaric acid interfere with the determination as they form stable complexes with quinquevalent molybdenum.\*

### CONCLUSIONS

A new photometric method for determining small amounts of molybdenum by means of 8-hydroxyquinoline-5-sulphonic acid (after its reduction to the quinquevalent state by means of hydrazine hydrochloride) is developed. The method permits the determination of 3–20 mg/ml. Large amounts of tungsten, and also magnesium, calcium, barium, nickel, cadmium, aluminium, thorium, manganese<sup>II</sup>, chromium<sup>III</sup> and small amounts of bismuth, copper and uranium do not interfere with the molybdenum determination.

**Zusammenfassung**—Eine neue photometrische Methode wurde entwickelt, um kleine Mengen von Molybdän (nach Reduktion zur fünfwertigen Stufe) mit 8-Oxin-5-sulfonsäure zu bestimmen. 3–20  $\mu\text{g/ml}$  können erfasst werden. Grosse Mengen von W, sowie Mg, Ca, Ba, Ni, Cd, Al, Th, Mn(II), Cr(III) und kleine Mengen von Bi, Cu und U stören nicht.

**Résumé**—Les auteurs ont mis au point une nouvelle méthode photométrique de dosage de faibles quantités de molybdène (après sa réduction à l'état pentavalent par le chlorure d'hydrazinium) à l'aide d'acide sulfo-5 oxy-8 quinoléine. Cette méthode permet de doser de 3 à 20  $\mu\text{g/ml}$  de Mo. De grandes quantités de tungstène, ainsi que de magnésium, calcium, baryum, nickel, cadmium, aluminium, thorium, manganèse(II), chrome(III) et de faibles quantités de bismuth, cuivre et uranium ne gênent pas le dosage du molybdène.

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\* Although the compound formed between molybdenum<sup>V</sup> and 8-hydroxyquinoline-5-sulphonic acid is less stable than the compound formed with Complexone III, it is not suitable as a complexometric indicator for titrating quinquevalent molybdenum because of the unsharp colour change at the end-point (both at room temperature and on heating).



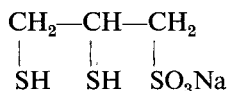
## UNITHIOL AS A REAGENT FOR MOLYBDENUM\*

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**Summary**—Unithiol (sodium 2,3-dimercaptopropanesulphonate) forms coloured complexes with molybdenum in acid solutions. The nature of these complexes is discussed, and it is concluded that  $\text{Mo}^{\text{VI}}$  is reduced to  $\text{Mo}^{\text{V}}$  by the reagent. Coloured complexes contain molybdenum<sup>V</sup> and probably molybdenum<sup>VI</sup>. Unithiol is a promising reagent for molybdenum. It has a high degree of selectivity. Cr and  $\text{Hg}^{\text{II}}$  do not give colours in acidic solution,  $\text{Hg}^{\text{I}}$  gives a greyish-brown precipitate, and  $\text{Pb}^{\text{II}}$  gives a yellow precipitate.

UNITHIOL (sodium 2,3-dimercaptopropanesulphonate)



is a white fine crystalline substance, readily soluble in water and sufficiently stable in solution. Its synthesis has been worked out.<sup>1</sup> Unithiol is used in medicine as an antidote against heavy metal poisoning. As far as can be judged from the first publication,<sup>2</sup> unithiol is also a valuable analytical reagent.

Unithiol is capable of forming stable complex compounds with a series of metals. The complex compounds of unithiol with some metals are in some cases more stable than the corresponding complexonates. This enables it to be employed for masking when carrying out complexometric determinations, in particular when titrating in an ammoniacal medium.

Quinque- and sexavalent molybdenum (the latter at acidities of pH 4 to 0.5*M* in hydrochloric acid) interact with unithiol in an acidic medium, giving yellow colorations. The colour appears rapidly when the reagent is present in a large excess. The maximum colour is developed on standing for some time. In a neutral or alkaline medium quinque- and sexavalent molybdenum do not form coloured compounds. The optimum optical density of the solutions for molybdate concentrations of  $10^{-4}$ *M* and unithiol concentrations of  $10^{-3}$ *M* is obtained at pH 1.5–2.7.

The absorption curves of the solutions obtained when mixing compounds of quinque- and sexavalent molybdenum with unithiol are shown in Fig. 1. All of the solutions were prepared in the following manner:

The necessary amount of sexa- and quinquevalent molybdenum salt (final molybdenum concentration  $10^{-4}$ *M*) was placed in a 25-ml calibrated flask, then hydrochloric acid was added until the desired pH had been attained. A ten-fold molar amount of the reagent was added and the solution made up to the volume with water. The optical densities of the solutions were determined with respect to water, after 1.5 hr in the case of compounds of molybdenum<sup>V</sup> and after 12 hr in the case of compounds of molybdenum<sup>VI</sup>. Solutions of the reagent alone absorbed practically no light in the region of long wavelengths at which the solutions of molybdenum compounds absorb.

The absorption curve (Fig. 1, curve 1) of solutions of compounds of molybdenum<sup>V</sup> exhibits a maximum at 335  $\mu$ . Absorption curves of solutions obtained by mixing

\* Translated from the Russian: *Zhur. Vsesoyuz. Khim. Obschestva im. D. I. Mendeleeva*, 1961, 6, 237.

molybdate with unithiol, also exhibit a maximum at 335  $m\mu$  (Fig. 1, curve 2). When using a hundred-fold molar amount of unithiol the absorption maximum undergoes practically no change. All of these curves have roughly the same region of maximum absorption and, consequently, characterise absorption of the same molybdenum compound.

The coincidence of the absorption curves of compounds of quinquevalent molybdenum with those of compounds obtained starting from sexavalent molybdenum

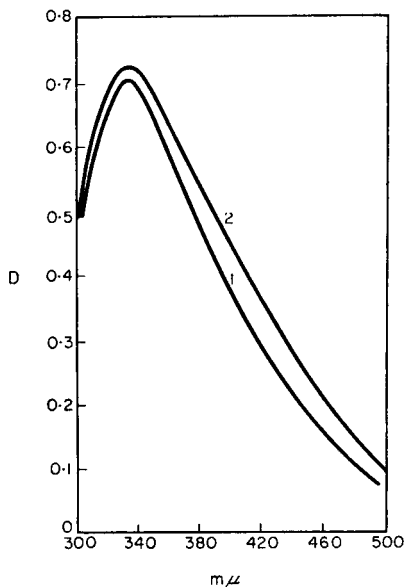


FIG. 1—Absorption curves of solutions of molybdenum<sup>VI</sup> and molybdenum<sup>V</sup> with unithiol:  
1—Molybdenum<sup>V</sup> at pH 2; 2—Molybdenum<sup>VI</sup> at pH 1.52.  
Concentration of molybdenum<sup>VI</sup> and molybdenum<sup>V</sup>  $1.03 \times 10^{-4}M$ , concentration of unithiol  $10^{-3}M$ .

leads to the conclusion that molybdenum<sup>VI</sup> is reduced by unithiol to the quinquevalent state and that the compounds of molybdenum<sup>V</sup> are stable. However, there also undoubtedly exists a compound of molybdenum<sup>VI</sup> with unithiol.

The apparent molar absorption coefficient of solutions of compounds of quinquevalent molybdenum at 335  $m\mu$  is equal to 7000 (pH 2). The optical density was measured after 1.5 hr. The apparent molar absorption coefficient of solutions obtained by mixing molybdate and unithiol was found to be equal to 7200 at 335  $m\mu$  (pH 1.5, 2 and 2.3). The optical density was measured after 12–15 hr.

The molar ratio in the interaction of molybdenum<sup>V</sup> or molybdenum<sup>VI</sup> was established by the method of isomolar series. Different volumes of a 0.00943  $M$  solution of sodium molybdate or a salt of quinquevalent molybdenum were mixed with an 0.00943  $M$  neutral unithiol solution in such a way that the sum of the molar concentrations of the two components in the final solution was always constant and equal to  $7.55 \times 10^{-4}M$ . The concentration of the unithiol solution was determined by iodometric titration. The acidity was adjusted to pH 2 by the careful addition of a calculated amount of hydrochloric acid. After dilution to the mark with water the pH was checked by means of a glass electrode. The solutions were left to stand for

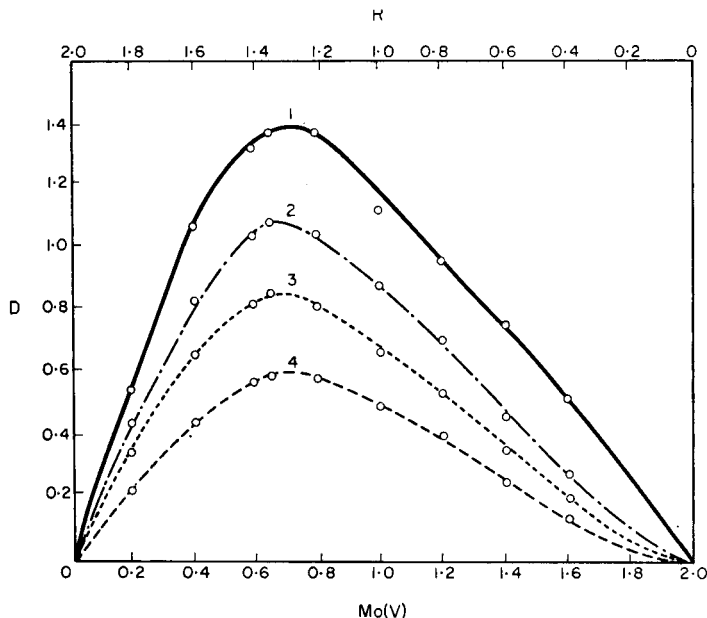


FIG. 2—Molar ratios in the interaction of unithiol with molybdenum<sup>V</sup> (pH 2):  
 1—335 mμ; 2—370 mμ; 3—430 mμ.  
 The optical density was determined 3 hr after preparation of the solutions, with reference to water.

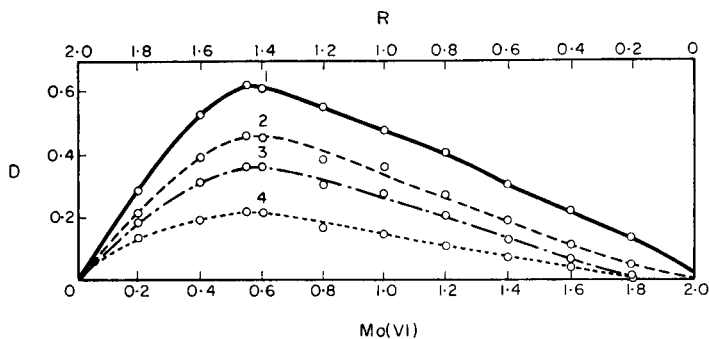
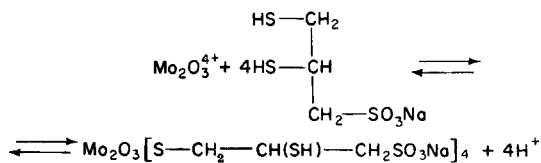


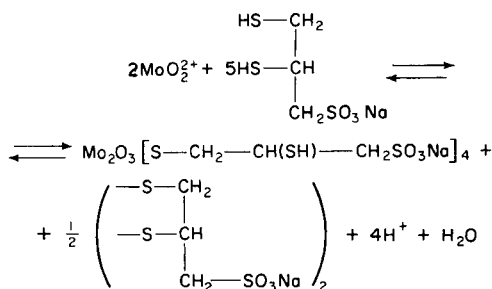
FIG. 3—Molar ratios in the interaction of unithiol with molybdenum<sup>VI</sup> (pH 2):  
 1—335 mμ; 2—370 mμ; 3—390 mμ; 4—430 mμ.  
 The optical density was measured 24 hr after preparation of the solutions, with reference to water.

3 hr in the case of molybdenum<sup>V</sup> (Fig. 2) or 24 hr in the case of molybdenum<sup>VI</sup> (Fig. 3). The optical density was measured at 335, 370, 390 and 430 mμ.

Fig. 2 shows that the maximum of the optical density for solutions of the compound of quinquevalent molybdenum and unithiol occurs at a molar ratio of 1:2. On the basis of this, the following equation can be written for the reaction:



The maximum optical density for molybdenum<sup>VI</sup> at pH 2, occurs at molar ratios of molybdenum to unithiol equal to 2:5 (Fig. 3). This confirms our conclusion that molybdenum<sup>VI</sup> is reduced to molybdenum<sup>V</sup> which also forms a coloured compound with unithiol. Evidently, 2 moles of molybdenum<sup>VI</sup> are reduced by 1 mole of unithiol to the quinquevalent state and following this 4 moles of unithiol interact with 2 moles of molybdenum<sup>V</sup>:



The reduction of sexavalent molybdenum to the quinquevalent state by unithiol was also confirmed by titration with iodine of a mixture of molybdate and unithiol solutions at pH 2. Three solutions containing known amounts of sodium molybdate and an excess of unithiol were prepared in 25-ml flasks. The solutions were prepared in the usual manner and on the next day they were titrated against a 0.01M solution of iodine in the presence of starch. At pH 2, quinquevalent molybdenum is not oxidised by iodine. A gradual weakening of the yellow colour is observed during the titration and close to the end-point the solution is completely colourless. The end-point of the titration is marked by the sharp transition to blue on addition of 1 drop of iodine, which does not disappear for several min. From the amount of iodine required to complete the titration the amount of unreacted unithiol is calculated, and the difference gives the amount of unithiol used in reducing molybdenum<sup>VI</sup>. Unithiol bound to molybdenum is not oxidised by iodine. Thus, it was established that the reduction of 2 moles of sexavalent molybdenum requires 1 mole of unithiol. The results of the iodometric titration confirm the above proposed scheme for the interaction of unithiol with sexavalent molybdenum.

Unithiol as a reagent for molybdenum has a high degree of selectivity. Chromium and mercury<sup>II</sup> do not give a coloration with unithiol in an acidic medium, mercury<sup>I</sup> gives a greyish-brown precipitate at pH 2 and lead<sup>II</sup> gives a yellow precipitate.

Thus, unithiol is undoubtedly a very promising reagent for molybdenum.

**Zusammenfassung**—Unithiol (Natrium-2,3-dimercaptopropansulfonat) bildet in saurem Medium farbige Komplexe mit Mo (V) und Mo (VI). Aus experimentellen Studien wurde geschlossen, dass Mo (VI) durch das Reagens zu Mo (V) reduziert wird. Unithiol ist ein vielversprechendes Reagens für Molybdän und zeigt einen hohen Grad von Selektivität. Chrom und Hg (II) geben keine Färbung in saurer Lösung, Hg (I) gibt einen graubraunen, Pb (II) einen gelben Niederschlag.

**Résumé**—L'unithiol (2,3-dimercapto-propane sulfonate de sodium) forme des complexes colorés avec Mo (V) et Mo (VI) en solution acide. Les auteurs discutent la nature de ces complexes et concluent que Mo (VI) est réduit en Mo (V) par ce réactif. L'unithiol est un réactif intéressant pour le molybdène; il est très sélectif. Le chrome et le mercure (II) ne donnent pas de couleurs en solution acide, le mercure (I) donne un précipité brun grisâtre, et le plomb (II) donne un précipité jaune.

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## IMPROVED ELECTRODES FOR THE CONTINUOUS MEASUREMENT OF SODIUM AND POTASSIUM

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**Summary**—A method for constructing sodium and potassium selective glass electrodes is described. The electrodes are capable of continuous, accurate, and reproducible recording of  $\Delta(\text{Na}^+)$  and  $\Delta(\text{K}^+)$ . The pair of electrodes is able to discriminate a change of less than 0.5 mequiv/l. of sodium and 0.5 mequiv/l. of potassium when used in mixed sodium and potassium solutions in the biological range of 130–150 mequiv/l. of sodium and 2–6 mequiv/l. of potassium. When used for continuous measurements a simple circuit reduces the “sodium error” inherent in the potassium electrode to less than 0.25 mequiv/l. of potassium with changes in sodium from 130 to 150 mequiv/l.

### INTRODUCTION

UNTIL the recent development of sodium and potassium sensitive glass electrodes, no reliable reproducible method for continuous measurement of these cations in blood and tissues was available. Previous methods necessitated repetitious sampling of the specimen with obvious disadvantages. Eisenman, Rudin and Casby,<sup>1</sup> elaborating on the previous work of Horovitz<sup>2</sup> and Lengyel and Blum,<sup>3</sup> developed a sodium sensitive glass designated NAS<sub>11-18</sub>.<sup>\*</sup>

They also defined the cation selectivity of an electrode glass in terms of the parameter  $k_{AB}$  of a new empirical equation:

$$E = E^\circ + \frac{RT}{F} \ln \left[ (A^+)^{1/n_{AB}} + k_{AB}^{1/n_{AB}} (B^+)^{1/n_{AB}} \right]^{n_{AB}} \cdot \dagger$$

The original NAS<sub>11-18</sub> sodium selective electrode glass described by Eisenman, Rudin and Casby had a sodium selectivity with regard to potassium of 250 to 1 at pH 7.6 ( $k_{\text{NaK}} = 4 \times 10^{-3}$ ). Electrodes constructed from this glass had limited practical value because no insulating glass had been found to which the sensitive glass could be sealed. Friedman and associates<sup>4,5</sup> constructed a capillary type of

\* The designation NAS<sub>11-18</sub> describes the final composition of the glass as determined by analysis, namely: Na<sub>2</sub>O, 11 moles%; Al<sub>2</sub>O<sub>3</sub>, 18 moles%; SiO<sub>2</sub>, 71 moles%. The NAS<sub>11-18</sub> glass we utilised was obtained from Corning Glass Works and was prepared to approximate the original composition.

†  $E$  = measured e.m.f.;  $E^\circ$  = standard potential;  $R$  = ideal gas equation constant;  $T$  = temperature (absolute);  $F$  = Faraday constant;  $(A^+)$  and  $(B^+)$  = activity of ionic species  $A^+$  and  $B^+$ ;  $n_{AB}$  and  $k_{AB}$  = empirical constants for a given glass composition and ionic pair  $A^+$  and  $B^+$ . For the cation pair sodium and potassium (above pH 6), this equation simplifies at 22° to  $E = E^\circ + 58 \log [(Na^+) + k_{\text{NaK}}(K^+)]$ , since  $n_{\text{NaK}} = 1$  for both glasses described.

For the described glasses, above pH 6, a value of  $k_{\text{NaK}} = 0.01$  indicates that 0.01 mole ( $\text{Na}^+$ ) is equivalent to 1.0 mole ( $\text{K}^+$ ) in determining electrode potential. A value of  $k_{\text{NaK}} = 10$  indicates that 0.1 mole ( $\text{K}^+$ ) is equivalent to 1.0 mole ( $\text{Na}^+$ ) in determining electrode potential. The value  $k_{\text{NaK}}$  can be determined by measuring the potentials ( $E$ ) of two solutions, one containing pure  $\text{Na}^+$  of known activity and the other pure  $\text{K}^+$  of known activity. The values for  $E$  at a known ( $\text{Na}^+$ ) and zero ( $\text{K}^+$ ), and at a known ( $\text{K}^+$ ) and zero ( $\text{Na}^+$ ) are thus determined and the two equations obtained are solved simultaneously for  $k_{\text{NaK}}$ .

sodium sensitive electrode by silvering the external surface of a capillary made of  $\text{NAS}_{11-18}$  glass, thus making a glass-to-silver electrode. This electrode had a 48 mV slope rather than the theoretical 58 mV slope for ten-fold dilutions of sodium activity at 22°. Using a special microforge, Hinke<sup>6,7</sup> was able to seal  $\text{NAS}_{11-18}$  to a high resistant insulating glass to produce microelectrodes. In this communication we describe a new method for constructing all glass sodium sensitive electrodes using  $\text{NAS}_{11-18}$ .

Potassium selective glass electrodes have been constructed from a new glass,  $\text{KAS}_{20-5}$ , developed in co-operation with Eisenman. This glass,  $\text{KAS}_{20-5}$ , has an initial or pre-melt composition of  $\text{K}_2\text{O}$ , 20 moles %;  $\text{Al}_2\text{O}_3$ , 5 moles %; and  $\text{SiO}_2$ , 75 moles %.\* It has a potassium selectivity with regard to sodium of 10 to 1 ( $k_{\text{NaK}} = 10$ ) which is close to the theoretical limit for glasses of the ternary systems: alkali metal oxide,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ .<sup>8,9</sup> This glass is superior in selectivity and physical properties to potassium selective glasses composed of  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , made available to us by Eisenman. These NAS-type potassium selective glasses have only a 3–5 to 1 selectivity factor and relatively low softening point, about 500° as compared to 800° for  $\text{KAS}_{20-5}$ .

## EXPERIMENTAL

### *Construction of the electrodes*

Both sodium and potassium selective glass electrodes can be made utilising the following newly devised compression seal technique.† To make a probe type of electrode (Fig. 1), the sodium ( $\text{NAS}_{11-18}$ ) or potassium ( $\text{KAS}_{20-5}$ ) selective glass is drawn into a capillary having a diameter of approximately 1 mm and a wall thickness of approximately 0.1 mm. One end of the capillary is sealed and the glass capillary is then cut 8–10 mm from the closed end. The open end of the capillary is then inserted into the open end of a 5-mm diameter tube of a suitable insulating glass such as modified Fischer thermometer glass, a lead-containing glass having a softening point around 600–650°. By slowly rotating the end of this insulating glass in a gas-oxygen flame, the end is brought to working temperature and allowed to flow about the  $\text{NAS}_{11-18}$  or  $\text{KAS}_{20-5}$  glass. On cooling, a compression seal is formed between the two glasses.

Formation of the capillary electrode is very similar except that a capillary of  $\text{NAS}_{11-18}$  or  $\text{KAS}_{20-5}$  glass is placed through the centre of the cross bar of the T-shaped supporting tube made of the suitable insulating glass. A compression seal is then formed at each end of this T-piece as illustrated in Fig. 1. After some experience these electrodes can be made without significant breakage.

The glass electrode is completed by filling the insulating glass stem with 0.1N sodium chloride or 0.1N potassium chloride solution, respectively, for the sodium selective and potassium selective electrodes. It is usually preferable to buffer the solution to an alkaline pH. Tris-hydroxymethyl-aminomethane is a convenient buffer. We have found it advantageous to layer a column of mineral oil or silicone fluid‡ above the filling solution. These are both good insulators (especially the latter) and also tend to reduce spurious electrical discharges by eliminating the fluid layer present on the inside surface of the insulating glass. A chlorided silver wire attached to a flexible shielded cable is used to complete the electrode.

### *Function of the electrode*

Electrodes constructed from the  $\text{NAS}_{11-18}$  and  $\text{KAS}_{20-5}$  glasses gave theoretical slopes for ten-fold dilutions of the respective sodium or potassium ion activity as tested with varying dilutions of pure sodium chloride and potassium chloride solutions (above pH 6.0) using both a calomel reference

\* Both  $\text{NAS}_{11-18}$  and  $\text{KAS}_{20-5}$  may be obtained from Dr. Martin E. Nordberg, Research and Development Division, Corning Glass Works, Corning, New York, U.S.A., as Corning Code #172 AVN and #X172 BHI, respectively.

† The glass electrode shells used in this study were constructed by Mr. Walter Angst, 18639 Blue Island Court, Roseville, Michigan, U.S.A., who devised the compression seal technique.

‡ Dow Corning 200 Silicone Fluid (#350), Dow Corning, Midland, Michigan, U.S.A.

electrode with liquid junction\* and a Ag-AgCl electrode without liquid junction.† Though Eisenman, *et al.*<sup>1</sup> report a selectivity of 250 to 1 for electrodes constructed from their original NAS<sub>11-18</sub> glass, the glass which we utilised had about one-half this selectivity (100 to 1).‡ As mentioned before, the potassium selective glass, KAS<sub>20-5</sub>, has a 10 to 1 potassium to sodium selectivity as determined in pure sodium chloride and potassium chloride solutions.

#### Compensating the potassium electrode

It was deemed advisable to have the potassium electrode indicate only changes in potassium and not the combination of potassium and sodium as dictated by a selectivity factor ( $k_{\text{NaK}}$ ) of only 10. Without some form of compensation the potassium electrode would respond to a change in sodium

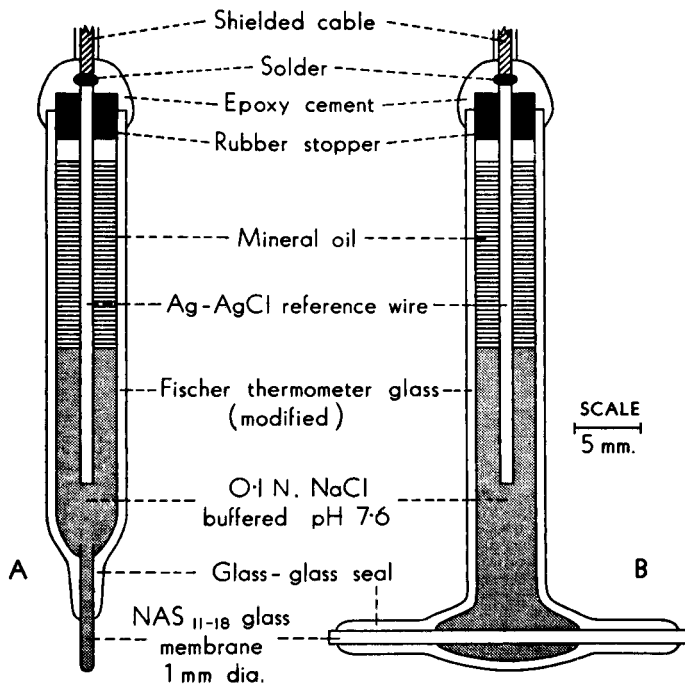


Fig. 1—Details of construction of the probe (A) and capillary (B) sodium sensitive glass electrodes. Similar potassium selective glass electrodes may be constructed by utilising KAS<sub>20-5</sub> glass as the glass membrane and 0.1N potassium chloride for the filling solution.

from 130 to 150 mequiv/l. by an alteration in potential equivalent to about 1.5 mequiv/l. of potassium. A simple electronic circuit effectively reduces this "sodium error" when utilised in the biological range of sodium and potassium.

The output of each of the electrodes was amplified by a Radiometer PHM22 pH meter coupled to a Grass Model 5 Polygraph by a calibrated coupling unit. The circuitry of the coupling unit was modified as illustrated in Fig. 2. By placing the output of the sodium and potassium selective electrodes in opposition, the former output being modified by a voltage divider, A, the effect of sodium change on the potassium selective electrode can be minimised. If the voltage divider, A, is

\* When using these electrodes with a liquid junction reference electrode in solutions of greater concentration than 0.2N sodium chloride, the values obtained for ( $\text{Na}^+$ ) are progressively higher than those obtained by calculation utilising mean activity coefficients. No such discrepancy occurs when using a Ag-AgCl reference electrode without liquid junction or in measuring ( $\text{K}^+$ ) regardless of reference electrode used. Hinke<sup>7</sup> has found a similar deviation at high concentrations of ( $\text{Na}^+$ ).

† The mean activity coefficients for the calculation of sodium chloride and potassium chloride activity were obtained from tables in H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd Edition. Reinhold Publishing Co., New York, 1958.

‡ See footnote on page 1.



properly adjusted, calculations based on the formula of Eisenman, *et al*\* reveal that, for changes in sodium concentration from 130 to 150 mequiv/l. and potassium in the range of 2–6 mequiv/l., there is a potassium error of less than 0.25 mequiv/l. at the extremes of sodium and potassium concentration.

### Testing the electrodes

In order to test the electrodes in continuously changing solutions of varying sodium and potassium concentration, a test apparatus was designed which almost completely eliminated artifacts caused by variations in flow and which was simple and easy to use. The particulars of this apparatus are described more fully elsewhere<sup>10</sup> but are schematically represented in Fig. 2. The electrodes were

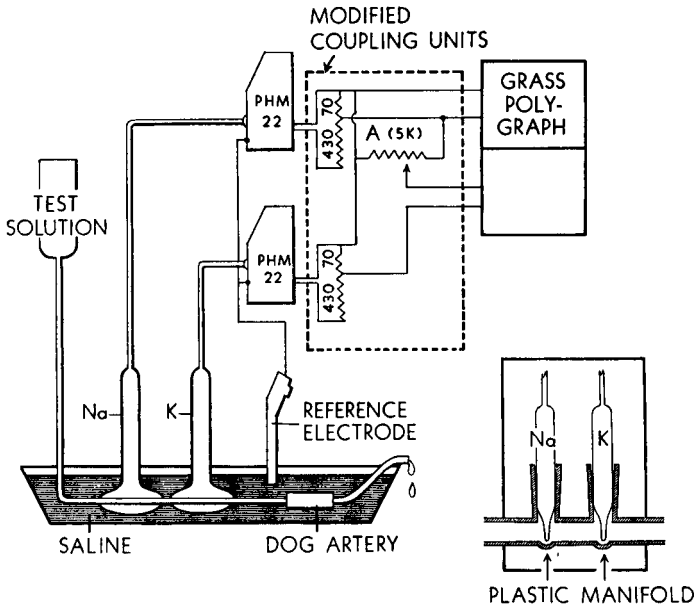


Fig. 2.—Apparatus for testing the sodium and potassium selective electrodes. Note the diagram of the modified coupling units for use with Radiometer PHM22 pH meters and Grass model 5 Polygraph with low level d.c. pre-amplifiers. Voltage divider A is adjusted as described in the text to minimise “sodium error” of the potassium electrode. The plastic manifold used for testing the probe electrodes is illustrated in the insert.

placed in series such that the test solutions ran first through the sodium electrode, then through the potassium electrode. (A second potassium electrode was used so as to be able to compare changes in potential from a potassium electrode with and without electronic compensation.) Solutions were changed by pouring the new solution into the test solution flask when the flask contained no more than a few ml of old solution. Under these circumstances the solutions could not be instantaneously changed and there was always a little admixture of old and new solution.

The voltage divider “A” (Fig. 2) was adjusted so that there was a minimal variation in recorded potential from the potassium selective electrode when solutions of 130 and 150 mequiv/l. of sodium

\* The assumption is made that the sodium electrode measures solely sodium ion activity. With a selectivity factor ( $k_{NaK}$ ) of  $1 \times 10^{-2}$  or less, this assumption should be valid for sodium and potassium concentrations in the biological range. The potential changes derived from the sodium ( $\Delta E_s$ ) and potassium ( $\Delta E_p$ ) electrodes on change from 130 to 150 mequiv/l. sodium with a constant potassium concentration in the range of 2–6 mequiv/l. are:

$$\Delta E_s = E_s^\circ + 58 \log (Na_{150}^{+}) - [E_s^\circ + 58 \log (Na_{130}^{+})]$$

$$\Delta E_p = E_p^\circ + 58 \log [(Na_{150}^{+}) + 10 K_{2-6}^{+}] - (E_p^\circ + 58 \log [(Na_{130}^{+}) + 10(K_{2-6}^{+})]).$$

Since  $E_s$  is the larger of the two potential changes, it must be reduced by a factor, A, in order for the net change of potential for the electrodes placed in opposition to be zero ( $A \Delta E_s - \Delta E_p = 0$ ). In the circuit, this alteration in  $E_s$  is accomplished by the voltage divider, A. Calculations based on these formulae were made assuming activity coefficients for sodium and potassium of 0.76 and 0.92, respectively.

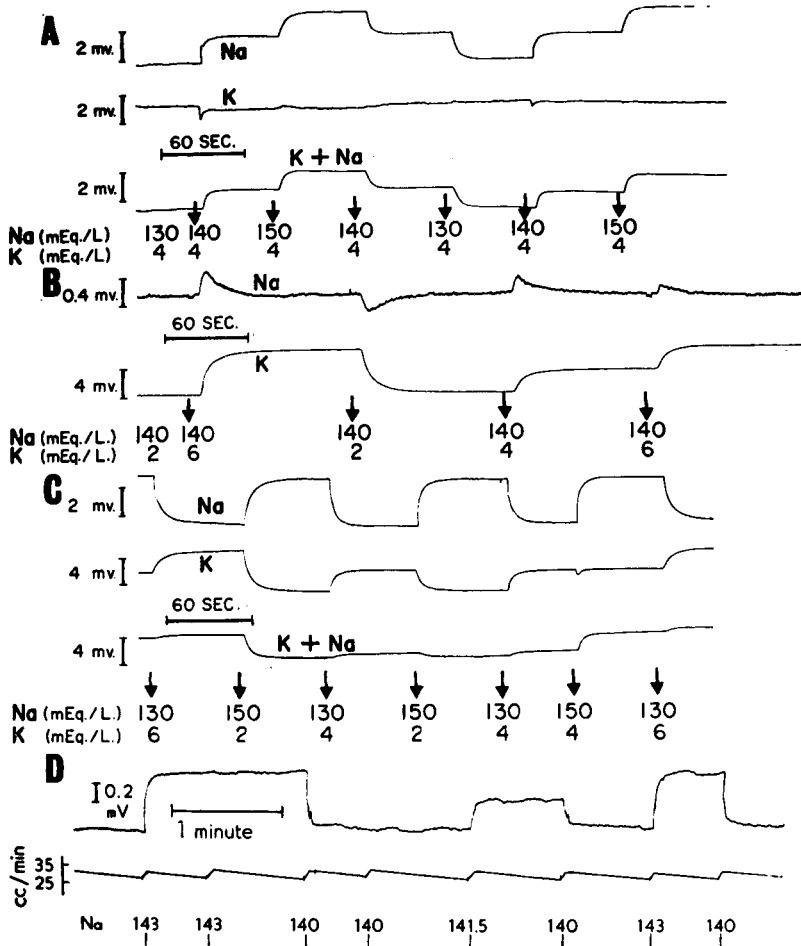


Fig. 3

A: Na, sodium electrode; K, compensated potassium electrode; K + Na, uncompensated potassium electrode. With voltage divider A (Fig. 2) adjusted, as directed in the text, change in sodium concentration from 130–150 mequiv/l. produces less than 0.2 mequiv/l. error in potassium. The transient positive and negative waves following the addition of a new solution are caused by (1) the unequal initial response time to changes in sodium of the sodium and potassium electrodes in opposition, and (2), in this study, the new solution coming into contact first with the sodium and then the potassium electrode. The sodium and uncompensated potassium electrode show similar potential changes. The delay between the pouring in of a new solution into the flask and the initial response of the electrodes is primarily determined by the time required for the new solution to traverse the rubber tubing.

B: Except for the transient positive and negative waves (see text), the sodium electrode shows almost no change when potassium is varied between 2 and 6 mequiv/l. The potassium electrode responds faithfully to the change in potassium.

C: Comparison with the response of compensated and uncompensated potassium electrodes to changes in both sodium and potassium. When recording from the uncompensated potassium electrode, a decrease in potassium tends to be nullified by a simultaneous increase in sodium, and *vice versa*.

D: Na in mequiv/l. Small changes in sodium concentration are readily detected and recorded by the sodium selective electrode. Changes in rate of flow (lower trace) at a constant sodium concentration do not significantly alter potential.

chloride each containing 4 mequiv/l. of potassium chloride, were alternatively flowed through the electrodes. Following this procedure, the effect of varying the sodium concentration in the presence of a constant potassium concentration was tested. As illustrated in Fig. 3A, variations in sodium concentration from 130 to 150 mequiv/l. of sodium at a constant potassium concentration of 4 mequiv/l. produced an error in the voltage recorded from the KAS<sub>20-5</sub> electrode corresponding to about 0.2 mequiv/l. potassium. By comparison, the potential variation recorded from the potassium selective electrode of Friedman *et al.*<sup>11</sup> (not compensated) was approximately equivalent to 4 mequiv/l. potassium for a similar change in sodium.

A similar test of the selectivity of the sodium electrode was likewise carried out by varying the potassium concentration through the biological range and keeping the sodium concentration constant at 140 mequiv/l. (Fig. 3B). Except for a transient change in potential which lasts less than 1 min, the potential derived from the sodium electrode remains practically unchanged (verifying the assumption upon which the electronic compensation of the potassium electrode is based). The transient increase and decrease in potential seen when the potassium concentration increased or decreased, respectively, was also noted by Friedman *et al.*<sup>11</sup> and appears to be a function of the sodium electrode.

The ability of the electrodes to discern small changes in concentration is good as can be seen from Fig. 3 (A, B, D) in which changes in sodium and potassium in the biological range are easily discernable. In Fig. 3D it should also be noted that changes in the rate of flow (lower trace) without changes in sodium concentration do not significantly alter the recorded potential.<sup>10</sup>

The probe electrodes were tested in a similar continuous flow system using the plastic manifold illustrated in Fig. 2 (insert). The results from the probe electrodes were essentially identical with those from the capillary electrodes.

*Acknowledgements*—The authors wish to thank Dr. George Eisenman for his many helpful suggestions during the course of this study. The work was aided by a grant from the Kresge Foundation.

**Zusammenfassung**—Eine Methode zur Konstruktion von Na- und K-empfindlichen Glaselektroden wird beschrieben. Die Elektroden sind imstande  $\Delta(\text{Na}^+)$  und  $\Delta(\text{K}^+)$  kontinuierlich, genau und reproduzierbar anzuzeigen. Das Elektrodenpaar ist imstande eine Änderung von weniger als 0.5 mVal/Liter  $\text{Na}^+$  und  $\text{K}^+$  anzuzeigen, wenn in Na-K-Lösungen im biologischen Bereich von 130–150 mVal/L Na und 2–6 mVal/L K gearbeitet wird. Wenn zu kontinuierlichen Anzeigen verwendet, ist es möglich durch einen einfachen Stromkreis den "Natriumfehler" der K-Elektrode auf weniger als 0.25 mVal/L herabzudrücken.

**Résumé**—Les auteurs décrivent une méthode de fabrication d'électrodes de verre sélectives pour Na et K. Les électrodes sont capables de donner des valeurs continues, précises et reproductibles de  $\Delta(\text{Na}^+)$  et  $\Delta(\text{K}^+)$ . La paire d'électrodes est susceptible de mettre en évidence une variation de moins de 0.5 meq./l. de Na et 0.5 meq./l. de K, quand elle est utilisée dans des mélanges de solutions de Na et de K dans le domaine biologique de 130–150 meq./l. de Na et 2–6 meq./l. de K. Pour des mesures continues, un simple circuit réduit "l'erreur de sodium" inhérente à l'électrode de K à moins de 0.25 meq./l. de K pour des variations de Na de 130 à 150 meq./l.

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## SPECTROPHOTOMETRIC STUDIES ON TECHNETIUM AND RHENIUM

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**Summary**—The behaviour of technetium and rhenium with three reagents, potassium ferrocyanide, sulphosalicylic acid, and  $\alpha$ -picolinic acid is discussed. With the first reagent, technetium and rhenium in the presence of bismuth amalgam or stannous chloride, form coloured solutions which show maximum absorption at widely different wavelengths, thus permitting the spectrophotometric determination of both elements in the presence of one another. As little as 2  $\mu$ g of technetium can be determined by this method.

Sulphosalicylic acid with pertechnetate which has been reduced with stannous chloride produces an orange-red coloration suitable for the determination of the element. The method has the advantage that the element can be determined in the presence of fairly large amounts of rhenium, manganese and molybdenum.

When pertechnetate is reduced with ascorbic acid,  $\alpha$ -picolinic acid yields a yellow-red solution which provides a sensitive method for the spectrophotometric determination of the element.

The types of complex formed with the reagents are discussed.

ALTHOUGH the element technetium was first obtained<sup>1</sup> in 1937 by neutron bombardment of a molybdenum target, until recently the amount available has been very small. This has resulted in a lack of information on the general and analytical chemistry of the element.<sup>2</sup> With the availability of higher neutron fluxes for bombardment purposes and the development of a method for the isolation of milligram quantities of the element from irradiated uranium and fission-product waste solutions,<sup>3</sup> there has been an increase in the supply of technetium and a number of papers on its analytical behaviour<sup>4,5,6</sup> have appeared.

In 1959 Jasim, Magee and Wilson,<sup>7</sup> after an ultramicro qualitative investigation, reported several new reagents for the detection of technetium and, the following year, Foreman *et al.* carried the investigation of some of these and other reagents a stage further.<sup>3</sup> The latter authors found that while many of the reagents showed possibilities there were often associated disadvantages. Ammonium thiocyanate<sup>5</sup> gave a reaction similar to iron; dimethylglyoxime<sup>7</sup> was too insensitive; thioglycollic acid and diphenylcarbazine also form coloured complexes with rhenium. In none of the cases outlined, except ammonium thiocyanate, have absorption spectra been determined, nor have colorimetric methods been developed.

In the work in this department the expanding field of research with technetium and rhenium necessitated an accurate method for the determination of these two elements, with a knowledge of the influence of associated elements such as molybdenum, ruthenium and manganese. Investigations were therefore begun to discover reagents which would provide simple, direct and sensitive methods for the colorimetric determination of both elements. The results of the spectrophotometric investigations carried out in this connection are reported in this paper.

## NEW REAGENTS FOR TECHNETIUM

1. *Potassium Ferrocyanide*

When acted on by strong reducing agents such as stannous chloride, potassium ferrocyanide in the presence of hydrochloric acid produces a brownish yellow complex with the lower valent states of technetium. This coloured complex can be extracted into amyl alcohol from acid solution. If stannous chloride is replaced by bismuth amalgam, or mercury, or concentrated hydrochloric acid, a distinctive blue colour is obtained which may also be extracted into amyl alcohol. With hydrobromic acid in place of hydrochloric acid, formation of the technetium blue occurs more slowly. With sulphuric acid a transient blue colour turns to reddish-violet and, after some time, a dark violet compound is precipitated. This reagent may be used as a quantitative test for the presence of technetium.

*Detection of technetium*

*Procedure:* Place in the cavity of a spot plate, 1 drop of the test solution and 1 drop of a freshly prepared 5% solution of potassium ferrocyanide. (If iron is present an immediate blue colour is obtained). To the solution now add 1 or 2 drops of concentrated hydrochloric acid. In the presence of technetium the characteristic blue colour slowly begins to develop. To confirm the presence of this element, add to the solution 1 drop of 10% stannous chloride in 6*M* hydrochloric acid. The blue colour of technetium is immediately changed to colourless or slightly brownish-yellow, depending on the concentration of technetium. If to this solution 1 drop of 10% hydrogen peroxide is now added, the blue colour reappears but will pass right through to colourless with excess of the peroxide.

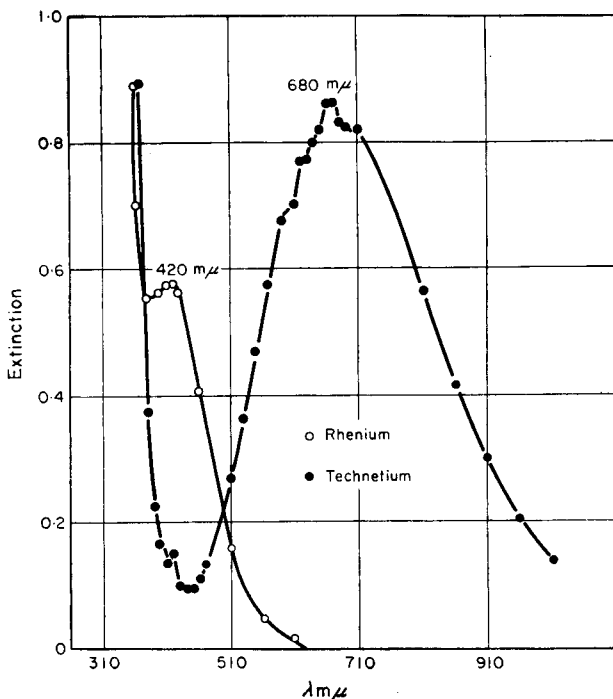


FIG. 1.—Absorption spectra of ferrocyanide complexes.

Metals which form colours or precipitates with ferrocyanide tend to obscure this test. It is, therefore, advisable to separate technetium (as pertechnetate) from these metals by a cation-exchange technique, before applying the test.

Molybdate, under similar conditions, forms a reddish-brown colour or produces a colloidal precipitate.<sup>8</sup> Perrhenate does not interfere unless stannous chloride<sup>9</sup> or bismuth amalgam is used, when red and brownish-yellow colorations, respectively are produced. With this reagent about 0.15  $\mu\text{g}$  of technetium can be detected.

*Spectrophotometric determination of technetium and rhenium with potassium ferrocyanide*

The success of potassium ferrocyanide as a qualitative reagent for technetium led to its investigation for the colorimetric determination of the element and, from preliminary studies, of rhenium also. The blue coloured complex of technetium was prepared and examined spectrophotometrically. This shows an absorption maximum at 680  $m\mu$ . As mentioned above, rhenium, under the same conditions, only produces a colour reaction with potassium ferrocyanide when reduced with bismuth amalgam in the presence of hydrochloric acid. In these circumstances a brownish-yellow complex is formed which, on examination spectrophotometrically, showed an absorption maximum at 420  $m\mu$ . The molar extinction coefficients were determined and found to be for technetium  $\sim 10,800$ , and for rhenium  $\sim 4000$ . The absorption spectra of both complexes are shown in Fig. 1. From this it will be seen that at the absorption maximum of technetium (680  $m\mu$ ) there is zero contribution from rhenium (see Note below), so that technetium may be determined in the presence of rhenium without prior separation. Furthermore, the contribution of technetium to the extinction of rhenium at 420  $m\mu$  is small, and by preparing a correction curve of technetium concentration versus extinction at 420  $m\mu$ , it is possible to determine rhenium in the presence of technetium without prior separation. The influence of rhenium on technetium at 680  $m\mu$ , and that of technetium on rhenium at 420  $m\mu$  for different concentrations, are shown in Fig. 2 and Fig. 3.

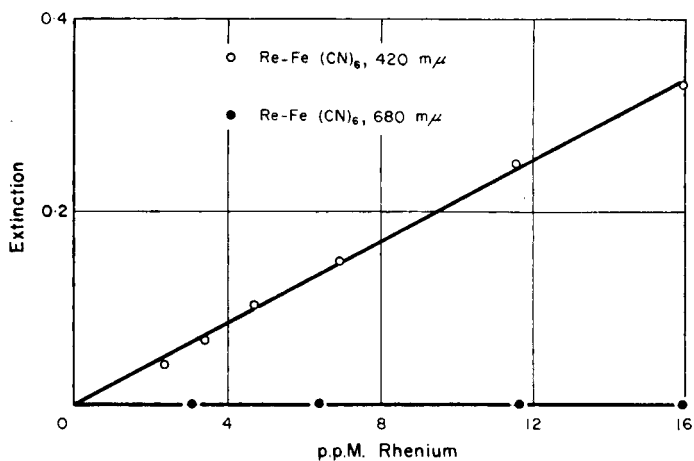


FIG. 2.—Influence of rhenium on technetium extinction.

## EXPERIMENTAL

### *Apparatus and reagents*

For the spectrophotometric investigations a Unicam spectrophotometer, SP600, was used with 1.000-cm silica cells.

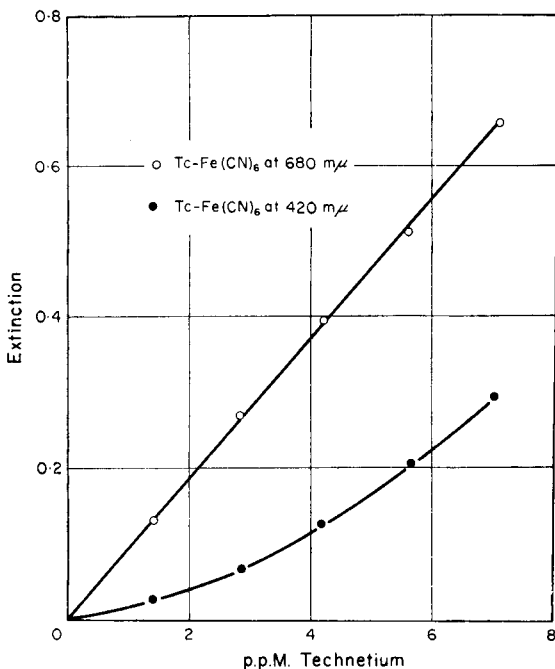


FIG. 3.—Influence of technetium on rhenium extinction.

*Caesium pertechnetate*: A standard aqueous solution containing 52  $\mu\text{g/ml}$  and 4.5M in hydrochloric acid.

*Potassium perrhenate*: A standard aqueous solution containing 116  $\mu\text{g/ml}$  of the "Specpure" compound in 4.5M hydrochloric acid.

*Potassium ferrocyanide*: A 5% aqueous solution of the AnalaR-grade reagent.

*Bismuth amalgam*<sup>10</sup>: Dissolve 3 g of granulated bismuth in 100 g of mercury in the presence of dilute sulphuric acid. Warm on a water bath and decant the amalgam.

#### Procedure

Place in a 30 ml separatory funnel 2 ml of 5.7M hydrochloric acid, and add to it a suitable aliquot of the test solution containing standard pertechnetate and perrhenate solutions. Add 2 ml of bismuth amalgam. It is advisable to wash the amalgam before use by shaking with several portions of 4.5M hydrochloric acid. Add 0.5 ml of 5% potassium ferrocyanide solution. Stopper and shake for 15 sec. Remove the amalgam, and allow the reduced solution to stand for 20 min in the dark.

Measure the extinction of technetium at 680  $m\mu$  and that of rhenium at 420  $m\mu$ . From a standard curve prepared from known amounts of the two elements, calculate the concentration of technetium and rhenium in the solution. It is desirable to correct by a blank carried through the same operations.

*Note*: If the concentration of rhenium is high, it can show a reading at the absorption maximum for technetium (680  $m\mu$ ). In these circumstances the most effective procedure is to determine technetium without interference from rhenium by the Procedure 2.

#### Procedure 2

In a 5-ml volumetric flask place an aliquot of the test solution and add to it sufficient concentrated hydrochloric acid to make it about 4-6M. Add 0.5 ml of 5% potassium ferrocyanide, mix well and set aside for 30 min in the dark. Carry a blank through the same procedure.

Measure the extinction of the technetium blue at 680  $m\mu$  in a 1.000-cm cell. From a calibration curve determine the amount of technetium present. There is no interference from rhenium.

## DISCUSSION

An attempt was made to elucidate the type of compound formed between the reduced perrhenate and potassium ferrocyanide. Attention was focussed on rhenium, to conserve technetium which is still, as far as we are concerned, a rare metal. The colour formed between perrhenate, stannous chloride and ferrocyanide is stable, can be extracted into solvents such as amyl alcohol, butyl alcohol and higher ketones. Its formation is strictly dependent on the acid concentration—at low acid concentration it is pale yellow, while at higher concentrations the yellow becomes pinker in appearance. The complex is readily sorbed on an anion-exchanger, suggesting that it is an anionic complex. Several experiments were carried out to find the molar ratio of rhenium to ferrocyanide. This was done by adding, in one experiment, an excess of rhenium to a known volume of ferrocyanide solution of the same concentration. In the second experiment an excess of ferrocyanide was added to the same quantity of rhenium as in the first experiment. In both experiments, the colour was developed in the usual way and the extinctions were measured at 470  $m\mu$ , where this complex showed an absorption maximum. The ratio of the absorbancies to the ratio of rhenium and ferrocyanide was found to be 3 : 1. This suggests that these two components form a type of double salt co-ordinated with hydrochloric acid molecules. With different acid concentrations the absorption maximum shifts along the wavelength axis.

If bismuth amalgam is used in place of stannous chloride, the complex produced has an absorption maximum at 420  $m\mu$ . This complex is also sorbed by an anion-exchange resin, and the colour is dependent on the acid concentration and ferrocyanide concentration. The optimum molarity of the acid is between 3 and 5, and the optimum potassium ferrocyanide concentration is  $\sim 5\%$ . The colour is time-dependent, full development occurring in 20–25 min.

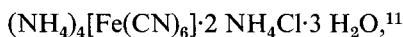
From the information obtained about the complexes produced by stannous chloride and bismuth amalgam, it is suggested that with the former reagent in high acid concentration the perrhenate is first reduced to rhenium<sup>IV</sup> and then forms a complex of the following type:



The reduction with bismuth amalgam is not so powerful, so that rhenium<sup>V</sup> is produced which reacts with ferrocyanide to give a complex of the type:—



These may be compared with double salts of the type



and addition compounds with sulphuric acid  $H_4[Fe(CN)_6] \cdot xH_2SO_4$  where  $x = 5$  or 7.

As already mentioned, technetium with bismuth amalgam and ferrocyanide forms a blue complex. This is anionic in character, as shown by ion-exchange studies, and is probably similar in structure to the rhenium complex, the technetium first being reduced to the Tc<sup>V</sup> or Tc<sup>VI</sup> state with bismuth amalgam. (Technetium is more easily reduced than rhenium.) With stannous chloride in place of bismuth amalgam, technetium yields a yellowish-brown complex.



## 2. Sulphosalicylic Acid

Pertechnetate yields no colour with this reagent alone, but when first reduced with stannous chloride in an acid medium, a red colour is produced. The colour is stable for several days. Iron<sup>III</sup>, rhenium, manganese and molybdate do not interfere with the test.

### *Spectrophotometric determination of technetium with sulphosalicylic acid*

The complex formed between technetium and sulphosalicylic acid was examined spectrophotometrically. Fig. 4 shows the absorption spectrum of the complex. A

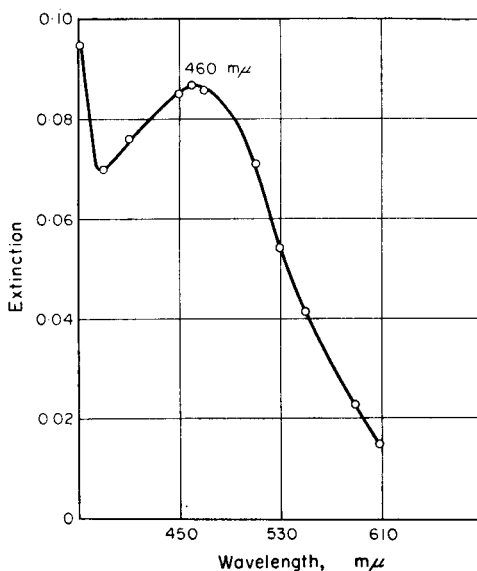


FIG. 4.—Absorption spectrum of technetium sulphosalicylate.

maximum occurs at wavelength 460 mμ. At this wavelength there is little or no interference from manganese, rhenium, molybdenum, thorium, iron or a number of other elements. It is possible to determine several μg of technetium in the presence of 3.0 mg of manganese, 0.2 mg of rhenium and 0.3 mg of molybdenum.

## EXPERIMENTAL

### *Reagents*

*Stannous chloride solution:* Dissolve 20 g of AnalaR stannous chloride dihydrate in sufficient 6M hydrochloric acid to dissolve the solid on warming. Dilute to 100 ml with 6M hydrochloric acid.

*Sulphosalicylic acid:* Dissolve 10 g of the acid in distilled water and dilute to 100 ml.

*Buffer solution:* Mix 97 ml of 0.2M hydrochloric acid and 50 ml of 0.2M potassium chloride (AnalaR) giving a solution of pH 1. Dilute to 200 ml with distilled water.

### *Procedure*

To a 5-ml volumetric flask add 2 ml of buffer solution and an aliquot of pertechnetate solution. Add 0.5 ml of the sulphosalicylic acid reagent and 0.1 ml of the stannous chloride reagent. Mix thoroughly and dilute to the mark with buffer solution.

Measure the extinction of the orange-red solution after 30 min at 470 mμ in a 1.000-cm cell. From a standard curve calculate the amount of technetium present.

## DISCUSSION

The complex is not extracted from aqueous solution by chloroform, amyl alcohol, toluene, or ether. This suggests that the technetium ion is co-ordinated with the hydroxyl oxygen and the carboxyl group, leaving the sulphonate group free.

The technetium is probably first reduced to the  $Tc^V$  state. The complex is moderately sensitive to acid concentration. The intensity decreases with increasing acid strength, probably because of a tendency of the complex to decompose at higher acidity. In the buffered solution the colour is, however, stable and maximum intensity occurs when the acidity is about 0.3M.

3.  $\alpha$ -Picolinic Acid

$\alpha$ -Picolinic acid (pyridine-2-carboxylic acid), when added to pertechnetate, produces no colour, but on the addition of stannous chloride or ascorbic acid a red colour appears slowly. The reaction appears to be highly selective for technetium.

*Spectrophotometric determination of technetium with  $\alpha$ -picolinic acid*

The complex formed between technetium and the reagent was examined spectrophotometrically. Fig. 5 shows the absorption spectra, with a maximum at 470-480  $m\mu$

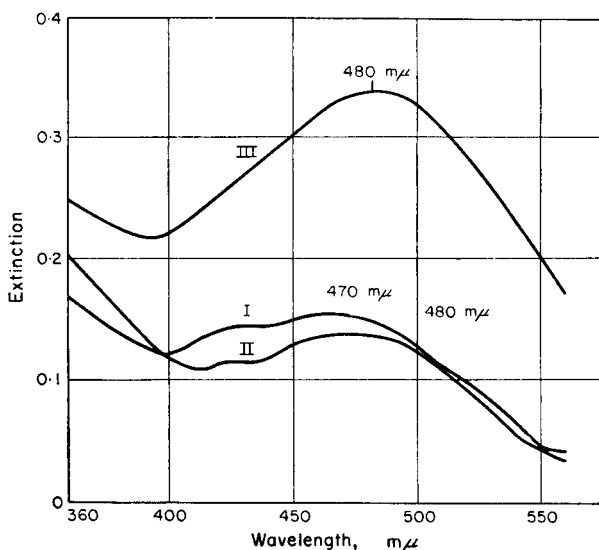


FIG. 5.—Absorption spectrum of technetium  $\alpha$ -picolinate. I—After 20 min, 4.3 ppm of technetium: II—After 20 hr, 2.4 ppm of technetium: III—After 20 hr, 5.7 ppm of technetium.

At this wavelength there is interference from no element except molybdenum.

## EXPERIMENTAL

*Reagents*

*$\alpha$ -Picolinic acid:* A 10% aqueous solution.

*Ascorbic acid:* A 10% aqueous solution.

*Buffer solution:* Prepare a KCl/HCl buffer solution of pH 2.0 from 10.6 ml of 0.2M HCl and 50 ml of 0.2M KCl, and dilute to 200 ml.

*Procedure*

In a 10-ml volumetric flask, place an aliquot of pertechnetate together with 5 ml of buffer solution, 0.5 ml of picolinic acid solution and 1 ml of ascorbic acid. Mix the contents well and place on a water bath maintained at 80° for 20 min. Cool, and dilute to the mark with buffer solution.

Measure the extinction of the yellow-red solution at 480 m $\mu$  against a blank treated in the same way. From a standard curve calculate the amount of technetium present.

## DISCUSSION

If ascorbic acid is used as the reductant the solution shows a slightly more reddish tinge than when stannous chloride is used as reductant. The former shows a higher molar extinction coefficient of the order of 4400. The technetium is probably reduced to the 4- or 5-valent state by the reductants. Both species are partially extracted from aqueous solution by chloroform.

**Zusammenfassung**—Das Verhalten von Technetium und Rhenium gegenüber drei Reagentien: Kaliumferrocyanid, Sulfosalizylsäure und  $\alpha$ -Picolinsäure wird diskutiert. Mit dem ersten Reagens formen Technetium und Rhenium in Gegenwart von Wismutamalgam oder Stannochlorid gefärbte Komponenten mit Absorptionsmaxima bei stark verschiedenen Wellenlängen. Dies gestattet die Bestimmung beider Elemente in einer Lösung. Bis hinab zu 2  $\mu$ g Technetium können derart bestimmt werden.

Pertechnat, nach Reduktion mit Stannochlorid, erzeugt mit Sulfosalizylsäure eine orangefarbene Färbung, was zur Bestimmung ausgewertet werden kann. Der Vorteil der Methode liegt darin, dass das Element in Gegenwart von ziemlich grossen Mengen von Rhenium, Mangan und Molybdän bestimmt werden kann.

Nach Reduktion mit Ascorbinsäure gibt Pertechnat mit  $\alpha$ -Picolinsäure eine rötlich-gelbe Färbung, die zur empfindlichen photometrischen Bestimmung herangezogen werden kann.

Die Typen der gebildeten Komplexe werden diskutiert.

**Résumé**—Les auteurs discutent du comportement du technétium et du rhénium en présence de trois réactifs: ferrocyanure de potassium, acide sulfosalicylique et acide  $\alpha$  picolinique. Avec le premier réactif, le technétium et le rhénium, en présence d'amalgame de bismuth ou de chlorure stanneux, forment des solutions colorées qui ont une absorption maximale à des longueurs d'onde très différentes; cela permet le dosage spectrophotométrique des deux éléments l'un en présence de l'autre. On peut doser par cette méthode une quantité aussi faible que 2  $\mu$ g de technétium.

L'acide sulfosalicylique donne avec le pertechnétate, qui a été réduit par le chlorure stanneux, une coloration rouge-orangé convenant pour le dosage de cet élément.

La méthode présente l'avantage suivant: l'élément peut être dosé en présence de très grandes quantités de rhénium, manganèse et molybdène.

Avec le pertechnétate réduit par l'acide ascorbique, l'acide  $\alpha$  picolinique donne une solution jaune-rouge qui fournit une méthode très sensible de dosage spectro-photométrique de l'élément.

Les auteurs discutent le type de complexes formé avec ces réactifs.

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## THE DETERMINATION OF INTERSTITIAL ELEMENTS IN THE REFRACTORY METALS

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**Summary**—A review is presented of current and potentially applicable methods for the determination of oxygen, nitrogen, hydrogen and carbon in molybdenum, tungsten, niobium, and tantalum.

### INTRODUCTION

MOST of the material which follows was summarised from the files of the Defence Metals Information Centre and the open literature as of April, 1961. This brings up to-date an earlier DMIC review.<sup>1</sup>

The determination of the interstitials, oxygen, hydrogen, nitrogen and carbon, in the refractory metals, molybdenum, tungsten, niobium and tantalum, are most conveniently discussed when considered as to the interstitial element sought. This discussion follows such a system.

### OXYGEN METHODS

A number of methods have been considered in connection with the determination of oxygen in molybdenum.<sup>2</sup> Where feasible for molybdenum, they can usually be applied with some modification to the other refractory metals. A number of possible methods are reviewed below.

#### *Neutron activation*

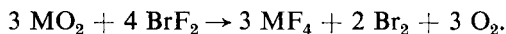
*Thermal neutrons.* In this method, the sample is irradiated with neutrons in a pile and the radiation emanating from the sample after irradiation is studied by suitable radiation counters. Unfortunately, oxygen has an almost zero cross-section to thermal neutrons. Therefore, the method is not suitable for oxygen, the most potent impurity in molybdenum. The method seems to offer some promise for the determination of hydrogen in metals and is excellent for detecting small amounts of rare earths.

*Fast neutrons.* Fast (14 MeV) neutrons have been used successfully for determination of oxygen in beryllium<sup>3,4</sup> and the method may prove satisfactory for molybdenum and the other refractory metals. The reaction produces protons and radioactive <sup>16</sup>N according to the equation, <sup>16</sup>O(n,p)<sup>16</sup>N. The <sup>16</sup>N decays with a half life of 7.4 sec by emission of  $\beta$ -rays with a maximum energy of 10 MeV (used for the oxygen analysis) along with high energy  $\gamma$ -rays.

#### *Fluorination*

This method has been applied to a number of metal oxides, salts<sup>5</sup> and titanium.<sup>6</sup>

In analysis, the sample is dissolved in bromine trifluoride by heating at 75° for 2 hr in a static vacuum. The reagent converts combined oxygen to free molecular oxygen according to the following reaction:



Oxygen is determined from pressure measurements after freezing out the other products and cooling the reaction tube to liquid-nitrogen temperature. In the case of some metals, nitrogen also may be released quantitatively. Oxygen is then determined from the drop in pressure observed when the oxygen-nitrogen mixture is passed over copper turnings at 400°. The residual pressure is due to nitrogen.

The method presumably can be applied to the determination of oxygen in niobium, tantalum and tungsten since no interference was found in the analysis of the oxides.<sup>5</sup> However, molybdenum oxide yielded a stable intermediate, MoOF<sub>4</sub>, which is retained in the reaction medium.<sup>6</sup>

#### *Other halogenation*

Several other halogenation methods have been used for other metals and may prove workable for the refractory metals. The better known ones involve volatilisation of the metal by gaseous bromine, chlorine,<sup>7</sup> or hydrogen chloride<sup>8</sup> to leave oxygen as an oxide residue. The residue is weighed and the percentage of oxide in the residue estimated. Corrections are made for contaminants in the residue and for oxygen loss by reduction of oxide by the carbon content of the metal. The latter reaction was used as the basis of a modified method; that is, the bromination-carbon reduction method<sup>9,10</sup> in which all of the oxygen is converted to carbon monoxide and estimated as in the vacuum-fusion method. This method has been successfully used by several analysts. Bromination methods are not applicable to niobium and tantalum because volatile oxybromides are formed during the reaction. This prevents isolation of oxygen as a measurable species.

#### *Fractography*

Metallographic methods on polished sections of molybdenum are unsuitable because the amount of oxygen as inclusions appears to remain the same over rather wide composition ranges. Examination of a fractured surface is much more rewarding. Somewhere in the range 0.001 to 0.005% of oxygen, the oxide changes from discrete particles to a continuous sheet at the grain boundaries. Fractographs of specimens can be compared and their mechanical and other behaviour related to the impurity content without necessarily knowing the absolute amount of impurity in the samples. The fraction of the grain surface area covered with oxide is proportional to the oxygen content. This technique can be refined by using standards evaluated by primary analytical methods. Unfortunately, the method is not a quantitative one and in addition suffers several disadvantages. It is most useful for coarse-grained arc-cast molybdenum ingots. The grain size of most wrought molybdenum is too fine for fractographic methods to be most effective. Also the fracture obtained in samples of low oxygen content is nearly always transgranular so that it is hard to extend the fractographic method to very low oxygen contents. The method might be of some use for tungsten but would be of no practical value for niobium and tantalum which have higher oxygen solid solubilities.

#### *Mass spectrometry*

Mass spectrometry is not an independent method but an adjunct to a gas extraction method such as vacuum fusion.

The sensitivity of the mass spectrometer is such that  $10^9$  molecules per sec gives unit deflection. Unfortunately, the  $H_2O$ ,  $CO$ ,  $CO_2$  and  $N_2$  in which we are interested are the very gases normally present as residual gases in all vacuum systems, including that of the mass spectrometer. Hence, these gases are always background gases in the spectrometer, which reduces its sensitivity to them. Even so, the precision of  $\pm 0.0001\%$  on a 1-gram sample, which is believed desirable in analysing molybdenum, is 10 to 100 times the minimum sensitivity of the spectrometer. The advantage of using the spectrometer to analyse the gases evolved in vacuum fusion is that much smaller samples can be used and the identification of the gases is positive. The modern mass spectrometer can distinguish between carbon monoxide and nitrogen without difficulty. It should be emphasised that this method (mass spectrometer analysis of gases evolved by vacuum fusion) is *not* the isotopic dilution method which appears to involve the difficulties of both vacuum fusion and mass spectrometry.

### *Solid mass spectrometry*

Solid mass spectrometry is a relatively new development which is capable of measuring very low concentrations. For example, rare earth metal impurities in graphite can be measured at levels of 0.01 atomic part per million. Unfortunately vacuum characteristics limit the detection of carbon, oxygen and nitrogen below 100 to 200 atomic parts per million. There is some possibility that hydrogen could be detected at lower levels.

### *Isotopic dilution*

The method of isotopic dilution<sup>11</sup> is based on the equilibration of the sample's content of normal (99.757%  $^{16}O$ ) oxygen with a known amount of oxygen enriched in  $^{18}O$  as for example from a master alloy. Assuming that the extraction of oxygen-containing gas from the equilibrated complex is not affected by mass difference, only a fraction of the total gas need be removed to arrive at an assay of the total oxygen content. The extracted gas is analysed on a mass spectrograph to determine the degree of dilution of the  $^{18}O$  during the equilibration. The original oxygen content of the metal sample can then be computed. The effect of  $^{17}O$  enrichment does not seriously complicate the procedure. The method should be workable for niobium and tantalum at intermediate and high oxygen contents. Dilution and equilibration of oxygen in metals such as molybdenum and tungsten with low oxygen solubilities and containing precipitated oxides in the grain boundaries would seem to present insurmountable difficulties. Where applicable, the method is much more time-consuming and complicated than the vacuum-fusion method and certainly no more reliable.

### *Emission spectrometry*

Emission spectrometry is a recent method now developed to a stage permitting consideration for application to most metals. To-date, it has been applied to niobium and tantalum.<sup>12,13,14</sup> A 100-mg specimen pressed into intimate contact with a small amount of platinum is arced in a graphite anode. Arcing is done in a chamber which is previously evacuated and filled with pure argon. The oxygen content of the specimen is evolved as carbon monoxide which is dissociated to atomic carbon and

oxygen. The lowest oxygen values obtained to date appear to be 20 ppm. Technique-wise the method is much simpler and faster than vacuum fusion. Potentially 70 to 80 specimens can be analysed in a day using a direct reader recording device.

### *Vacuum fusion*

The familiar vacuum-fusion method<sup>2</sup> is the referee method for the determination of oxygen and hydrogen in most metals. It involves melting a metal sample in a graphite crucible in vacuum and collecting, measuring, and analysing the evolved gases. The extraction is usually made at 1600° or higher and the gas is principally carbon monoxide, hydrogen and nitrogen. Results are usually reported as percentages of oxygen, hydrogen, and nitrogen based on the weight of the metal sample.

*Bath techniques.* Individual metals require modification of the basic method. The refractory metals have melting points exceeding feasible operating temperatures for the vacuum-fusion furnace. To overcome this, specimens are sometimes dissolved in a degassed bath of another metal contained in the vacuum-fusion crucible. Iron,<sup>15</sup> iron-tin,<sup>16</sup> platinum,<sup>17</sup> platinum-tin,<sup>18</sup> or other metals are used. Extraction temperatures with a platinum bath may be as high as 2000°. It is essential that the bath dissolve carbon to reduce oxides and not form higher melting point intermetallic compounds at concentrations up to at least 10 weight % of the specimen metal.

*Flux techniques.* Sometimes refractory metals are melted by dropping the specimen and the fluxing metal simultaneously into the graphite crucible. The flux is usually tin or platinum and preferably is in intimate contact with the specimen. The specimen may be imbedded in the flux by pressing or may be wrapped in the flux. In the case of titanium,<sup>19</sup> the specimen and tin flux are dropped onto a bed of graphite chips contained in the crucible. This permits dispersion of the specimen in thin layers in intimate contact with graphite and aids the reduction of the oxygen of the titanium. The metal soon solidifies because of evaporation of the tin and the gradual conversion of the titanium to the high-melting carbide. The last gas removed is often released by diffusion-extraction from the solid.

The platinum flux<sup>20</sup> technique requires no graphite chips and has the advantage that the residue remains molten throughout the gas extraction.

*Gas separation and identification.* The gas extracted in the vacuum-fusion method is analysed in a number of ways. Low pressure analysis through absorption by dry chemicals or through fractional freezing are most commonly used. The gas also can be analysed by mass spectrograph, wet chemical (Orsat) apparatus, gas chromatograph, and other means.

### *Inert-gas fusion*

In the inert-gas fusion method, an inert gas is purified and passed over an inductively heated graphite crucible (in a reaction tube) containing the sample. Oxides in the sample are reduced to carbon monoxide and are carried by the inert gas through an oxidising agent. The carbon dioxide thus formed is then measured in a conductivity cell where the change in resistance is read. This change is translated to % of oxygen by means of a graph prepared from results on primary standards. At oxygen levels below 100 ppm this method has limitations. Estimates of sensitivity range from 5 to 10 ppm oxygen on a 1-g sample. The measurement is indirect and requires repeated calibration. There is some indication of trouble caused by variation of the oxygen

content of the platinum flux used with low oxygen niobium. This difficulty may be overcome by using a bath technique. No measurement of nitrogen or hydrogen is obtained by this method. A commercial apparatus for inert-gas fusion is sold by LECO, Laboratory Equipment Corporation, St. Joseph, Michigan.

### *Practical Application of Oxygen Methods*

#### *Molybdenum*

A vacuum-fusion iron bath technique<sup>2,15</sup> for oxygen in molybdenum was developed in the course of a co-operative study of this analysis through the Office of Naval Research Advisory Committee on Molybdenum. Work was done through a sub-committee on the Analysis for Gases in Molybdenum. Recommended details of the technique were that:

- (1) Graphite parts (crucibles, *etc.*) be halogen purified.
- (2) Extraction be carried out for a minimum of 20 min.
- (3) Extraction temperature be 1600 to 1650° to avoid the solidification of the bath experienced at higher temperatures.
- (4) Molybdenum content of the bath be limited to 30 weight %.

On molybdenum containing about 60 ppm of oxygen, the reproducibility within several individual laboratories was to  $\pm 2$  ppm. However, laboratory averages ranged from about 40 ppm to 70 ppm. Recovery seemed to increase as the operator gained experience with the technique. Work by the same group with molybdenum containing about 10 ppm of oxygen showed greater relative variation. Need for further study at this level was indicated.

More recently the work on molybdenum was continued under the guidance of the Task Group on Oxygen in Molybdenum, Division M, Committee E-3, ASTM. The most recent meeting of the Task Group was held at Westinghouse Research Laboratories, November 19 and 20, 1959. Results obtained with an iron-tin bath were discussed. The analytical specimens were of the same high- and low-oxygen molybdenum studied with the iron bath. This time the results for the high-oxygen molybdenum ranged from about 60 to 80 ppm oxygen and averaged close to 70 ppm. The statistical significance of the data is presently being determined. The higher average is probably caused by the greater experience of the analysts rather than to any slight difference in analytical method entailed with the addition of tin to the bath. The low-oxygen molybdenum gave laboratory averages from 3 to 11 ppm and averaged about 8 ppm. It was concluded that results at the 60 or 70 ppm level are reasonably satisfactory but better reproducibility is needed below the 10 ppm level. It was agreed to prepare a description of the iron-tin method to submit to the ASTM for consideration. The outline of the method is as follows. Use a 2-g sample cleaned by filing. Degas the graphite crucible at 2350°. About 2 hr is required. Reduce temperature to 1650° and take a 30-min blank, then drop 10 g of iron and 0.3 g of tin to form a bath. Degas for a minimum time to obtain a satisfactory blank. Drop sample and extract gas for 30 min. Drop 0.3 g of tin between samples. If tin has a measurable oxygen content, degas before dropping the molybdenum sample. Periodically drop additional iron between samples to keep the molybdenum concentration of the melt below 30 weight %. Analyse the extracted gas.

One of the laboratories (Bureau of Mines, Boulder City) of the Task Group used a bath of 80 platinum-20 tin and a bath temperature of 1650°. This takes advantage



of the eutectic in the platinum-tin system (72 Pt: 28 Sn, 1080°). The bath is quite fluid and the tin content is said to be quite stable and not readily lost by vaporisation. The platinum is degassed above its melting point and the temperature dropped to 1650° before adding tin. The Task Force proposes a future investigation of this technique.

Earlier, a platinum bath at 1850° was used by Wilkins.<sup>2</sup> Iron was added to the platinum bath before the introduction of molybdenum samples.

A diffusion-extraction technique was used by Fagel, Witbeck and Smith.<sup>21</sup> In this method the solid sample is heated in a degassed graphite crucible in a vacuum-fusion apparatus. Oxygen diffuses to the surface of the specimen and is released as carbon monoxide. Nitrogen and hydrogen are also evolved. The extracted gases are analysed as in the vacuum-fusion method.

The LECO conductimetric oxygen analyser (inert gas fusion apparatus) is reported by the company to have been used to analyse for oxygen in molybdenum, tungsten, tantalum and niobium.

Several other papers<sup>22,23,24,25</sup> on the determination of oxygen in molybdenum have appeared. Most deal with versions of the iron bath technique which differ only in detail with descriptions already given.

### *Tungsten*

The methods for the analysis of molybdenum are often used without modification for the analysis of tungsten. The principal methods reported are the iron bath,<sup>21,23</sup> diffusion extraction<sup>21</sup> and inert gas fusion.<sup>26</sup> The concentration of tungsten should not exceed 30 weight % in the iron bath.<sup>24</sup> The volume of extracted gases is the same at 1650° as at 1800°, but the 1650° results are more reproducible.<sup>23</sup>

The National Research Corporation<sup>27</sup> has reported the use of a platinum bath at 1850° for determining oxygen in tungsten. Samples weigh about 0.5 g and several are run in a 25 to 30 g platinum bath.

### *Niobium*

Oxygen in niobium has been determined by the emission spectrographic method. Success was achieved by fluxing the sample with platinum.<sup>12,13</sup>

A diffusion extraction method for niobium was developed by Hansen and Mallett.<sup>28</sup> Oxygen as carbon monoxide is quantitatively removed from a 0.3-g sample at 2000° in vacuum in 30 min. The sensitivity of the method was about 20 ppm for this size of sample.

The LECO inert gas fusion method<sup>26</sup> has also been used for this analysis. A sensitivity of 2 ppm for a 1-g sample is claimed. The temperature of extraction is about 2200°.

The vacuum-fusion method for niobium has been described by at least two investigators.<sup>23,29</sup> The conditions specified by Harris<sup>29</sup> include the use of 0.25-g samples melted in a platinum bath (weight not specified) at 1950°. Complete gas extraction required only 10 min. A probable sensitivity of 5 ppm is reported.

Mikhailova *et al.*,<sup>23</sup> used the same vacuum-fusion procedure as for molybdenum and tungsten. Extraction was made with an iron bath at 1650°.

Benner<sup>30</sup> lists the use at 1850° of both the iron bath and the platinum bath for the analysis of niobium.

In June, 1959, the Oxygen Sub-Group, Niobium Task Group, Division M, Committee E-3, ASTM, met to discuss the results of an interlaboratory round-robin study<sup>31</sup> of the analysis of niobium for oxygen. The test specimens were prepared from niobium ingots, hot rolled at 1200° to 5/8 inch, round surface ground to remove oxide and cold forged to 1/4 inch round. It was concluded that a method worthy of write-up for consideration by ASTM had been achieved. Results based on an average value from each of nine laboratories, seven by vacuum fusion and two by inert gas fusion, averaged 299 ppm of oxygen with a standard deviation of 17 ppm; the coefficient of variation was 5.8%. In vacuum fusion most of the laboratories used platinum either as a flux dropped with the sample or as a bath or a combination of flux and bath. Extraction temperatures ranged from 1790 to 1950° and extraction times from 10 to 50 min. It appears that 1900° for 15 min could be recommended. It was generally agreed that the niobium content of the bath should not exceed 20 weight %.

One laboratory used a nickel bath at 1800° with a 10-min extraction time. Again the niobium concentration was limited to 20 weight %.

The Task Group members using the inert gas-fusion method extracted the gas in 6 to 10 min at 2200°. A platinum bath and iron bath plus a 1:1 platinum flux was used.

### *Tantalum*

Direct references to methods of determining oxygen in tantalum are fewer than for the other refractory metals. Good results by the inert gas fusion,<sup>26</sup> the diffusion extraction<sup>21</sup> and emission spectrographic<sup>13</sup> methods are reported.

Beach and Guldner<sup>16</sup> analyse tantalum by the same vacuum-fusion iron-tin bath technique used by them for molybdenum. A 2-g sample is dropped into a bath containing initially 6 g of iron and 0.3 g of tin. Intermittent additions of iron are made to keep the iron content between 25 and 40 weight %. Each sample is wrapped in 0.3 g of tin sheet before dropping.

It is interesting that Smiley<sup>32</sup> using perhaps the earliest form of the inert gas fusion technique (his capillary-trap technique) found the platinum bath did not work for tantalum (molybdenum, tungsten and niobium). Recent unpublished work at Battelle indicates that the use of a platinum-bath vacuum-fusion technique yields excellent and rapid results. Gas extraction is complete in 5 min at 1850°. Up to 50% of tantalum can be tolerated in the bath. For a 1-g sample the usual sensitivity of the analysis is 7 ppm. For total gas contents below 100  $\mu$ l (equivalent to 70 ppm of oxygen for a 1-g sample), a sensitivity of 0.2 ppm is realised.

### HYDROGEN METHODS

The determination of hydrogen in metals is considered to be simpler than the determination of oxygen and nitrogen. Hydrogen is removed rapidly and quantitatively from nearly all metals when melted in vacuum. Thus good hydrogen results are often obtained in the trial of unsuccessful vacuum-fusion techniques for oxygen. The Serfass Gas Analyser<sup>33</sup> which utilises a specially designed palladium diffusion valve appears particularly well suited to the rapid determination of hydrogen alone by vacuum fusion. A sensitivity of 0.2 ppm is indicated.

Hydrogen is also readily removed by diffusion from solid samples. The most satisfactory extraction rates are obtained at 1000° and higher. In the case of titanium,

extractions are made at 1350° for 20 min and the evolved gas is relatively pure hydrogen. For practical purposes the gas need only be measured (not analysed). Benner<sup>30</sup> reports the use of a molybdenum bucket in vacuum at 1400° for hydrogen extraction from titanium and zirconium in 2 to 3 min. The sensitivity of the analysis is about 2 ppm at the 50 to 100-ppm level. There is no apparent reason why this technique should not be directly applicable to the refractory metals. If other gases are evolved, the hydrogen is readily separated by diffusion through a heated palladium tube. The hydrogen content of the gas can also, of course, be determined by conventional oxidation and absorption techniques, or by thermal conductivity, mass spectrometry, or gas chromatography techniques.

The equilibrium pressure method applied by McKinley<sup>34</sup> to titanium would appear also applicable to tantalum and niobium. However, the method would probably lack sensitivity in the low concentration range, for it is based on the amount of gas evolved in a closed system at a constant temperature (1050° for titanium). When an equilibrium pressure is reached, the volume of gaseous hydrogen is calculated. The volume of hydrogen remaining in the metal at this pressure is computed from experimental equilibrium data for the metal. The total hydrogen is a summation of these two volumes.

A tin bath method<sup>35</sup> has been used for steels. The sample is dissolved in tin at 1100 to 1200° and the hydrogen is readily evolved and measured. Only minor amounts of other gases are evolved. It is unlikely that such low-temperature fluxing of the refractory metals will be found possible.

A combustion method in which the sample is ignited in oxygen in the presence of a flux<sup>36</sup> has been used for titanium. The method was never widely used because it is cumbersome compared to other methods.

Specific references to the determination of hydrogen in refractory metals by vacuum fusion were made by Hansen and Mallett (molybdenum),<sup>2</sup> Mikhailov *et al.* (molybdenum, tungsten, niobium)<sup>23</sup> and Henry and Sloman (molybdenum).<sup>25</sup>

Hydrogen values (molybdenum, tungsten, niobium) were obtained by Fagel *et al.*,<sup>21</sup> in the course of diffusion extraction at 2000° for oxygen. Results by emission spectroscopy (niobium) were reported by Fassel.<sup>12,13</sup>

#### NITROGEN METHODS

The following discussion of the solution distillation method used at Battelle for the determination of nitrogen in refractory metals was prepared by Chase.<sup>37,38</sup>

##### *Solution-Distillation Method*

When determining nitrogen in niobium-, tantalum-, molybdenum- and tungsten-base alloys, the major problem is in the digestion and complete dissolution of the samples. Depending upon the type and quantity of alloying elements present various digestion procedures must be used. In general, one tries to avoid using an acid that will produce an insoluble film or residue with any major element in the alloy.

The following procedures have proved useful in dissolving the above metals in the pure state or alloyed with metals having similar solubilities.

##### *Molybdenum and molybdenum alloys*

Transfer a 0.5 to 1.0-g sample to a 30-ml micro-Kjeldahl flask. Add 6 ml of 1:1 sulphuric acid and 1 ml of 60% phosphoric acid. Heat on the digestion rack until the excess water is driven off and the

acid refluxes about half way up the neck of the flask. Continue digestion until no residue remains.

#### *Niobium, tantalum, tungsten and their alloys*

Transfer a 0.5-g sample to a 40-ml platinum crucible. It is desirable to have the sample in the form of >40 mesh chips. Add 5 ml of 1:1 sulphuric acid along with 2 ml of hydrofluoric acid and 1 ml of 30% hydrogen peroxide. Cover with a platinum lid and heat on a hot plate until the major part of hydrofluoric acid is driven off. If a residue remains, repeat the additions of hydrofluoric acid and hydrogen peroxide and continue heating until all of the sample has reacted. Also, one must make sure that all of the hydrogen peroxide has decomposed before proceeding to the distillation.

Regardless of the type of acid attack on the samples, the following procedure is applicable.

#### *Apparatus and reagents*

*Distillation apparatus.* The Parnas-Wagner apparatus is modified by the addition of an electrically heated steam generator consisting of a 2-litre reaction vessel with immersion heater and a three-way stopcock placed between steam generator and still. This allows the steam to be exhausted to the drain while the still empties without interrupting the heat supply.

*38% Sodium hydroxide solution:* Dissolve 1.5 lb of sodium hydroxide in 2 litres of distilled water, add 1.0 g of Devarda's alloy, and boil until the volume is 1800 ml.

*Mixed indicator solution:* Dissolve 0.0166 g of methyl red and 0.0834 g of bromocresol green in 100 ml of neutral ethanol.

*Boric acid solution:* A stock solution is made up by dissolving 40 g of C.P. boric acid in 1000 ml of tepid water. A dilute boric acid solution is prepared by diluting 40 ml of the 4% solution to 1000 ml with water.

*Standard sulphuric acid:* Make up a stock solution of sulphuric acid of approximately 0.07*N*. The stock solution is diluted to 0.007*N* for the determination of nitrogen in the range of 0.001 to 0.100%. For samples above 0.100% in nitrogen use the 0.07*N* sulphuric acid.

#### *Procedure*

Transfer the diluted sample solution to the Parnas-Wagner still and add 25 ml of sodium hydroxide solution. Distil and collect the condensate in a 50-ml Erlenmeyer flask containing 4 drops of mixed indicator solution and 10 ml of dilute boric acid solution. For samples containing more than 0.100% of nitrogen, use 10 ml of 2% boric acid solution as the ammonia collector. Adjust the heat input by a variable transformer so that 5 min after distillation begins, 10 ml of condensate will have been collected.

Titrate the collected ammonia with standard acid, and make a blank determination using the same amounts of all reagents as in the sample determination. An alternative method used by others<sup>39</sup> is to determine the ammonia in the condensate spectrophotometrically with Nessler's reagent.

#### *Alkali-Fusion Method*

Harris of the Westinghouse Research Laboratories analysed niobium for nitrogen<sup>29</sup> by an alkali-fusion method previously used in that laboratory for the analysis of boron, tungsten and molybdenum.<sup>40</sup> The fusion apparatus consists of a Vycor tube, 30 inch long and 1-1/4 inch in diameter, fitted with ground glass joints at each end and tubes for the passage of carrier gas. A nickel boat containing a fusion mixture is placed inside a nickel sleeve which protects the combustion tube from spattered alkali. The mixture is heated with a 12-inch split-tube furnace.

The niobium, in the form of fine powder or millings, is fused with sodium hydroxide at 600° for 1-0.5 hr in a slow stream of hydrogen. The ammonia formed during the fusion is absorbed in water or boric acid and determined by the usual titrimetric or colorimetric techniques. A blank is determined in the same way. Blanks as low as 1 µg can be obtained by prefusing the sodium hydroxide before use. Otherwise, the blank amounts to 20 to 25 µg of nitrogen which may be tolerable at high nitrogen levels.

### *Other Methods*

The vacuum diffusion-extraction was developed for molybdenum by Mallett and Griffith.<sup>15</sup> Extraction was made at 1800° for 30 to 50 min. The same method at 2000° for 20 to 30 min was used for molybdenum, tungsten and tantalum by Fagel, Witbeck and Smith.<sup>21</sup> Other methods include the use for one or more of the refractory metals, of the vacuum fusion iron bath,<sup>23,25</sup> iron-tin bath<sup>21</sup> and the emission spectrograph.<sup>13</sup> In general, vacuum-fusion nitrogen values for metals other than steels amount to no more than numbers obtained incidental to oxygen determinations. The findings were never properly verified by work with standards. A steel containing 0.89% of titanium yielded only half the solution-distillation value.<sup>41</sup> For chromium and its alloys, nitrogen (vacuum fusion) recovery approaches 80%. In the case of titanium, no nitrogen is recovered by the dry-crucible (tin flux) technique. The platinum bath technique has yielded some apparently satisfactory results but the conclusion<sup>42</sup> is that the "vacuum-fusion technique, as at present operated, does not furnish very reliable nitrogen figures for those elements forming very stable nitrides." No concentrated effort has been made to determine the conditions required for quantitative recovery of nitrogen from refractory metals by vacuum fusion.

It appears that wet chemical methods may be adequate for determining nitrogen levels above 10 or 20 ppm. No method exists for levels lower than this.

### CARBON METHODS

The determination of carbon in metals is normally carried out by a combustion technique in which the carbon is converted to carbon dioxide for measurement. The three most common methods<sup>37,38</sup> of measurement and their areas of application are as follows.

#### *Gravimetric procedure*

In this method the sample, with appropriate flux, is combusted in a Globar furnace. The resulting carbon dioxide, after removal of impurities, is collected and weighed in an absorption bulb containing Ascarite. The working detail can be found in such standard works as *ASTM Methods of Chemical Analysis of Metals* or *Scott's Standard Methods of Chemical Analysis*. At Battelle, the gravimetric method is usually reserved for those samples containing more than 1% of carbon.

#### *Gasometric procedure*

The combustion step is carried out just as in the gravimetric procedure. The gas mixture from the combustion, after the removal of impurities, is collected and measured in a gas burette. The carbon dioxide is then removed from the gas mixture by absorption in potassium hydroxide solution. The volume of gas is measured again and from the loss in volume one can calculate the carbon content of the sample. The method is rapid and reliable, and the working details can be had from the manufacturers of such apparatus. This procedure is most useful in determining carbon contents of from 0.03 to 2.0 %.

#### *Conductometric procedure*

This is a modification of a method reported by Bennet, Harley and Fowler<sup>43</sup> for

the determination of carbon in steel. This procedure is useful in the range of from 5 to 400 ppm of carbon. Since, presently, most interest is centered in metals and alloys in this range of carbon content, this method will be described more fully.

In the conductometric determination of carbon, a sample is combusted in pure oxygen in a high-frequency induction furnace, and the amount of carbon dioxide resulting is established by measuring the change in conductivity of a barium hydroxide solution in which the carbon dioxide is adsorbed. A commercial apparatus using these principles is manufactured by Laboratory Equipment Corporation. Full operating details may be obtained from the manufacturer.

In determining the carbon content of niobium, tantalum, molybdenum, and tungsten by the conductometric technique, the main difficulty is in obtaining a quantitative combustion. These metals and their alloys do not properly load the induction coil, and an incomplete combustion results. To overcome this difficulty, the use of several different combustion accelerators has been proposed. High-purity iron and tin are most widely used for this purpose and have been found satisfactory for the metals and alloys mentioned above. Since these materials contain small amounts of carbon and therefore introduce a significant blank value, they must be used with intelligence. One must use sufficient accelerator to ensure complete combustion, but avoid excessive amounts and their attendant high blank values.

For most metals of this type, one may use a 1-g sample along with 1 g of high-purity iron and 1 g of C.P. tin. The tin has such a low blank that it need not be weighed, but simply measured out with a small scoop. For those samples which are still more difficult to burn, one may use a 0.5-g sample with 1 g of iron plus 1 g of tin. For those materials more easily burned, one may cut the amount of iron to 0.5 g with 1 g of sample and 1 g of tin. To test for complete combustion, the cooled melt may be broken up with a hammer and examined for unburned metal under a low-power magnifier.

Finally, in the determination of low amounts of carbon in metals one of the most important and sometimes overlooked precautions is cleanliness. Since carbon in its many forms is such a common contaminant, one must keep the apparatus and its surroundings as clean as possible. Equally important, it must be impressed upon all who handle the sample in its various stages of preparation that the analysis is only as good as the weakest link in the chain of sample preparation.

**Zusammenfassung**—Eine Übersicht über die derzeitigen Methoden zur Bestimmung von Sauerstoff, Stickstoff, Wasserstoff und Kohlenstoff in Mo, W, Nb, und Ta wird gegeben.

**Résumé**—L'auteur présente un compte-rendu des méthodes électrochimiques applicables au dosage de l'oxygène, de l'azote, de l'hydrogène et du carbone dans le molybdène, le tungstène, le niobium et le tantalé.

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## THE FLAME PHOTOMETRIC DETERMINATION OF LEAD IN LEAD ALLOYS

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**Summary**—Methods are described for the determination of lead in lead alloys by flame photometry. The samples analysed contained from 4 to 85% of lead and the results obtained were reproducible to  $\pm 5\%$  of the amount of lead present. The analyses were accurate to within  $\pm 5\%$  of the lead content.

LEAD exhibits weak emission lines in the mantle of an oxygen-fuel flame and the emission at  $405.8\text{ m}\mu$  has been successfully applied to the determination of tetra-ethyl lead in gasoline.<sup>1-3</sup> This lead line is subject to spectral interference from manganese and potassium, but if necessary this interference can be avoided by using the lead line at  $368.3\text{ m}\mu$ .<sup>4</sup>

The lead line at  $283.3\text{ m}\mu$  has been used together with the atomic absorption spectrophotometric technique by Elwell and Gidley<sup>5</sup> for the determination of lead in copper-base alloys and steel and by Robinson<sup>6</sup> for the determination of lead in gasoline.

The determination of lead in alloys by simple flame photometry has not received much attention because of the very low emission sensitivity of the lead lines. The studies described in this paper indicate the precision and accuracy that may be obtained in alloy analysis using this technique.

### EXPERIMENTAL AND RESULTS

#### *Equipment*

The apparatus used consisted of a Hilger H700 Uvispek Spectrophotometer fitted with a Hilger H868 Flame Photometer attachment.

In accordance with the manufacturer's instructions, the oxygen-hydrogen flame was fed with oxygen at a pressure of 30 lb/sq. in. and hydrogen at a pressure of 20 lb/sq. in.

The emission of the most sensitive lead line, *i.e.*,  $405.8\text{ m}\mu$ , was measured using the normal UV photocell with the  $\times 5$  amplification switch in operation. The width of the slits was adjusted to 0.15 mm (corresponding to  $0.5\text{ m}\mu$ ), and the flame photometer mirror was adjusted to give maximum signal.

Correction for flame background was made by adjusting the instrument zero with the shutter open while distilled water was sprayed into the flame. The "check" (or 100% transmittance) adjustment was then made by spraying a standard lead solution of concentration greater than that of the samples to be tested into the flame. The intensity of emission from the standard lead solution was thus made to correspond to the 100% reading of the transmittance scale on the instrument. This scale was then used to measure the emission intensity of test solutions relative to the intensity of the standard solution in terms of "% transmittance". The constancy of the "zero" and "check" settings was used as a guide to the reproducibility of the flame conditions and rate of atomisation. In most cases, variations in these settings were traced to partial clogging of the capillary sampling tube.

Multiple readings of the percentage transmittance of test samples were then made, with constant checking of the "zero" and "check" adjustments.



### Selection of concentration limits

Because of the low emission sensitivities of the lead lines, high concentrations of lead are required in the test solutions. For the 405.8  $m\mu$  line, Dean<sup>4</sup> reports a sensitivity of 14 ppm of Pb per % transmittance, which indicates that the check or 100% transmittance standard should contain at least 1400 ppm of Pb.

A standard solution of lead nitrate containing 2000 ppm of Pb was prepared by dissolving 1.598 g of AnalaR  $Pb(NO_3)_2$  in 500 ml of distilled water. Standards containing lower concentrations of lead were prepared by dilution of this stock solution.

The % transmittance of a series of the diluted standards were then measured using the 2000 ppm of Pb solution as the "check" standard. A plot of % transmittance *versus* concentration of lead yielded a straight line. Erratic results were obtained when the measurements were repeated using the 1000 ppm of Pb solution as "check" standard. It therefore appears that the emission sensitivity of lead using the Hilger apparatus, is of the same order as that observed by Dean. Thus in all subsequent studies the concentration of lead in the check solution was kept greater than 1400 ppm.

For *direct measurement*, *i.e.*, where the content of lead in the unknown is calculated from the relationship

$$\text{ppm of Pb}_{(\text{unknown})} = \%T \times 10^{-2} \times \text{ppm of Pb}_{(\text{check})}, \quad (1)$$

the concentration of lead in the unknown should preferably be just slightly less than the concentration of lead in the "check" standard solution. Apart from reducing any effects from self-absorption of radiation, this condition also reduces the % error in the final result introduced by any error in measurement of emission. For example, curve A in Fig. 1 represents the possible % error that may be obtained in the final result with samples giving different transmittance readings, assuming that there is a 1% error in the actual transmittance reading. It is obvious from this curve that the concentration of lead in the unknown solution should be large enough to yield a reading of at least 40% transmittance. This, with a minimum concentration of 1400 ppm of Pb in the "check" standard, corresponds to 550 ppm of Pb. If the test solution is prepared by dissolving 1 g of alloy and diluting to 100 ml, this 550 ppm of Pb corresponds to 5.5% of Pb in the alloy. The method therefore appears to be mainly suitable for alloys containing an appreciable content of lead.

In the analysis of metal alloys, difficulty arises in preparing standard "check" solutions of composition comparable to that of the assay solution. In these circumstances, a method based on the *standard*

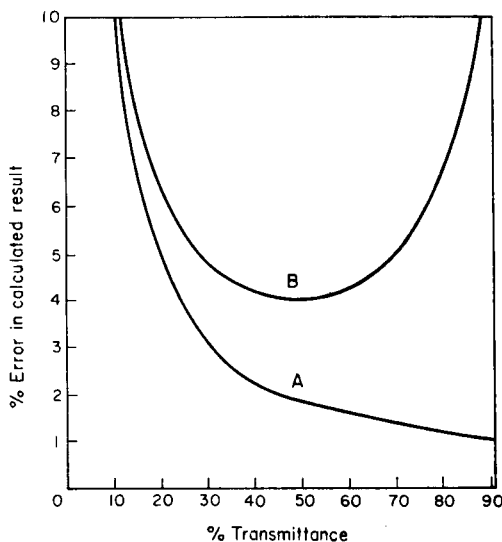


FIG. 1.—Percentage error introduced into calculated lead content of sample by 1% error in transmittance reading.

Curve A: Assay measured directly against a standard lead solution.

Curve B: Assay measured against a reference standard prepared by the standard addition method

addition technique was considered preferable. The same principle was adopted by Smith and Palmby<sup>3</sup> for the determination of lead in gasoline.

In the standard addition technique, the emission of the test solution is compared with the emission of an aliquot of the test solution to which a known amount of standard lead solution has been added. Because the concentration-transmittance curve was found to be linear, the unknown concentration of lead could be calculated from the relationship

$$\frac{x \cdot (v_1 + v_2)}{v_1x + v_2y} = \%T \cdot 10^{-2} \quad (2)$$

where

$x$  = concentration of Pb in unknown solution,  
 $y$  = concentration of Pb in added standard solution,  
 $v_1$  = volume of test solution aliquot,  
 $v_2$  = volume of standard added,

and  $\%T$  = observed transmittance reading.

Using this technique, an error in the observed transmittance reading is magnified by the calculations, and Curve B, Fig. 1 represents the error in the final result that may be introduced by a 1% error in the transmittance reading. From this curve, it can be seen that transmittance readings should preferably lie between 40% and 60% if the calculation errors are to be kept to a minimum. This corresponds to a minimum of 550 ppm and a maximum of 850 ppm of Pb in the test sample, using a check solution containing the suggested minimum content of 1400 ppm of Pb. These limits may be increased to higher values by using check solutions containing higher concentrations of lead but experience has indicated that the maximum concentration in the check solution should be limited to 2000 ppm of Pb. Above this limit the calibration curve began to deviate from a linear relationship, and precision was impaired because scale divisions corresponded to larger units of lead concentration.

The optimum conditions for the flame photometric determination of lead using the Hilger Flame Photometer appears to be the adjustment of the test solution so that it contains 700–1000 ppm of Pb and the adjustment of the check solution (by addition of standard lead solution) so that it contains approximately twice the concentration of lead in the test solution. The precision studies (*cf.* Table 1) have confirmed the suitability of these limits.

#### Preparation of test solutions

One of the problems associated with solution of lead alloys is the ready hydrolysis of the salts of tin and antimony which are commonly found in association with the lead.

Elwell and Gidley<sup>5</sup> satisfactorily overcame this problem with copper-base alloys by dissolving the alloys in a mixture of nitric and hydrochloric acids.

In the present study, metals were retained in solution as citrate complexes following solution of the sample in concentrated sulphuric acid.

Several g of ammonium citrate were added to the sulphuric acid solution of the alloy and the acid was carefully neutralised with concentrated ammonia solution. During neutralisation, some cloudiness caused by lead sulphate appeared, but this largely disappeared on complete neutralisation of the acid. To ensure complete lead recovery and a perfectly clear solution for testing, the citrate solution was filtered through a fine sintered-glass crucible (P4), and the residue in the crucible was treated with hot ammonium acetate extraction solution. The filtrate was then diluted to a standard volume, so as to give a lead concentration of 700–1000 ppm.

With white metals containing a low concentration of lead, it was found advisable to isolate the lead initially as lead sulphate, and subsequently to dissolve it in hot ammonium acetate solution.

Check solutions were then prepared by carefully adding, with constant agitation, 0.15 to 0.20 ml of a standard lead solution (0.1000 g of Pb per ml) from an Agla Micro Syringe to a 20-ml aliquot of the test solution. Under these conditions, each addition of 0.10 ml gives an increase of approximately 500 ppm in the concentration of lead in the aliquot.

No detrimental effects from the presence of the citrates and acetates in the test solutions were observed in the subsequent flame photometric determinations. However, because of the poisonous nature of lead fumes, the flame attachment was housed in a fume chamber.

TABLE I.—PRECISION OF FLAME PHOTOMETER READINGS

Sample	No. of readings	Conc. of test soln., ppm of Pb	Conc. of "Check" soln. ppm of Pb	Precision* (Std. deviation, ppm of Pb)	
				Individual results	Mean of 3 readings
Lead nitrate solutions	15	1040	2080	±71	±26
	15	520	2080	±57	±33
	15	260	2080	±56	±22
	15	520	1040	±95	±78
Solder A, 43% Pb	15	860	1360	±51	±42
	18	860	1860	±43	±23
	15	860	2360	±62	±51
Solder B, 60% Pb	25	1200	1700	±111	±72
	25	1200	2200	±120	±103
	20	1200	2700	±130	±72
	42	900	1900	±79	±28
White metal A, 3.9% Pb	54	780	1780	±69	±35
White metal B, 84.5% Pb	27	850	1700	±43	±10

\* The standard deviation was calculated from the formula  $m = \sqrt{\sum x^2/n - 1}$  where  $x$  is the deviation from the mean and  $n$  the number of readings taken.

#### Precision of instrument readings

The errors associated with the analysis of lead in alloys can be broadly divided into two groups, namely, those associated with the dissolution of the sample, preparation of test solution, addition of standard solution, *etc.*, and those associated with instrumental variables such as flame fluctuations, atomising rates, *etc.*

The magnitude of the former group can be assessed from a study of the accuracy and reproducibility obtained in the analysis of a series of alloys. These results are discussed in the next section.

The magnitude of the error associated with instrumental variables can be assessed from a study of the precision of a series of readings on the same sample.

Multiple transmittance readings were therefore made using standard solutions of lead nitrate in water and using test solutions prepared from lead alloys. The precision of the readings was then calculated in terms of the standard or root mean square deviation using the formula

$$\text{Standard Deviation, } m = \sqrt{\sum x^2/n - 1} \quad (3)$$

where  $x$  is the deviation from the mean reading and  $n$  the number of readings.

For comparison purposes the mean of every three readings was calculated, and the precision of these means was then determined.

The results of the precision calculations are summarised in Table I.

A number of deductions may be made from this Table. First, the worst precision was obtained with samples whose concentrations varied from the optimum limits previously suggested. For example, the test solution of Solder B, which contained 1200 ppm of Pb, gave poorer precision than the same sample prepared so as to have a lead concentration of 900 ppm. Similarly, poorer precision was obtained with lead nitrate solutions when a "check" solution containing only 1040 ppm of Pb was used.

Secondly, precision is greatly improved by considering only the mean of each three readings, which emphasises that multiple readings should be taken with every test solution.

Thirdly, the magnitude of the standard deviations emphasises the large errors that may be introduced in the final evaluation stage of analysis. Taking a single reading, the average standard deviation indicates the possibility of errors of the order of  $\pm 10\%$  in the calculated lead content of the sample. On the other hand, using the mean of three readings and considering only those samples which satisfy the concentration limits previously suggested, a precision of  $\pm 3-5\%$  of total content may be predicted.

Using similar Hilger equipment together with a photo-multiplier attachment and the atomic absorption technique, Elwell and Gidley<sup>5</sup> obtained a precision (*i.e.*, standard deviation) of  $\pm 0.06\%$  for copper-base alloys containing 2.5 to 4% of lead. Thus the precision of the atomic absorption technique for the analysis of lead would appear to be at least twice as good as that obtainable by direct flame emission measurements.

#### *Accuracy and reproducibility*

Multiple samples of a number of alloys containing a certified lead content were analysed using the flame photometric method. The lead content of each sample analysed was obtained by substituting the mean of at least six transmittance readings in equation (2). The results obtained with these individual samples have been used to calculate the reproducibility of the sample preparation and final evaluation. This reproducibility (expressed in terms of a standard deviation) is summarised in Table II. It can be seen from this Table that the lead determinations were reproducible to within 4-6% of the total lead content.

The lead content of each alloy was finally calculated by averaging the results obtained with three samples of the alloy. The results thus obtained for the alloys are summarised in Table III and it can be seen from this Table that an accuracy of about  $\pm 5\%$  of the total lead content was achieved. The composition of the alloys used is given in Table IV.

In order to improve the poor precision obtained with individual instrument readings (*cf.* Table I), a number of readings had to be taken for each sample.

TABLE II.—REPRODUCIBILITY OF LEAD ANALYSES

Sample	No. of assays	Mean Pb content, %	Max. dev. from mean	Standard deviation, %	Std. dev. as % of Pb content
Solder A	9	40.9	4.1	$\pm 2.5$	6.2
Solder B	12	60.1	5.3	$\pm 3.8$	6.3
White metal A	4	3.63	0.21	$\pm 0.15$	4.2
White metal B	3	84.5	4.0	$\pm 3.7$	4.3

This need for multiple readings has been noted by workers using the flame photometric method for the determination of lead in gasoline. Smith and Palmby<sup>3</sup> used the standard addition method for calibration, and the lead determinations were found to be accurate to about 2% of the amount of lead present in the gasoline. This higher degree of accuracy in comparison with the values quoted in Table III may be attributed in part to the tenfold increase in emission sensitivity obtained by burning gasoline samples, in part to the use of a photo-multiplier in the detection unit, and in part to the use of an atomiser-burner.

Using the atomic absorption technique for the estimation of lead, a reproducibility of the order of 2% and an accuracy (expressed as standard deviation) of 0.025% on samples containing 2.5 to 4% lead was obtained.<sup>5</sup> This again demonstrates the superiority of the atomic absorption technique over direct emission studies. However, the results obtainable using the normal flame photometric technique are sufficiently accurate for routine testing and even with multiple readings the method is faster than conventional gravimetric or titrimetric procedures.

#### *Method for the analysis of solder*

Transfer weighed samples of solder containing 0.0700-0.1000 g of lead to 250-ml Erlenmeyer flasks and add 5-10 ml of concentrated sulphuric acid. Cover with a watch glass, and heat to dissolve

TABLE III.—ACCURACY OF LEAD ANALYSES

Sample	Determined Pb content, %	True Pb content, %	Error % Pb	Error as % of lead content
Solder A	39.9	43.0	-3.1	7.2
	41.4		-1.6	3.7
	41.3		-1.7	4.0
Solder B	62.7	60.1	+2.6	4.3
	57.0		-3.1	5.2
	60.0		-0.1	0.1
	60.7		+0.6	1.0
	White metal A		3.63	3.90
White metal B	84.5	84.5	0.0	0.0

Standard Deviation  $\pm 4.7\%$

TABLE IV.—COMPOSITION OF ALLOYS USED

Solder A	43.0% Pb, 56.9% Sn.
Solder B	60.1% Pb, 39.6% Sn.
White Metal A	3.90% Pb, 84.0% Sn, 7.50% Sb, 4.10% Cu.
White Metal B	84.5% Pb, 5.09% Sn, 10.4% Sb.

the alloy. Cool slightly, dilute with 10 ml of water, and add 5 ml of 50% ammonium citrate solution. From a pipette carefully add 15*N* ammonia solution down the sides of the flask (with constant swirling) to neutralise the acid (Note 1). Heat the solution on a hot plate for a few min. Decant the solution through a fine sintered-glass crucible (P4), using slight suction. Collect the filtrate.

Add 10 ml of boiling ammonium acetate extraction solution (Note 2) to the flask, heat to dissolve any residue of PbSO<sub>4</sub>, and filter the contents of the flask through the same glass crucible. If any residue remains in the flask or crucible, repeat the extraction with a further 5 ml of the ammonium acetate solution. Wash the crucible with water. Combine all filtrates and transfer to a 100-ml standard flask, diluting to the mark with water. This is the "test" solution.

Take a 20-ml aliquot of this test solution, and from an Agla Micro Syringe carefully add 0.15–0.20 ml of standard lead solution (Note 3). This is the "standard" solution.

Set the wavelength drum of the flame photometer to 405.8 m $\mu$ , and adjust the zero control while spraying distilled water into the flame. Adjust the instrument to give 100% transmittance on the introduction of the "standard" solution. Measure the transmittance of the "test" solution.

Take the mean of a series (Note 4) of transmittance readings. Calculate the percentage of lead in the original alloy by substitution in the equation

$$\% \text{ Lead} = \frac{\alpha \cdot v_1 \cdot 10^{-4} \cdot v_3 \cdot c}{[(1 - \alpha) \cdot v_2 + v_3] \cdot w}$$

where

- $\alpha$  = % transmittance of sample  $\times 10^{-2}$ .
- $v_1$  = Volume of test solution after dilution (e.g. 100 ml)
- $v_2$  = Volume of aliquot used for "check" solution.
- $v_3$  = Volume of standard lead solution added.
- $c$  = Concentration of standard lead solution (ppm).
- $w$  = Weight of alloy taken (g).

#### Notes

1. Most of the precipitate present in the early stages disappears when neutralisation is complete.
2. The ammonium acetate extraction solution is prepared by diluting a saturated solution of ammonium acetate with twice its volume of distilled water and adding 30 ml of 80% acetic acid to each litre of solution.<sup>7</sup>

3. A suitable standard lead solution may be prepared by dissolving 15.9850 g of AnalaR  $\text{Pb}(\text{NO}_3)_2$  in 100 ml distilled water. This is equivalent to  $10^5$  ppm of Pb or 0.1000 g of Pb per ml.

4. A minimum of six readings is recommended.

Although this method has been developed for the analysis of solder, only minor modification is required to permit its application to other forms of alloys containing lead.

If the lead content of any type of alloy be first isolated as lead sulphate, then solution of this precipitate in ammonium acetate provides the required "test" solution and the analysis can be completed as already described. The presence of some ammonium citrate in the acetate extraction mixture ensures solution of any co-precipitated metal ions. This approach was tested with two white metal samples, containing 3.9 and 84.5% of Pb respectively, and it can be observed from Tables II and III that the reproducibility and accuracy achieved was slightly better than that obtained in the solder analysis. This improvement coincides with improved precision in the individual measurements. Because of the lower concentration of salts in the solution, the rate of atomisation was similar to that of lead nitrate solutions and the precision obtained was of the same order (*cf.* Table I).

#### *Method for the analysis of white metal*

Transfer weighed samples of white metal containing 0.0700–0.1000 g of lead to 250-ml Erlenmeyer flasks, add 10 ml of conc. sulphuric acid and cover with a watch glass. Heat till the sample is dissolved and the residue is white. Cool (but not below  $60^\circ$ ), dilute carefully with 50 ml of water, and heat to boiling until the precipitate settles quickly on the removal of heat. Maintain above  $60^\circ$  until the precipitate settles completely. Decant solution through a fine sintered-glass crucible (P4). Retain most of the precipitate in the flask and discard the filtrate.

Add 5 ml of 50% ammonium citrate and 5 ml of boiling ammonium acetate extraction mixture to the flask. Heat to dissolve the precipitate. Filter the contents of the flask through the same glass crucible and collect the filtrate.

Extract the contents of the flask once more with 5 ml of boiling ammonium acetate extraction mixture. Collect the filtrate and wash the flask and crucible with water. Combine all the filtrates and make up to volume with water to provide the "test" solution. Complete the determination as in the solder method.

#### DISCUSSION

One of the main attributes of flame photometry is the relative speed with which analyses can be performed when compared with other standard techniques. Often the penalty paid for the increased speed is a loss in accuracy.

The flame photometric determination of lead possibly provides the extreme case, since the excitation of lead salts by an oxygen-fuel flame results in lines of very low intensity. However, it has been shown in this study that satisfactory analysis can still be performed if suitable limits of lead concentration are chosen and multiple readings are made. The lead determinations were reproducible to  $\pm 5\%$  of the total lead content, and the accuracy of the determinations was of the same order.

It is emphasised that the results obtained in this study represent the accuracy and precision that may be obtained using the standard instrument. Improved results can be obtained by using a photo-multiplier attachment,<sup>3,5</sup> and the advantages of the atomic absorption technique have been clearly demonstrated.<sup>5,6</sup>

An alternative approach to improved accuracy and precision is that recommended by Dean,<sup>8</sup> who suggests the extraction of lead into organic solvents and direct aspiration of the organic phase into the flame. The enhancement of emission sensitivity caused by the organic phase has been clearly demonstrated with gasoline, but for safety reasons organic solvents should only be used with flame photometers fitted with an integral type of burner-atomiser. The Hilger attachment is fitted with a separate glass atomising chamber. As a consequence the beneficial effect of organic solvents could not be investigated in this study because of the danger of explosion within the chamber.

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**Zusammenfassung**—Methoden zu flammphotometrischen Analyse von Bleilegerungen werden beschrieben. Die untersuchten Proben enthielten 4–85% Blei. Reproduzierbarkeit und Genauigkeit der resultate war  $\pm 5\%$  des Bleigehaltes.

**Résumé**—Les auteurs décrivent des méthodes d'analyse d'alliages de plomb par photométrie de flamme. Les échantillons analysés contenaient de 4 à 85% de plomb et les résultats obtenus étaient reproductibles à  $\pm 5\%$  de la quantité de plomb présent. La précision des analyses était de  $\pm 5\%$  de la teneur en plomb.

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## CHELOMETRIC TITRATIONS WITH AMPEROMETRIC END-POINT DETECTION

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**Summary**—Anodic chelon waves may be used as indicator waves in the amperometric titration of metal ions which exhibit poorly defined reduction waves. By this method, also, mixtures of metal ions whose  $\log K$  values differ by less than 4 units may be selectively titrated. Buffers and chelons may be selected to improve selectivity, and the procedure is more rapid than the usual amperometric methods. Results are given for selected ions and mixtures of ions. The interference of halide ions must be overcome.

THREE different methods have been proposed for amperometric titrations with ethylenediaminetetra-acetic acid, EDTA. The most obvious uses the decrease in reduction wave height of the uncomplexed metal ion during the course of the titration.<sup>7</sup> This method is applicable when the reduction waves of the free metal ion and the metal chelonate are sufficiently well separated, and where that of the free metal ion occurs at a reasonably accessible region of potential. Since such conditions do not always exist, some alternative methods are desired.

One is to add an *indicator ion*; this is a metal ion species which is reducible at some practical potential and which, under the solution conditions chosen, forms a weaker complex with the chelon than the metal ion to be determined. The amperometric titration of calcium, for example, was accomplished by addition of zinc ion (zincate ion under the solution conditions chosen); a decrease in the diffusion current of zincate ion commenced after calcium was complexed and served to mark the end point.<sup>5</sup>

A second alternative is based on the appearance of an *anodic wave for the free chelon* after the end-point.<sup>6,10</sup> This electrode reaction may be written:



This method offers several advantages which have made its further investigation profitable and interesting.

A significant advantage of this latter method arises from the fact that the titration may be performed at a potential where the reduction wave of oxygen does not interfere. Hence the time-consuming operation of removing oxygen from the solution before analysis and after the addition of titrant is eliminated. Also, metals with large negative reduction potentials, such as calcium or barium, may be titrated without the introduction of "indicator" ions into the solution. Metal ions which exhibit ill-defined reduction waves may also be analysed conveniently. Furthermore, metal ions, such as zinc, may be easily titrated in the presence of a more readily reducible species, such as nitroaniline. This method should be readily adaptable to the use of rotary mercury electrodes in cases where higher sensitivity is desired.

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The disadvantages of the proposed method include those common to amperometric analysis, with the exception of the oxygen interference mentioned above. The presence of halide ions interferes<sup>10</sup> and must be avoided.

#### SELECTION OF POTENTIALS FOR ANALYSIS

A principal operational difference between the anodic wave method and the other methods is, of course, the potential applied during the titration. In the first two methods, a potential at which one of the metals in the solution is reduced is applied. In the anodic method, the potential applied should correspond to a point on the diffusion plateau (anodic wave) for the chelon.

In order to select a suitable potential, it is expedient to consider polarograms which illustrate the various factors affecting the limits of the chelon wave (see Fig. 1). Either the initiation of the oxygen reduction wave, *a*, or the onset of the chelon wave (where mercury is anodically oxidised), *b*, establishes the negative limit of useful potentials. The less negative of the two values determines this limit and is designated as  $E_{\min}$ . The positive limit of the potential is always controlled by the buffer present in solution and is denoted as  $E_{\max}$ . Hence, the potential region useful for analysis,  $\Delta E$ , is dependent on the buffer type and concentration and on *either* the oxygen wave or the chelon wave. Consequently, each of these factors was investigated.

##### *Oxygen wave*

The oxygen wave is difficult to characterise in a definitive manner because a number of different features determine its reduction potential. Kern<sup>4</sup> dismisses the special effects of pH and buffer components as adsorption effects, and takes the electron transfer step as the rate-determining step. In this study, the potential value at which the oxygen wave begins was found to vary from 0.05 V *vs.* S.C.E. at pH 1 to 0.10 V at pH 10.9; this is in agreement with the results found by Kern.

To determine practical limiting values of  $E_{\max}$  and  $E_{\min}$ , a suitable current level was first established. For this purpose, consider the practical titration where one drop (0.05 ml) of chelon in excess of the equivalence point is added to 50 ml of solution; the current given by this concentration of free chelon may be calculated using the Ilkovič equation and known diffusion coefficients. The resultant current will be 0.40  $\mu\text{A}$  for the chelon hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), and 0.48  $\mu\text{A}$  for diethylenetriaminepenta-acetic acid (DTPA). The values given in Table I were obtained by taking the experimentally observed EMF corresponding to a current of 0.4  $\mu\text{A}$  in various buffers. Although the concentration of chelon used here is somewhat arbitrary, it nevertheless represents a practical choice applicable to the titration of approximately 0.25 mmoles of metal in a 50-ml volume.

##### *Buffer wave*

The maximum potential that may be applied in the absence of a buffer depends on the formation of mercury<sup>I</sup> ions or mercury<sup>II</sup> oxides. Because of the necessity of having a buffer present, the limit is less, since the buffers complex with the mercury<sup>II</sup> to some extent. Consequently the type and concentration of buffer establishes the maximum potential limit for an anodic wave titration.

The effect of buffers on potentiometric chelometric titrations using the mercury electrode was studied by Reilley and Schmid.<sup>9</sup> The upper potential limit, corresponding

TABLE I.—EFFECTS OF BUFFERS ON LIMITING POTENTIALS

Buffer	pH	Conc., molar	$E_{\max}$	$E_{\min}$	$\Delta E$
HNO <sub>3</sub>	1.0	0.10	0.290	0.050	0.260
Hexamethylenetetramine	4.62	0.10	0.285	0.042	0.243
		0.075	0.290	0.042	0.248
		0.05	0.301	0.040	0.261
		0.025	0.330	0.030	0.300
Acetate	4.7	0.10	0.290	0.050	0.240
Potassium acid phosphate	5.5	0.10	0.220		0.190
Triethanolamine	7.8	0.10	0.108	0.025	0.083
		0.075	0.118	0.025	0.095
		0.05	0.120	0.025	0.095
		0.10	0.160	0.046	0.114
Trishydroxymethylaminomethane	7.91	0.10	0.095	0.039	0.056
		0.075	0.102	0.032	0.070
		0.05	0.110	0.035	0.075
		0.01	0.150	0.049	0.101
Diethanolamine	8.8	0.10	0.084	0.002	0.082
		0.05	0.096	0.007	0.091
		0.01	0.125	0.016	0.109
Ammonia	9.3	0.10	0.042	-0.007	0.049
		0.075	0.048	-0.008	0.056
		0.050	0.057	-0.005	0.062
		0.025	0.062	-0.007	0.094
2-aminoethanol	9.5	0.10	0.030	-0.027	0.057
		0.05	0.052	-0.025	0.077
		0.025	0.064	-0.023	0.087
		0.01	0.080	-0.025	0.105
3-aminopropanol	10.0	0.10	0.028	-0.050	0.078
		0.05	0.040	-0.050	0.090
		0.025	0.053	-0.050	0.103
Diethylamine	10.9	0.10	0.007	-0.102	0.109
		0.05	0.013	-0.096	0.109

to  $E_{\max}$ , was discussed, and was shown, as expected, to be largely dependent on the stability of the mercury<sup>II</sup> buffer complex.

The existence of mixed complexes containing mercury, buffer ( $B$ ), and chelon ( $Y$ ) was also considered. Mercury<sup>II</sup>-EDTA forms a complex of the type  $HgBY$  with most nitrogen-containing buffers. On the other hand, chelons like ethyleneglycol bis-( $\beta$ -aminoethyl ether)- $N,N'$ -tetra-acetic acid (EGTA), and diethylenetriamine-penta-acetic acid (DTPA) have little tendency to form such complexes. In contrast,

oxygen type buffers, such as acetate and phthalate, do not form stable mixed complexes with mercury<sup>II</sup>-EDTA. When a complex of the type  $HgBY$  is formed, the minimum potential limit imposed by the onset of the chelon wave is shifted favourably to more negative values. On the other hand, this imposes a further complication when stability constants are measured polarographically, in that another equilibrium must be considered in interpreting the half-wave potentials.

The positive potential limit may be decreased by the formation of insoluble mercury<sup>I</sup> halides in solutions which have high halide concentrations. Consequently, care should be taken that the titration solution be kept relatively free of halide ions.

In view of the above, the ideal buffer should form a relatively weak complex with mercury. Taking this into consideration, only buffers which gave a  $\Delta E$  value greater than 0.08 V were used, with the exception of ammonia, where  $\Delta E$  is 0.049 V (see Table I). The use of ammonia necessitates a more careful control of both pH and applied potential.

In an actual analysis, each sample is neutralised to a pH near 7 *before* the addition of buffer; this permits use of a minimum quantity of buffer consistent with ample buffer capacity.

#### Chelon wave

Fig. 1 shows that either the chelon wave or the initiation of the oxygen wave may establish the negative potential limit. Since only the diffusion plateau of the chelon

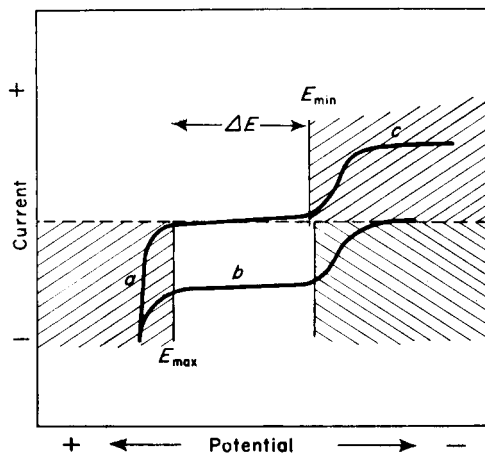


FIG. 1.—Polarographic waves affecting choice of potential.  
 A. Anodic oxidation of mercury in the presence of a buffer.  
 B. Anodic oxidation of mercury in the presence of a chelon.  
 C. Cathode reduction of oxygen.

wave is truly useful for analytical purposes, the potential where the current departs from this plateau is taken as the limiting potential.

Polarographic and potentiometric studies indicate the properties which one can expect for a given chelon in a practical titration. Fig. 2 represents the results of the investigation of a typical chelon, *N*-hydroxyethylethylenediaminetriacetic acid, HEDTA. Line *b* is the anodic oxidation of mercury in the presence of free chelon,

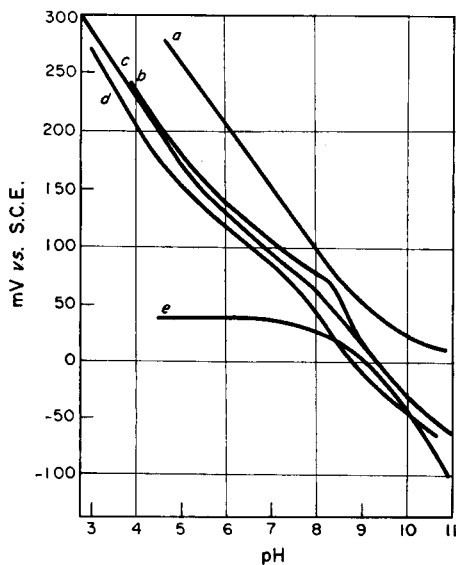


FIG. 2.—HEDTA polarographic and potentiometric waves.  
 A.  $E_{\max}$  vs. pH  
 B. Anodic oxidation of mercury in  $1.342 \times 10^{-3}M$  HEDTA.  
 C. Potentiometric-pH study of equimolar mixture of Hg-HEDTA and HEDTA, ( $1.342 \times 10^{-3}M$ ).

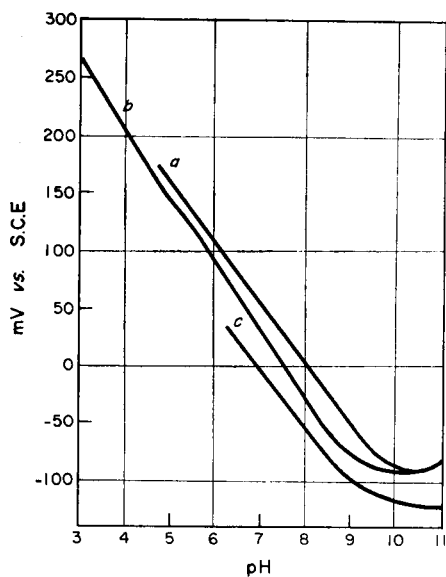


FIG. 3.—EGTA polarographic and potentiometric waves.  
 A. Anodic oxidation of mercury in  $0.972 \times 10^{-3}M$  EGTA.  
 B. Potential-pH curve of equimolar Hg-EGTA and EGTA, both  $0.972 \times 10^{-3}M$ .  
 C. Cathodic reduction of  $0.972 \times 10^{-3}M$  Hg-EGTA.

and line *d* is the cathodic reduction of the mercury<sup>II</sup>-chelionate, the e.m.f. shown being the polarographic half-wave potentials. Line *c* is the potentiometric-pH relationships of an equimolar mixture of mercury<sup>II</sup>-chelionate and free chelon. This line should coincide with the  $E_{\frac{1}{2}}$ -pH line of a solution of the same composition if the diffusion coefficients of the mercury<sup>II</sup>-chelionate and free chelon are identical. However, even when corrections are made for diffusion-coefficient differences (which actually are small), coincidence is still not observed because of the degree of overall irreversibility of the electrode reactions. In fact, the separation of the anodic and cathodic lines (see Figs. 2, 3, and 4) serve as an indication of this, the more widely separated being the more irreversible. Thus, it may be seen that, while DTPA and

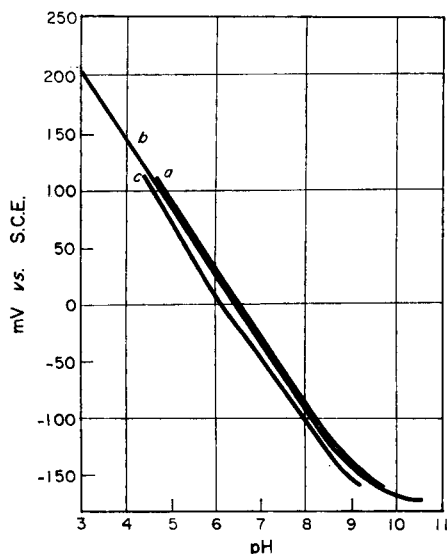


FIG. 4. —DTPA polarographic and potentiometric waves.

- A. Anodic oxidation of mercury in  $1.088 \times 10^{-3}M$  DTPA.
- B. Potential-pH curve of equimolar Hg-DTPA and DTPA, both  $1.088 \times 10^{-3}M$ .
- C. Cathodic reduction of Hg-DTPA,  $1.088 \times 10^{-3}M$ .

HEDTA undergo fairly reversible reactions, EDTA is much less reversible. (Corrections for IR drop in the polarographic system were found to be insignificant.)

From polarographic and potentiometric data, the stability constants of the mercury<sup>II</sup>-chelionates were calculated. The method of Goffert, Michel, and Duyckaerts<sup>1</sup> was used to calculate the stability constants from polarographic data, while the method of Schmid and Reilley<sup>11</sup> was used with the potentiometric data. Table II lists the calculated values and values previously reported in the literature.

#### SELECTION OF TITRATION CONDITIONS

The metal ion or mixture of metal ions to be analysed ultimately determines the conditions necessary for a successful analysis. Principles which govern the selection of an appropriate pH in any chelometric analysis are valid here, and the pH effect, *i.e.* the change of pH for selective titrations of the components of a mixture, can be employed to advantage. However, a corresponding change in applied potential

TABLE II. MERCURY CHELONATE STABILITY CONSTANTS

Chelon	log $K$ , calculated	Method of determination	log $K$ , literature	Reference	log $K_{HM}^H$
HEDTA	20.1	potentiometric	20.1	2	8.37
DTPA	27.0	potentiometric	27.0	2	11.79
	27.2	polarographic			
EDTA	23.9	potentiometric	23.8	11	11.95
	23.9	polarographic			
CyDTA	23.7	potentiometric	24.3	12	10.32

is necessary for an effective analysis of mixtures. Fig. 5 illustrates the results of such a titration for a mixture of copper and nickel with triethylenetetramine, trien. As shown above, the potential range suitable for the analysis is governed by the buffer and the chelon.

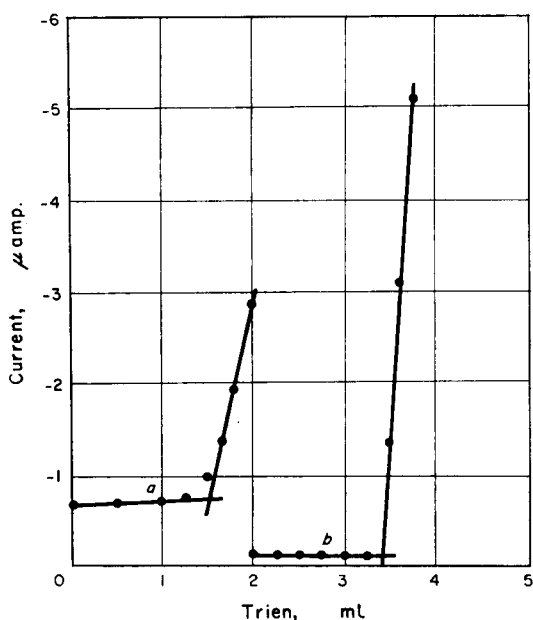


FIG. 5.—Titration of a Cu-Ni mixture with trien.

- A. Titration of  $\text{Cu}^{2+}$  in phthalate buffer at a pH of 5.5.  
 B. Titration of  $\text{Ni}^{2+}$  in ammonia buffer at pH 9.3.

Selective titrations can sometimes be effected by the use of two different chelons, often with no change in pH. This method has more stringent thermodynamic and kinetic limitations, however. This may be illustrated by the titration of a mixture of zinc and calcium. These components in a single aliquot may be selectively analysed in ammonia buffer by first titrating zinc with trien and then titrating calcium with EDTA. Thermodynamic considerations require that the effective stability constant of calcium-trien be so low that essentially no calcium will complex with trien after the zinc end-point is reached. In addition, the exchange shown by reaction 2 must not proceed in the forward direction.



When such conditions are met, the metal components are easily titrated selectively. Fig. 6 represents a combination of this method with the pH effect. Table III shows the results of this analysis.

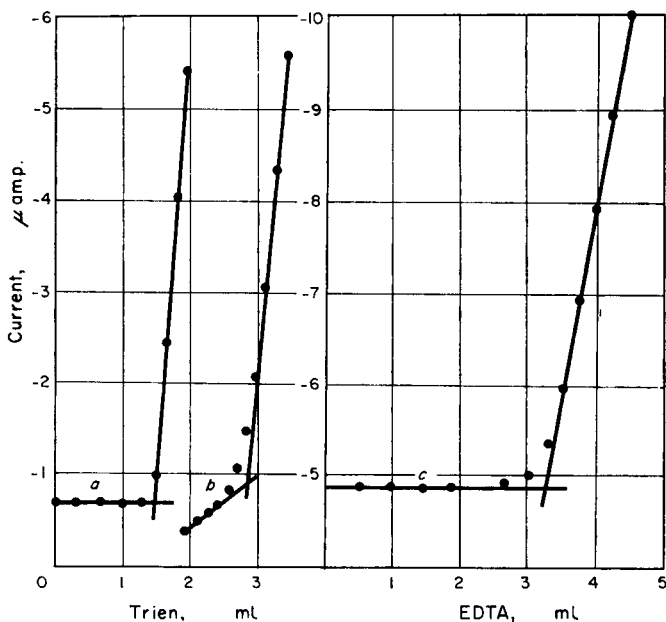


FIG. 6.—Titration of a Cu-Ni-Ca mixture.

- A. Titration of  $\text{Cu}^{2+}$  in phosphate buffer at a pH of 5.5 with trien.
- B. Titration of  $\text{Ni}^{2+}$  ammonia buffer at a pH of 9.3 with trien.
- C. Titration of  $\text{Ca}^{2+}$  ammonia buffer at pH 9.3 with EDTA.

Fig. 7 illustrates typical curves obtained for several titrations of this type. A nickel-magnesium analysis (Fig. 7a) is not feasible since the effective  $\log K$  value for nickel-EDTA is nearly 10 units greater than the value for magnesium-EDTA. Consequently, reaction 2 would take place in the forward direction to a large extent and there would be little, if any, magnesium-EDTA formed. The EDTA added beyond the nickel-trien end-point would simply replace the trien from the nickel-trien chelate.

The analysis of a zinc-magnesium mixture by this method is also impossible. However, Fig. 7b shows a trend that can be interpreted as the occurrence of a reaction similar to reaction 2, but to a smaller extent than in the case of the nickel-magnesium mixture.

In the case of the nickel-calcium mixture in Fig. 7c, the titration curve appears useful. Nevertheless, the experimental results indicate that the second end-point occurs too soon. Obviously some of the EDTA added during the titration reacts with the nickel-trien.

The zinc-calcium mixture represented by Fig. 7d fulfils the thermodynamic and kinetic requirements, and may be successfully titrated by this method. Table III gives the results of this titration.

## EXPERIMENTAL

### Apparatus

*Instruments:* All polarographic and amperometric studies were made with a Leeds and Northrup

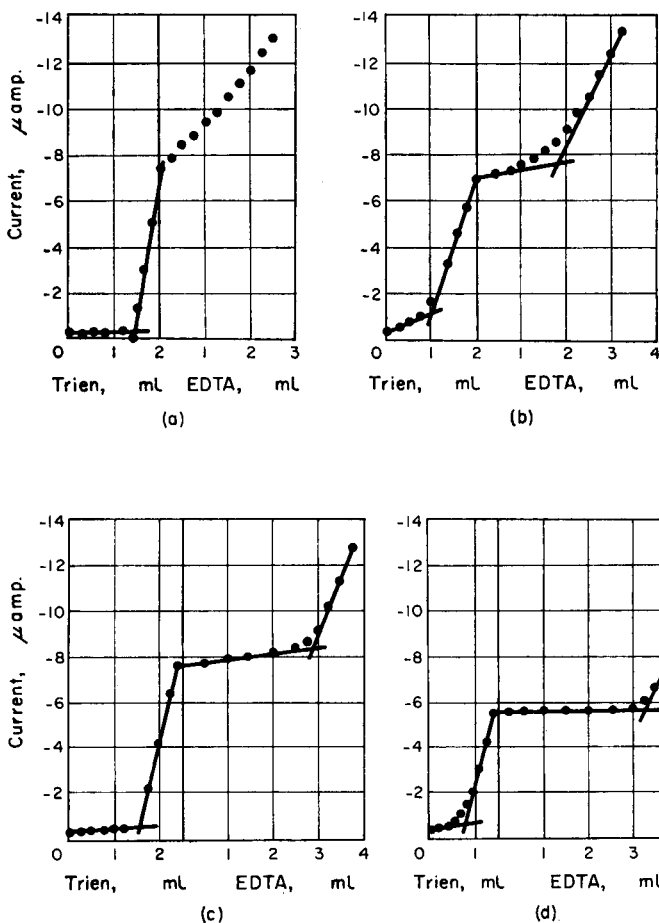


FIG. 7.—Selective titrations with *no* pH change.  
 A. Titration of Ni-Mg mixture in ammonia buffer at pH 9.3 with trien and EDTA.  
 B. Titration of Zn-Mg mixture in ammonia buffer at pH 9.3 with trien and EDTA.  
 C. Titration of Ni-Ca mixture in ammonia at pH 9.3 with trien and EDTA.  
 D. Titration of a Zn-Ca mixture in ammonia at pH 9.3 with trien and EDTA.

Electrochemograph. A Leeds and Northrup pH indicator Type 7764 was used for pH measurements. Potential measurements were made with a Rubicon portable precision potentiometer, type 2730.

*Electrodes:* A saturated calomel electrode and a dropping mercury electrode were used for all polarographic and amperometric work. During titrations and during some polarographic runs a shield was used for the dropping mercury electrode to eliminate adverse stirring effects. Fig. 8 shows the shield fitted with a rubber bulb of the medicine-dropper type, which is repeatedly squeezed after the addition of each aliquot of titrant to ensure homogeneity of solution inside and outside the shield. Only a few seconds are necessary before the solution within the shield is sufficiently quiet for the current to be diffusion-controlled. With this device, stirring throughout the titration is possible without adverse effects, and the time required for an analysis is greatly reduced. (In performing other amperometric titrations where oxygen interferes and must be removed from the solution, bubbling with nitrogen may proceed throughout the titration so long as the bubbles do not enter the shield.)

A gold amalgam electrode was used for the potentiometric studies. Because halide ions interfere with the potentiometric results, the interior of the saturated calomel electrode (Leeds and Northrup



TABLE III. RESULTS OF TITRATIONS OF MIXTURES OF METAL IONS

Mixture	Metal titrated	Present, mg	Found, mg	Error, %
Ni + Cd	Cd	29.42	29.48	0.2
			29.55	0.4
			29.10	1.1
Ni + Cd	Ni	18.66	18.92	1.4
			18.99	1.8
			18.99	1.8
Cu + Ni	Cu	15.91	15.71	1.2
			15.81	0.6
			15.97	0.4
Cu + Ni	Ni	18.66	18.53	0.7
			18.53	0.7
			18.44	1.2
Ca + Zn + Cu	Cu	15.91	15.66	1.6
			15.50	2.6
			15.61	1.9
Ca + Zn + Cu	Zn	14.47	14.48	0.1
			14.75	1.9
			14.53	0.4
Ca + Zn + Cu	Ca	13.34	13.07	2.0
			13.07	2.0
			13.11	1.7
Ni + Zn	Ni	14.93	14.85	0.5
			14.93	0.0
			14.93	0.0
Ni + Zn	Zn	11.76	11.77	0.1
			11.77	0.1
			11.80	0.3
Cu + Zn + Ca	Cu	15.91	15.66	1.6
			15.50	2.6
			15.61	1.9
Cu + Zn + Ca	Zn	14.47	14.48	0.1
			14.75	1.9
			14.53	0.4
Cu + Zn + Ca	Ca	13.34	13.07	2.0
			13.07	2.0
			13.11	1.5

1199-31 reference electrode) was coated with a thin layer of agar-agar gel saturated with  $\text{KNO}_3$ . This effectively prevented the diffusion of chloride ions from the electrode into the reaction vessel. This type of reference electrode was also used in the bismuth titration, since formation of  $\text{BiOCl}$  would otherwise result.

#### Titants

Approximately 0.1M solutions were prepared from the salts and standardised against a standard copper nitrate solution. The latter was prepared by dissolving a weighed portion of electrolytic copper in nitric acid and diluting to an appropriate volume.

*Ethylenediaminetetra-acetic acid, EDTA*: A 0.1M solution was prepared by dissolving an appropriate amount of the disodium salt in water. It was standardised in acetate buffer at a pH of 4.6 with the standard copper solution, using SNAZOX<sup>18</sup> as an indicator.

*Hydroxyethylethylenediaminetriacetic acid, HEDTA*: Standardised in ammonia buffer at a pH of 8.0 with murexide as the indicator, using the standard copper solution. It is marketed as Chel DM Acid by Geigy Industrial Chemicals.

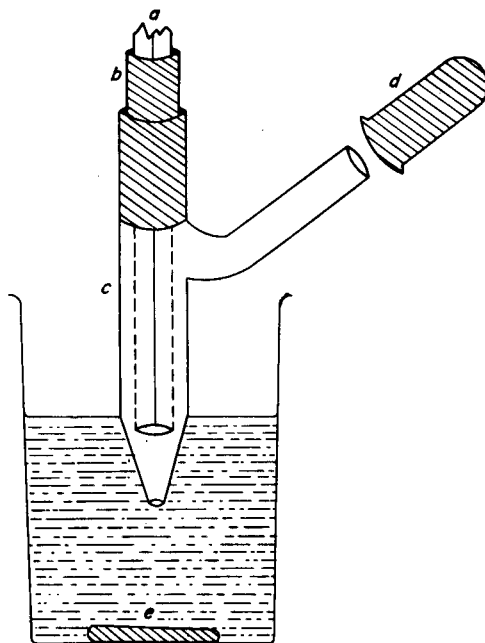


FIG. 8.—Amperometric titration assembly.

- A. Dropping mercury electrode.
- B. Gasket of rubber tubing.
- C. Electrode shield.
- D. Dropper bulb.
- E. Stirrer magnet.

*Diethylenetriaminepenta-acetic acid, DTPA* (Geigy Industrial Chemicals): Standardised with the standard copper solution at a pH of 4.5 in acetate buffer, using SNAZOXS<sup>18</sup> as an indicator.

*Ethyleglycol bis-(β-aminoethylether)-N,N',tetra-acetic acid, EGTA*, (Geigy Industrial Chemicals): Standardised potentiometrically in ammonia buffer with the standard copper solution at a pH of 8.5.

*Triethylenetetramine, trien*: Purified according to the method of Reilley and Holloway.<sup>8</sup> Standardised potentiometrically at a pH of 10 in ammonia buffer using the standard copper solution.

*Tetraethylenepentamine, tetren*: Standardised with copper potentiometrically in potassium acid phthalate buffer at a pH of 5.8. It was purified according to the method of Reilley and Holloway.<sup>8</sup> Both trien and tetren (technical grade) were obtained from Carbide and Carbon Chemical Company. A purified grade of trien disulphate is available from J. T. Baker Chemical Company.

#### Metal ions

*Standard copper nitrate solution*: Made by dissolving a weighed portion of electrolytic copper metal in nitric acid. The solution was heated gently to expel oxides of nitrogen and some excess acid, transferred to a volumetric flask, and diluted to an appropriate volume. Before weighing, the copper was cleaned with 1:3 nitric acid, washed with distilled water and then with ethanol, and dried at 85°.

*Mercury<sup>II</sup> nitrate solution*: Prepared in essentially the same manner as the copper nitrate solution. A weighed portion of the pure metal was dissolved in nitric acid and the solution was heated gently to expel oxides of nitrogen and some excess acid. This solution was standardised potentiometrically in pyridine buffer with EDTA.

All other metal solutions were made by dissolving approximately 0.1 mole of the nitrate salt in 1 litre of water.

*Calcium nitrate*: Standardised in diethylamine buffer at a pH of 12.2 with Calcon (C.I. 15705) as the indicator, using EDTA as the titrant.

*Zinc, cadmium and magnesium solutions*: Standardised in ammonia at a pH of 10.0 with EDTA using Eriochrome Black T (C.I. 14645) as the indicator. Nickel was standardised similarly using murexide as the indicator.

*Bismuth<sup>III</sup> nitrate solution:* Made by dissolving 0.1 mole of the salt in a litre of 0.1*N* nitric acid. This solution was standardised at a pH of 1 with SNAZOXS<sup>18</sup> as an indicator, using EDTA.

*Lead nitrate solution:* Standardised with EDTA at a pH of 5 in acetate buffer, using Xylenol Orange as the indicator.

*Barium nitrate solution:* Standardised at pH 12 in ammonia and NaOH with Eriochrome Black T (C.I. 14645) as the indicator, using EDTA as titrant.

#### *Buffer solution*

All buffer solutions were made by dissolving approximately 1 mole of the acid or base in 1 litre of water. Each solution was then half neutralised with concentrated HNO<sub>3</sub> or carbonate-free 50% NaOH. A pH meter was used to locate conveniently the exact half-neutralisation point where pH = pK. The buffer was added to each sample before analysis in an amount sufficient to give a concentration of 0.1*M* during the analysis.

### PROCEDURES AND RESULTS

The titrations were performed in a 150-ml beaker equipped with a magnetic stirrer as shown in Fig. 8. The stirrer could not be mounted on the same ring stand as the electrodes, since vibrations from the motor affected the formation of the mercury drop. Also, the beaker did not rest directly on the stirrer, but was held approximately 1 mm above it. This eliminated any effect which the vibration might have had on diffusion of species to the electrode surface. These precautions were necessary since the solution was stirred at all times during the analysis.

#### *Titrations of individual metal ions*

To test the feasibility of the proposed method, all metal ions were titrated individually before any mixtures were titrated. The results of these titrations are given in Table IV. In each case the buffer concentration was 0.1*M* and the supporting electrolyte was 0.1*M* KNO<sub>3</sub>; no maximum suppressor was found to be necessary. A 10-ml burette was used to deliver the titrant, and a single titration takes about 15 min.

*Calcium, magnesium, and zinc:* To a sample containing approximately 0.25 mmoles of calcium, magnesium, or zinc ions add 7.5 ml of 1*M* ammonia buffer and dilute the solution to 75 ml with 0.1*N* KNO<sub>3</sub>. Adjust the pH to 9.3 and perform the titration at 0.002 V applied potential *vs.* S.C.E. in each case. EDTA is used to titrate calcium and magnesium, while trien is used for zinc.

*Cadmium, nickel:* To a sample which contains approximately 0.25 mmoles of cadmium or nickel add 7.5 ml of 1*M* hexamethylenetetramine buffer, dilute the solution to 75 ml with 0.1*N* KNO<sub>3</sub>, and adjust the pH to 4.6. Titrate with HEDTA at an applied potential of 0.28 V *vs.* S.C.E.

*Copper:* To a sample of approximately 0.25 mmoles of copper ions, add 14 ml of 0.5*M* potassium acid phthalate buffer and dilute to 75 ml with 0.1*N* KNO<sub>3</sub>. Adjust the pH to 5.5 and titrate with trien at an applied potential of 0.25 V *vs.* S.C.E.

*Lead:* To a sample containing approximately 0.25 mmoles of metal ion, add 7.5 ml of 1*M* acetate buffer and dilute to 75 ml with 0.1*N* KNO<sub>3</sub>. Titrate lead with EDTA at a pH of 4.7 and a potential of -0.03 V *vs.* S.C.E.

*Bismuth:* To a sample containing approximately 0.25 mmoles of bismuth in 0.1*N* HNO<sub>3</sub>, add sufficient 0.1*N* KNO<sub>3</sub> to dilute the volume to 75 ml, and adjust the pH to 1.5 with HNO<sub>3</sub>. Titrate with DTPA at an applied potential of 0.36 V *vs.* S.C.E. BiOCl has a tendency to precipitate when chloride ions are present, so the calomel cell used a reference electrode should be treated as described above to prevent diffusion of chloride ions into the solution.

#### *Titrations of mixtures of metal ions*

*Nickel and cadmium:* To a solution containing approximately 0.25 mmoles of each metal ion, add 7.5 ml of 1*M* hexamethylenetetramine buffer and dilute to 75 ml with 0.1*N* KNO<sub>3</sub>. Adjust the pH to 4.0 and titrate with HEDTA at an applied potential of 0.32 V *vs.* S.C.E. The pH drops about 0.5 unit during the titration, which enhances the separation. Add NaOH to bring the pH to 4.6, and titrate cadmium with HEDTA at the same potential.

TABLE IV. RESULTS OF INDIVIDUAL METAL ION TITRATIONS

Metal	Present, mg	Found, mg	Error, %
Ca	10.67	10.64	0.3
		10.66	0.1
		10.68	0.1
Cd	29.42	29.55	0.4
		29.63	0.7
		29.55	0.4
Cu	15.91	15.76	0.9
		16.08	1.1
		16.03	0.8
		15.76	0.9
Ni	18.66	18.64	0.1
		18.64	0.1
		18.68	0.1
Pb	58.05	58.40	0.6
		58.50	0.8
Ba	27.53	28.12	2.1
		28.21	2.3
		27.92	1.4
		28.12	2.1
Mg	5.580	5.545	0.5
		5.534	0.9
		5.545	0.5
Zn	11.57	11.46	1.0
		11.54	0.3
		11.46	1.0
Bi	56.44	57.10	1.1
		56.74	0.5
		56.98	1.0

In this mixture, two metals are selectively titrated in the same buffer system at two different pH values. Since the pH range is narrow, the break at the equivalence point is very shallow. Nevertheless, it serves to prove that only small pH differences may permit selective titrations, and it emphasises the importance of pH control.

*Copper and nickel:* Copper and nickel may be selectively titrated in the presence of magnesium. To a solution containing approximately 0.25 mmoles of each metal ion, add 10 ml of 0.5M potassium acid phthalate buffer, dilute to 50 ml with 0.1N KNO<sub>3</sub>, and adjust the pH to 5.5. Apply a potential of 0.25 V vs. S.C.E., and titrate copper with trien. Add 7 ml of 1M ammonia buffer and adjust the pH to 9.3. The volume of the solution should be about 70 ml at this point. Titrate nickel with trien at a potential of 0.002 V vs. S.C.E. (see Fig. 5). Magnesium cannot be titrated at this point with another chelon such as EDTA. Apparently EDTA replaces some of the trien combined with nickel or copper ions before reacting with magnesium. Consequently, no well-defined end-point is obtained. The sum of copper, nickel, and magnesium may be easily obtained by titrating the mixture with EDTA in ammonia at a pH of 9.3 and a potential of 0.002 V vs. S.C.E.

**Calcium, zinc and copper:** To a solution containing approximately 0.25 mmoles of each metal ion, add 10 ml of 0.5*N* potassium acid phthalate buffer, dilute to 50 ml with 0.1*N* KNO<sub>3</sub>, and adjust the pH to 5.5. Titrate copper with trien at an applied potential of 0.25 V *vs.* S.C.E. Add 7 ml of 1*M* ammonia buffer, adjust the pH to 9.3, apply a potential of 0.002 V *vs.* S.C.E., and titrate nickel with trien. Without changing any of the existing conditions after the nickel end-point, titrate calcium with EDTA. The results of a titration of this type are shown in Fig. 6 and Table III.

**Nickel and zinc:** To a solution containing approximately 0.25 mmoles of each metal ion in 60 ml of 0.1*N* KNO<sub>3</sub>, add 40 ml of 0.5*M* potassium acid phthalate buffer and adjust the pH to 5.8. Titrate nickel with tetren at an applied potential of 0.22 V *vs.* S.C.E. Add 10 ml of 0.1*M* triethanolamine, adjust the pH to 7.8, and titrate zinc at an applied potential of 0.06 V *vs.* S.C.E.

This nickel-zinc ion analysis is interesting because the effective log *K* values for Ni-tetren and Zn-tetren differ by only 2.4 units. Potentiometrically a difference of 4 units is necessary for a selective titration using only the pH effect for selectivity. As would be expected, there is a great deal of rounding near the nickel end-point. Because of this, it is necessary to exceed the nickel end-point by more than the usual amount of chelon in order to obtain a linear curve, *i.e.*, where the current is diffusion-controlled. Consequently, the zinc concentration in the mixture must be sufficient to ensure that, when the pH is changed to 7.8 after the nickel end-point, enough uncomplexed zinc still remains to define the base line for zinc (see Fig. 9). The results of such a titration are given in Table III.

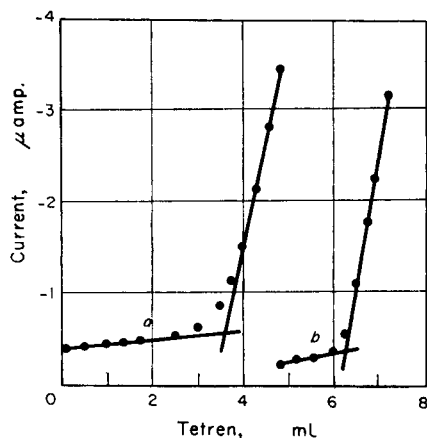


FIG. 9.—Titration of a Ni-Zn mixture.

- A. Titration of Ni<sup>2+</sup> in phthalate buffer at pH 5.5 with tetren.  
 B. Titration of Zn<sup>2+</sup> in ammonia buffer at pH 9.3 with tetren.

## CONCLUSION

The use of the anodic chelon wave as the indicator wave in amperometric titrations extends the usefulness of amperometric analysis by including those metal ions that exhibit ill-defined reduction waves. Furthermore, mixtures of metal ions whose log *K* values differ by less than 4 units can be titrated selectively, a procedure that is not practical by potentiometric analysis. This method allows the choice of both buffers and chelons in order to obtain optimum selectivity. The time required for an analysis is much less than for the usual amperometric methods since dissolved oxygen need not be removed from the system and the solution can be stirred continuously.

A primary disadvantage of the method is the interference from halide ions. However, with reasonable care, this difficulty is avoided by excluding halide ions from the analytical solution.

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**Zusammenfassung**—Die anodischen Wellen von Chelonen können als Indicatorwellen in amperometrischen Titrationen verwendet werden, wenn das Metallion schlecht definierte Reduktionswellen zeigt. Mittels dieser Methode ist es auch möglich Mischungen von Metallionen selektiv zu titrieren, deren log K-Werte einen kleineren Unterschied als 4 Einheiten zeigen.

Geeignete Wahl von Chelon und Puffer erlaubt Erhöhung der Selektivität. Die Methode ist rascher als die übliche amperometrische Titration.

Ergebnisse für ausgewählte Ionen und Ionenmischungen werden mitgeteilt. Es wird gezeigt wie Störungen durch Halidionen ausgeschaltet werden.

**Résumé**—Les vagues anodiques des "chelons" peuvent être utilisées comme indicatrices dans le titrage ampérométriques des ions métalliques qui présentent des vagues de réduction mal définies. Par cette méthode, des mélanges d'ions métalliques dont les valeurs de log K diffèrent de moins de 4 unités peuvent être titrés sélectivement. Les tampons et les "chelons" peuvent être choisis de manière à améliorer la sélectivité; cette méthode est plus rapide que les techniques ampérométriques usuelles. Des résultats sont donnés pour certains ions et mélanges d'ions. L'interférence des halogénures peut être éliminée.

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## THERMOGRAVIMETRIC ANALYSIS OF POTASSIUM HYDROGEN PHTHALATE

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**Summary**—The decomposition of potassium hydrogen phthalate in nitrogen yields potassium carbonate and a char at 800° when carried out in a thermobalance at a heating rate of 300° per hr. In air, only potassium carbonate is obtained at this temperature. The rate of decomposition in carbon dioxide is ~15 mg/g/hr at 235°. These results are compared with previous work.

### INTRODUCTION

THE thermogravimetric pyrolysis of potassium hydrogen phthalate in *nitrogen* has been reported<sup>1</sup> to proceed in three stages which are: (1) the formation of dipotassium phthalate and the volatilisation of phthalic anhydride and water; (2) the decomposition of dipotassium phthalate to yield volatile products and a residue of potassium carbonate and carbon (or "tar"); and, (3) the loss of the carbon leaving a residue of potassium carbonate in the stoichiometrically correct amount. The loss of carbon in the third step is rather surprising for a pyrolysis in nitrogen, and strongly suggests that the atmosphere was contaminated with oxygen. In an earlier paper, Erdey and Paulik<sup>2</sup> reported difficulty in maintaining an air-free nitrogen atmosphere in their study of the pyrolysis of BaC<sub>2</sub>O<sub>4</sub> and MnC<sub>2</sub>O<sub>4</sub>.

There is also a disagreement about the initial decomposition temperature of potassium hydrogen phthalate. The most recent value, 190°, is claimed to be more precise than values measured by conventional thermoanalytical methods which range from 125° to 235°.

A third peculiarity of this system is the unexplained weight gain maximum at about 450° shown in the thermogravimetric curves published by Dupuis and Duval<sup>3,4</sup> for the intermediate decomposition product of dipotassium phthalate heated in air.

### EXPERIMENTAL

The work was done with a pen-recording Chevenard thermobalance whose construction and performance have been described.<sup>5</sup> Experiments in static air were performed using a quartz liner tube and transparent top plate,<sup>6</sup> and in some cases with a quartz protective sleeve for the support rod as described by Soulen and Mockrin.<sup>7</sup> Experiments in controlled atmospheres were performed using a quartz tube as described by Duval,<sup>8</sup> modified by the addition of the quartz protective sleeve for the support rod. Even with this protective sleeve, which was very helpful, difficulty in obtaining good thermograms was sometimes experienced because the phthalic anhydride formed in the first stage of decomposition tended to deposit as long flexible needles which bridged the gap between the support rod and the wall of the sleeve and interfered with the motion of the balance. Coors porcelain crucibles were used, directly or with a platinum foil boat in the bottom. All weight changes were corrected for apparent weight gain. The potassium hydrogen phthalate was Bureau of Standards sample 84d. Samples weighing 0.1 g were used. Nitrogen was from the laboratory supply, and the carbon dioxide was the regular grade supplied by the Liquid Carbonic Co.

## DISCUSSION

The thermogram of potassium hydrogen phthalate,  $C_8H_5O_4K$ , heated in flowing air in a platinum boat held in a porcelain crucible, is shown in Fig. 1, curve 1, and other results for Run 1 are given in Table 1. The thermogram is very similar to that previously published<sup>1</sup> for a sample heated in nitrogen, and with the support of the additional results given below suggests that the atmosphere they used may have contained oxygen. None of the three major intermediate plateaus is horizontal, as also shown in the earlier work,<sup>1</sup> so that agreement between theoretical and observed weight changes is affected by the selection of the point chosen for calculation. The curve may be interpreted as showing four major reactions in sequence: (1) the first weight loss results from the volatilisation of water and phthalic anhydride and the formation of a residue of dipotassium phthalate; (2) the second weight loss is caused by the decomposition of this compound to  $K_2CO_3$  and char; (3) the char loses weight slowly and finally burns producing a third sharp weight loss and a residue of potassium carbonate; (4) the potassium carbonate decomposes with evolution of  $CO_2$ . In the last step the  $K_2O$  is "fixed" by reaction with the porcelain crucible which, by its roughened and crazed interior surface, clearly shows evidence of attack. The final product is indicated in the table and figure by " $[K_2O]$ ."

When a sample of  $C_8H_5O_4K$  was heated in static air in a porcelain crucible without a protective sleeve on the crucible support rod a weight gain was obtained at *ca.* 425-450° as shown by the dashed line, Fig. 1, curve 2. However, when samples were run in static air, flowing  $N_2$ , or flowing  $CO_2$  using a protective sleeve for the crucible support rod, this effect did not appear. It therefore seems likely that the effect is caused by evaporation of phthalic anhydride from the furnace walls with increasing temperature and its condensation on the crucible support rod. This probably also accounts for the generally smaller weight loss compared to 1 in the range 500-850°. Curve 2 otherwise follows curve 1 quite closely to about 870° when direct reaction of  $K_2CO_3$  with the crucible occurs with volatilisation of  $CO_2$ .

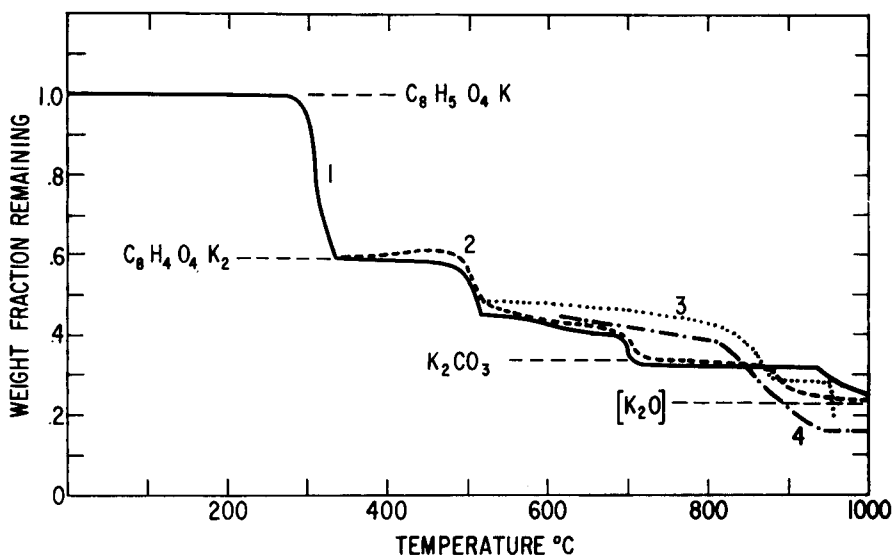


FIG. 1.—Thermograms of 0.1-g samples of potassium hydrogen phthalate at a heating rate of 300°/hr. See Table I for conditions.



TABLE I. DECOMPOSITION OF POTASSIUM HYDROGEN PHTHALATE

Substance	% Residue, calculated	Run 1 Flowing air, Platinum boat		Run 2 Static air, Porcelain crucible		Run 3 Flowing N <sub>2</sub> Porcelain crucible		Run 4 Flowing N <sub>2</sub> Platinum boat	
		T, °C	% Residue	T, °C	% Residue	T, °C	% Residue	T, °C	% Residue
C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> K <sub>2</sub> K <sub>2</sub> CO <sub>3</sub> + Char	59.3	400	59	400	60	400	60	400	56
	—	520	44	—	—	530	48	535	46
K <sub>2</sub> CO <sub>3</sub> [K <sub>2</sub> O]	33.8	900	32	700	36	900 <sup>b</sup>	29	—	42
	23.1	1040 max.	23 <sup>a</sup>	1000 max.	23 <sup>a</sup>	—	—	—	—
C <sup>c</sup>	14.7	—	—	—	—	950 max.	20 <sup>a,c</sup>	1000 max. <sup>a</sup>	17

<sup>a</sup> Based on final weighing on an analytical balance.<sup>b</sup> [K<sub>2</sub>O] + char<sup>c</sup> Air introduced at the end of the run to burn off char. Reaction complete in 1 min.<sup>d</sup> Assuming C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>K<sub>2</sub> → 2K + 3CO + H<sub>2</sub>O + H<sub>2</sub> + 5C

A sample of  $C_8H_5O_4K$  heated in flowing nitrogen in a porcelain crucible gave a thermogram similar to that in flowing air up to about  $500^\circ$ , but deviated thereafter as shown by the dotted line in Fig. 1, curve 3. In this run, the relative stability of the char in nitrogen is clearly shown and a sharp weight loss is not observed in the region of  $700^\circ$  as in air. The loss in weight from  $500^\circ$  to  $880^\circ$  results both from further decomposition of the char, of  $K_2CO_3$ , and also from the  $K_2CO_3$ —char reaction. The residue weight in  $N_2$  was constant at  $950^\circ$ , but the char burned very rapidly when air was admitted. The final residue weight was less than that expected and the crucible was left with a shiny black interior. This would seem to be indirect evidence for the formation of potassium, by the  $K_2CO_3$ —char reaction, and its attack of the crucible.

In order to avoid completely the interference from phthalic anhydride formed in the first stage of decomposition, a sample of  $C_8H_5O_4K$  in a platinum boat in a crucible was heated in an air oven for 1.5 hr at  $300^\circ$ . The residue was 57.9% compared to 59.3% calculated for  $C_8H_4O_4K_2$ . This residue in its platinum boat and crucible, when heated in flowing nitrogen, gave thermogram 4 in Fig. 1. This resembles thermogram 3 up to about  $880^\circ$ , but above this temperature it continues to lose weight. This undoubtedly arises from continuance of the  $K_2CO_3 + C$  reaction, whereas, in thermogram 3, the  $K_2CO_3$  had been partially consumed by reaction with the crucible. The final product at  $1000^\circ$  was a black porous char in the platinum boat, and a shiny black interior on the porcelain crucible containing the boat. In this run as in run 3, the quartz protective sleeve was also badly attacked.

The reaction between  $K_2CO_3$  and graphite has been studied by Kröger and Fingas.<sup>9</sup> In vacuum, the strong evolution of potassium was noted as low as  $700^\circ$ . The CO pressure increased rapidly above this temperature, was dependent on the sample size, and the reaction was not reversible. In the thermogravimetric runs in nitrogen, the onset of this reaction is obscured, because it overlaps the gradual weight loss from pyrolysis of the char, but it is evident at least as low as  $750^\circ$ . In air, of course, this reaction does not occur because of the prior removal of the char by oxidation.

If the reaction observed in the earlier work<sup>1</sup> above  $700^\circ$  is in fact an oxidation, this would cause the large exothermic effect which they observe by DTA. The complex DTA curves which they report cannot thus be easily interpreted without further experiments.

Fig. 1 shows a procedural decomposition temperature<sup>10</sup> of  $\sim 260^\circ$  for potassium hydrogen phthalate. This is the temperature at which a weight loss was first detected dynamically, and may be compared with  $170^\circ$ ,<sup>3</sup>  $236^\circ$ ,<sup>4</sup> and  $190^\circ$ <sup>1</sup> observed by others. These differences are not surprising, and the probable causes for this sort of difference have been discussed previously.<sup>11</sup> Such numbers are of little value in deciding the safe, long-term drying temperature for a primary standard substance.

The initial isothermal rate of decomposition of potassium hydrogen phthalate in carbon dioxide at  $235^\circ$  was measured to be  $\sim 15$  mg/g/hr. Previous studies by Caley and Brundin<sup>12</sup> plotted as log rate *vs.*  $1/T$  in the range  $149$ – $199^\circ$  may be extrapolated to give an initial decomposition rate in air of 7 mg/g/hr at  $235^\circ$ . The agreement is sufficient considering the great difference in experimental conditions. Duval<sup>4</sup> made isothermal runs at  $150^\circ$ ,  $160^\circ$ , and  $170^\circ$ , and observed no weight loss in 3 hr. If a sample weight of 0.5 g is assumed for his experiments, the changes expected from the results of Caley and Brundin are 0.004 mg, 0.011 mg, and 0.030 mg. These

changes are too small to be detected on the usual Chevenard thermobalance. It is therefore not surprising that Duval observed no weight changes and his observations do not conflict with those of Caley and Brundin. The only evidence contradictory to their recommendation that potassium hydrogen phthalate may be dried safely at 135° is the statement by Kolthoff<sup>13</sup> that the purified compound is dried at 125°, but not higher, since sublimation of phthalic anhydride takes place.

**Zusammenfassung**—Die Zersetzung von Kaliumhydrogenphthalat in Stickstoff gibt Kaliumcarbonat und Kohle bei 800°C, Dies wurde in einer Thermowaage mit einer Heizgeschwindigkeit von 300° per Stunde gefunden. In Luft wird nur Kaliumcarbonat erhalten. Die Zersetzungsgeschwindigkeit in Kohlendioxyd is etwa 15/mg/g/h bei 235°C. Die Ergebnisse werden mit früheren Untersuchungen verglichen.

**Résumé**—La décomposition du phthalate acide de potassium dans l'azote donne du carbonate de potassium et un produit de carbonisation à 800°C, quand elle est réalisée dans une thermobalance à la vitesse de chauffage de 300°C par heure. Dans l'air, seul le carbonate de potassium est obtenu à cette température. La vitesse de décomposition dans l'anhydride carbonique est environ 15 mg/gm/h à 235°C. Ces résultats sont comparés à ceux d'un travail antérieur.

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## SHORT COMMUNICATIONS

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### **Tetramethylguanidine: A new solvent for titration of weak acids**

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#### INTRODUCTION

THE titration of weak acids in non-aqueous media has been investigated by several workers.<sup>1-4</sup> In these previous studies the solvents used were ethylenediamine or pyridine. The necessity for the removal of small amounts of water in the titration of very weak acids and the hazardous nature of ethylenediamine are factors which limit its use. Pyridine is quite useful for the titration of all types of acidic compounds, but its offensive odour and its more hazardous nature present objections to its use. 1,1,3,3-Tetramethylguanidine (TMG) is a much less volatile material (B.P. = 159-160°) and may be used quite successfully in the presence of small amounts of water.

The titrants were standardised against benzoic acid using TMG as a solvent. In order to test the effectiveness of TMG for the titration of weak acids, various phenols were selected.

#### EXPERIMENTAL

##### *Reagents and apparatus*

The tetramethylguanidine was obtained from the American Cyanamid Company and purified by distillation. This material boiled between 159-161° at a barometric pressure of 738 mm. The commercial reagent was also used without any change in titrimetric properties.

The titrants used were tetrabutylammonium hydroxide, prepared according to the procedure of Harlow,<sup>2</sup> and the commercially available tetramethyl-ammonium hydroxide pentahydrate (Southwestern Analytical Chemical Company, Austin, Texas) dissolved in 4:1 benzene-methanol. Much larger end-point inflections were obtained using the tetrabutylammonium hydroxide. Most of the phenols were "white label" from Eastman Kodak, and were used without further purification.

Although preliminary potential measurements were made using the Beckman Model "G" pH meter, most of the titrations were performed using a Beckman "zeromatic" pH meter. A Beckman general purpose glass electrode No. 4990-80 was used for all the titrations. The Beckman fibre-type calomel electrode No. 39170 was used with saturated aqueous potassium chloride and a saturated solution of potassium chloride in methanol, designated hereafter as the modified calomel electrode. A 180-ml Berzelius beaker equipped with a rubber stopper was used as the titration cell. Two holes were bored in the stopper to house the electrodes; additional holes were bored for the burette, nitrogen inlet and outlet. A magnetic stirrer was used for all titrations.

##### *Procedure*

A sample containing 1 to 2 mequiv of acid was weighed into a 180-ml Berzelius beaker. Fifty ml of TMG were pipetted into the titration cell, and the system was deaerated with nitrogen. An atmosphere of nitrogen was maintained throughout the titration to prevent the absorption of carbon dioxide. The blank was determined for each series of titrations.

#### RESULTS AND DISCUSSION

All of the acids titrated produced satisfactory potential inflections in the region of the equivalence point, as indicated in Fig. 1. The dissociation constants of these phenols in water vary from  $10^{-4}$  to  $10^{-10}$ , thus indicating the wide range of acidity over which this solvent may be employed. Table I indicates the reliability of this solvent for the titration of weak acids. Titration curves with the distilled or undistilled solvent were identical.

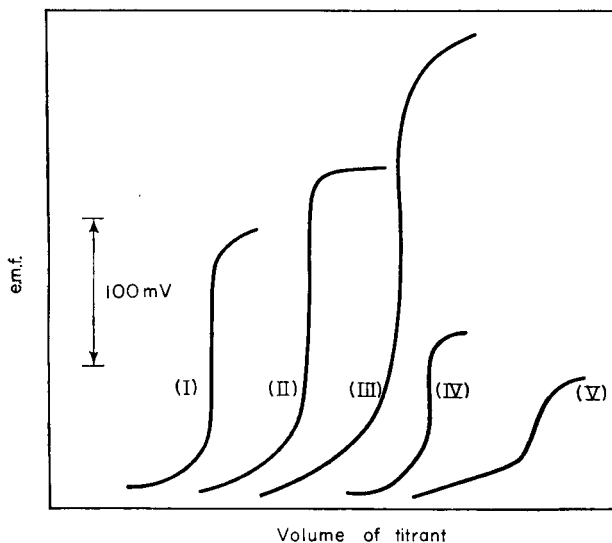


FIG. 1.—Titration of phenols with tetrabutylammonium hydroxide.

- (I)  $\beta$ -Naphthol
- (II) 2,4-Dichlorophenol
- (III) *p*-Bromophenol
- (IV) 2,4-Dibromophenol
- (V) *p*-Nitrophenol
- (VI) *m*-Nitrophenol
- (VII) Phenol

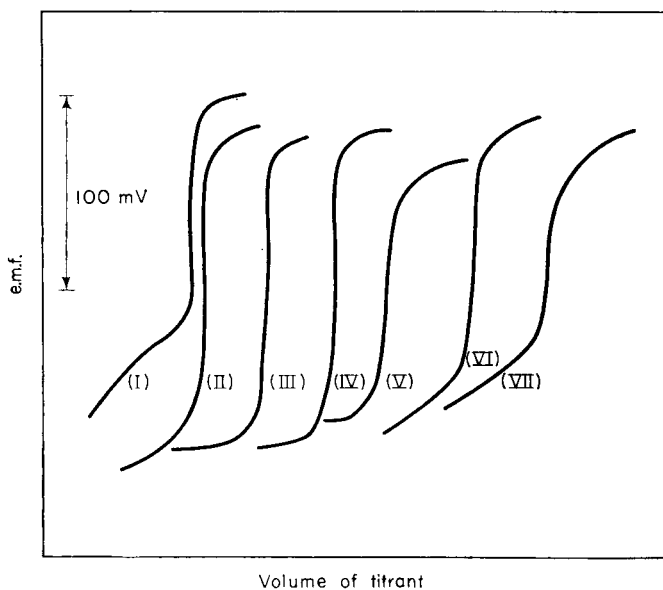


FIG. 2.—The effect of water on the end-point inflection of the titration of dinitrophenol with tetrabutylammonium hydroxide.

- (I) Anhydrous TMG with glass-modified electrode
- (II) Anhydrous TMG with glass-calomel electrode
- (III) 1% Water in TMG with glass-modified calomel electrode
- (IV) 3% Water in TMG with glass-modified calomel electrode
- (V) 10% Water in TMG with glass-modified calomel electrode

TABLE I

Compound	Taken, g	Found, g	Recovery, %
1. 2,4-Dinitrophenol	0.2154	0.2154	100.2
2. 2,4-Dinitrophenol	0.2180	0.2195	100.7
3. Succinic acid	0.0468	0.0461	98.5
4. <i>p</i> -Bromophenol	0.2227 0.2223	0.2175 0.2170	97.66 97.61
5. 2,4-Dichlorophenol	0.2004	0.1976	98.60
6. 2,4-Dichlorophenol	0.2090	0.2074	99.47
7. Phenol	0.2259	0.2252	99.69
8. Phenol	0.1822	0.1811	99.40

One may observe from Fig. 2 that small amounts of water, up to about 1%, are advantageous rather than harmful to the electrode response. Larger amounts of water have a deleterious effect on the electrode response. Further work is being performed to gain more information concerning the properties of this solvent.

*Acknowledgements*—The author would like to express appreciation to the American Cyanimid Company for the initial samples of TMG and to Helen Li for help with the experimental work.

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**Summary**—The use of 1,1,3,3-tetramethylguanidine (TMG) as a solvent for the titration of various phenols is described. The glass-calomel electrode system is employed using tetrabutylammonium hydroxide or tetramethylammonium hydroxide as the titrant. The effect of water on the electrode system is discussed. The commercially available solvent may be used without further purification.

**Zusammenfassung**—Die Verwendung von 1,1,3,3-tetramethylguanidin (TMG) als Lösungsmittel für die Titration verschiedener Phenole wird beschrieben. Ein Glas-Calomelektroden-Kombination wird verwendet; Tetramethylammoniumhydroxyd ist das Titrationmittel. Der Einfluss von Wasser auf das Elektrodensystem wird diskutiert. Käufliches Lösungsmittel kann ohne weitere Reinigung verwendet werden.

**Résumé**—Les auteurs décrivent l'utilisation de 1,1,3,3-tétraméthylguanidine (TMG) comme solvant pour le titrage de différents phénols. Le système d'électrode verre-calomel est utilisé; l'agent titrant est l'hydroxyde de tétrabutylammonium ou l'hydroxyde de tétraméthylammonium. L'influence de l'eau sur le système d'électrodes est discutée. Le solvant dont on dispose dans le commerce peut être utilisé sans purification.

## REFERENCES

- <sup>1</sup> D. B. Bruss and G. E. A. Wyld, *Analyt. Chem.*, 1957, **29**, 232.
- <sup>2</sup> G. A. Harlow, C. M. Noble and G. E. A. Wyld, *ibid.*, 1956, **28**, 784.
- <sup>3</sup> *Idem, ibid.*, 1956, **28**, 787.
- <sup>4</sup> J. S. Fritz and S. S. Yamamura, *ibid.*, 1957, **29**, 1079.

### Photophotometric titrations

(Received 14 October 1961. Accepted 21 October 1961)

A PHOTOELECTRIC titrator (such as that described by Flaschka and Sawyer<sup>1</sup>) employing a 1N2175 silicon photoconductive cell as detector with a low voltage battery as power supply can be markedly increased in sensitivity to light changes if the battery is replaced by a series of silicon photovoltaic cells (in the present work two "Heliodynes" consisting of eight silicon wafers each) also illuminated by light transmitted through the solution titrated (Fig. 1). Then an increase in transmitted light not only

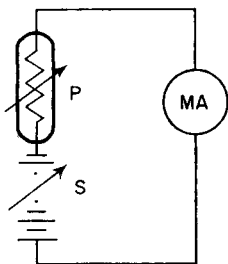


FIG. 1.—Electrical circuit for photophotometric titrations. P, 1N2175 photoconductive cell; S, a series of two Heliodynes; MA, 0-200 microammeter.

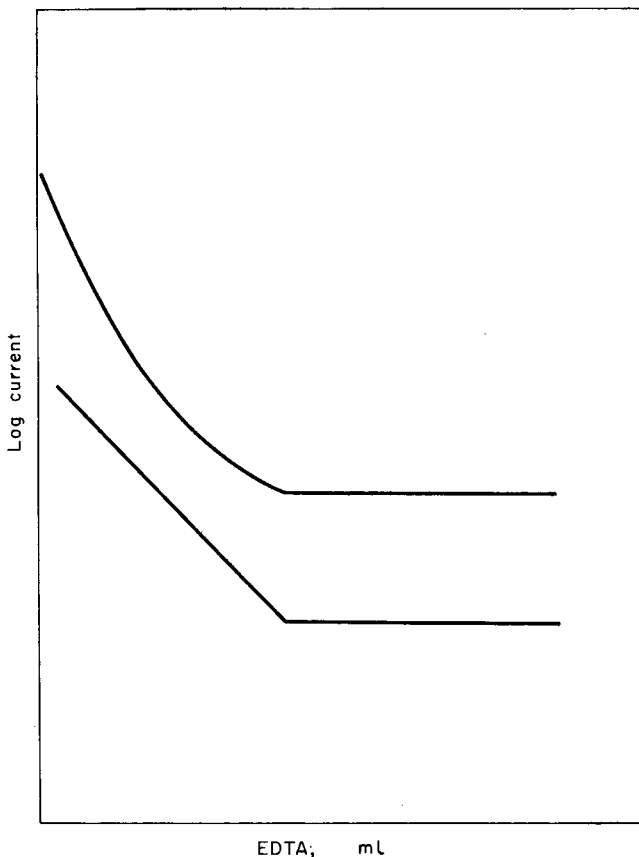


FIG. 2.—Photometric titrations of Cu with EDTA. Upper curve, with circuit of Fig. 1; lower curve, with 4.0-V battery in series with photoconductive cell.

decreases the resistance of the photoconductive cell but also increases the supply voltage from the photovoltaic cells. Despite the considerable impedance mismatch, the combination substantially increases high transmittancy readings and decreases low ones, as compared with results using the photoconductive cell and battery. In some circumstances the combination can give an improvement in photometric end-point sharpness.

Since the peak spectral response of both types of photocells is in the vicinity of the visible-near infrared border ( $975\text{ m}\mu$  for the 1N2175; about  $800\text{ m}\mu$  for the Heliodynes) the combination should be most suitable for titrations involving considerable changes in absorbancy in the  $700\text{--}800\text{ m}\mu$  region (or higher). As representative examples, respectively, of titrations with and without indicators in this region we have titrated copper with EDTA,<sup>1</sup> and sodium hydroxide with hydrochloric acid using Kryptocyanine as indicator. Sample results are given in Fig. 2 (Cu-EDTA) and Fig. 3 (NaOH-HCl-indicator). In both graphs the lower curve was obtained with a 4.0-V mercury battery in place of the Heliodynes. Obviously the variable supply voltage from the Heliodynes has the effect in Fig. 2 of making the end-point approach undesirably gradual, but in Fig. 3 a much larger end-point approach results. Thus, the new combination may be recommended only for titrations in which the end-point is marked by an increase in transmitted light, and in such titrations (with or without indicators) it has an amplifying action at the end-point.

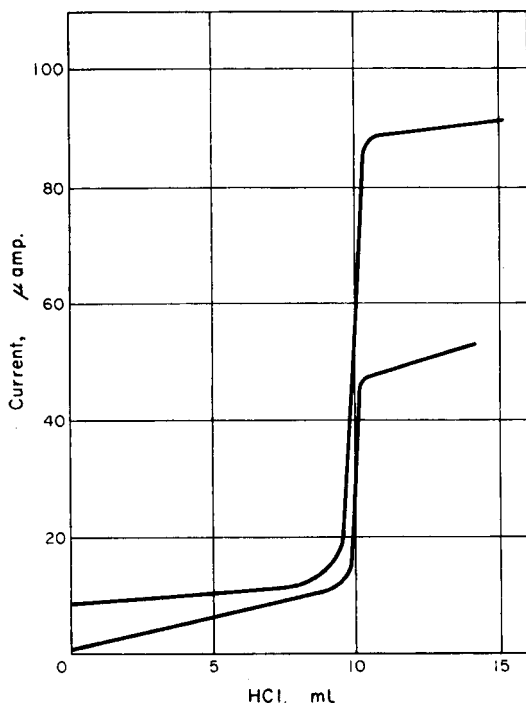


FIG. 3.—Photometric titrations of 10 ml of 0.1N NaOH with 0.1N HCl. Upper curve, with circuit of Fig. 1; lower curve, with battery and photoconductive cell.

Another possible way to combine end-point effects from different detectors is to use a potentiometric indicator (for example, quinhydrone-calomel electrodes in an acid-base reaction) in series with the photoconductive cell (perhaps with phenolphthalein as colour indicator). The extremely low operating voltages in this case require a galvanometer to measure the current change in the titration.

#### EXPERIMENTAL

All titrations were performed in a 400-ml beaker illuminated by a constant-intensity white light source on one side and with the 3 photocells (total area about  $1\text{ in}^2$ ) on the opposite side, the 1N2175 being mounted in a hole drilled in a 0.5-inch thick wood block with the Heliodynes



(Lafayette Radio Corp.) attached on either side. Light intensities were large enough to allow currents up to 200  $\mu\text{A}$  during a titration. Each titration was done three ways: with the Heliodynes alone (measuring voltage), with the 1N2175 cell in series with a 4.0-V battery, and with the circuit of Fig. 1. All titrations were done without benefit of filters, relying solely on the selective action of the photo cells for the 700–800  $\text{m}\mu$  region; considerable improvement might be expected if a narrow band filter appropriate to the system titrated were used.

A 200-ml portion of 0.005M copper sulphate was titrated with 0.1M EDTA,<sup>1</sup> taking current readings at 0.5-ml increments. The upper curve of Fig. 1 was obtained at slightly higher light intensity than the lower. In the acid-base titrations, 10 ml of 0.1N NaOH diluted to about 200 ml were titrated with 0.1N HCl, using a freshly prepared Kryptocyanine solution as indicator.

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**Summary**—Photometric titrations employing a photoconductive cell in series with a photovoltaic cell of approximately similar spectral response can give sharper end-points in titrations marked by an increase in transmitted light at the end-point.

**Zusammenfassung**—Eine instrumentelle Verbesserung für photometrische Titrationen mit Photozellen, die die Leitfähigkeit ändern, wird mitgeteilt. Die Photozelle wird mit einem Photoelement ähnlicher spektraler Empfindlichkeit in Serie geschaltet wodurch schärfere Endpunkte in photometrischen Titrationen erhalten werden.

**Résumé**—Les titrages photométriques utilisant une cellule photoconductrice en série avec une cellule photovoltaïque de réponse spectrale à peu près semblable peuvent donner des points équivalents plus nets, quand ceux-ci sont caractérisés par un accroissement de la lumière transmise.

#### REFERENCE

- <sup>1</sup> H. Flaschka and P. Sawyer, *Talanta*, 1961, **8**, 521.

## BOOK REVIEWS

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**Chromatography with Particular Consideration of Paper Chromatography.** E. MERCK AG, Darmstadt, Germany, 1961. pp. 185, DM 18.

THIS book, which is written in English, is the second edition of a work, of which the first edition appeared as *E. Merck, Chromatographie unter besonderer Berücksichtigung der Papierchromatographie*. Although the book contains a few quaint turns of phrase and some mis-spellings such as "anorganic" for "inorganic" on p. 5, and "jodine" for "iodine" on p. 84, it is very readable. There is a brief non-theoretical description of types of chromatography, methods of column chromatography, gas chromatography, thin-layer chromatography, and electrophoresis, but the greater part of the book (118 pages) is given over to paper chromatography. The authors state that in the main, only methods proven by them are described and the large section on the separation and identification of the constituents of many classes of organic compounds using paper chromatography should be of considerable value to chemists and biochemists.

The book contains twelve excellent plates of paper chromatograms and a list of 613 references. A most useful feature of the book is a detailed list of 139 colour reagents for paper chromatography.

Since the book is published by E. Merck AG, it is not surprising that most of the chemicals and reagents which are mentioned are those supplied by that company. However, at DM 18, the book is not expensive and should be of interest to all who may wish to employ chromatographic techniques in their work.

J. B. HEADRIDGE

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**An Introduction to Co-ordination Chemistry.** D. P. GRADDON, Pergamon Press Ltd., London, 1961. pp. 100, 25s.

THE past two decades have seen a remarkable resurgence of interest in the constitution and properties of co-ordination compounds. It is not surprising, therefore, that there should follow a number of monographs on various aspects of this rapidly growing branch of chemistry. Indeed, without the fairly frequent appearance of new texts and review articles on rather specialised topics, it would be almost impossible for research workers and teachers to keep abreast of current developments. Fortunately, several excellent books and reviews have recently become available. However, invaluable as these are to the specialist, those seeking an introduction to the subject often find them too advanced or too detailed for their purposes. It is against this background, then, that Dr. Graddon's *Introduction to Co-ordination Chemistry* makes a welcome appearance. Intended primarily for the student, it gives an exceptionally readable account of the development, the present scope and many of the more important aspects of co-ordination chemistry.

The book begins by tracing briefly the development of ideas on the constitution of complex compounds from the early eighteenth century, through Werner's classical studies, to Pauling's valence-bond theory and culminating with a simplified account of ligand-field theory. The success of the latter theory in accounting for the more outstanding features of co-ordination chemistry, *viz.* stereochemistry, magnetism, co-ordination number, *etc.*, is well illustrated. There follows a discussion of the factors determining the stabilities of complexes and an outline of the experimental methods commonly in use. The consequences of co-ordination on oxidation potentials and the stabilisation of valency states are given the emphasis they deserve. Most of the remainder of the book is devoted to an account of the constitution and bonding features of certain selected types of co-ordination compound, including carbonyls and sandwich  $\pi$ -complexes. The final chapter deals with some practical applications of complex formation.

Inevitably, in a short "introduction" the author is faced with the formidable problem of selection of material. He must omit much that is important and, to avoid confusion, must sometimes make non-rigorous generalisations so that it is not difficult to point to gaps and simplifications in this book. For example, it is to be regretted that the author felt compelled to omit an elementary account of the visible and ultraviolet spectra of transition metal ions; the treatment of ligand-field theory seems a

little bare without it. However, this book must be judged not only by its treatment of individual topics, but also by how well it presents to the newcomer an idea of the extensiveness of the occurrence of co-ordination. For too long, students have tended to regard co-ordination compounds as a rather special class featuring some unique kind of dative bond. Nowadays, on any broad definition such as emerges from a ligand-field description, co-ordination can be seen to embrace almost the whole of inorganic chemistry. Dr. Graddon's book gives a useful perspective and it will, undoubtedly, be a valuable aid to students and teachers alike.

The bibliography is adequate for the non-specialist reader and the book has been attractively produced at what is nowadays an easily accessible price for the undergraduate.

S. M. NELSON

**Computing Methods and the Phase Problem in X-Ray Crystal Analysis.** Edited by R. PEPINSKY, J. M. ROBERTSON and J. C. SPEAKMAN, Pergamon Press Ltd., 1960. pp. viii 326, 63s.

THIS book is a collection of twenty-eight papers read at the second conference on computing methods held at Glasgow in August 1960. Most of the papers are concerned with descriptions of crystallographic programmes written for a variety of computers. The machines for which programmes are given include the IBM 650 and 704, Ferranti Pegasus and Mercury, English Electric Deuce, X-RAC, Gamma 3B-AET and the Cambridge, Cardiff and Manchester University machines. The individual programmes, which are usually described in some detail, cover the whole range of structure calculations from prediction of interplanar spacings to the application of Monte Carlo methods of structure analysis.

Those papers not directly concerned with computers include discussions of direct methods of phase determination, structure factor algebra, the heavy atom method and the phase problem in protein structures.

The book represents a comprehensive account of the state of computational methods in 1960. It should prove most useful to any crystallographer requiring up-to-date information on available computer facilities and programmes.

B. J. McDONALD

**Treatise on Analytical Chemistry, Analytical Chemistry of the Elements, Volume 3 of Part II.** Edited by I. M. KOLTHOFF, and P. J. ELVING, with the assistance of E. B. SANDELL, Interscience Publishers, New York, 1961. pp. 380. \$13.25. (Subscription price \$12.00.)

ACCORDING to the editors, part II of the treatise critically reviews the analytical chemistry of the elements but is not intended to be encyclopædic. Section A deals with the analytical chemistry of the various elements. Volume 3 is divided into six parts, each treating an individual element. The authors of the material are W. C. Cooper (copper), G. B. Wengert, P. F. Reigler, and A. M. Carlson (magnesium), J. H. Kanzelmeyer (zinc), Q. Fernando and H. Freiser (cadmium), J. F. Coetzee (mercury), and M. Farnsworth and J. Pekola (tin).

The chapters are organised according to the following uniform outline: a brief discussion of the occurrence of the element, industrial processes, toxicology, a description of the important physical and chemical properties of the element, sampling procedures, separation and isolation techniques, qualitative and quantitative analysis, discussion of selected methods for the determination of the element in alloys, ores, minerals, biological samples, *etc.*, and some detailed laboratory procedures. Unfortunately, the space devoted to the material covered (36 pages to copper, 43 to magnesium, 61 to zinc, 51 to cadmium, 82 to mercury, 38 to tin), is such that the treatment of the analytical chemistry of the elements is only cursory. Thus, there are several important analytical techniques either not referred to at all or merely mentioned in passing. Examples of neglected or inadequate treatment are the determination of copper with neocuproïne, the precipitation of cadmium and zinc with benzotriazole (this reagent is mentioned in the material on copper), Umland and Hoffman's extraction method for magnesium, and the ion-exchange separation of cadmium and zinc in an iodide medium (mentioned under zinc, but not under cadmium).

With the exception of the excellent discussion of mercury, the book seems to offer little of value to the informed analyst.

J. O. HIBBITS

**Gravimetric Methods of Chemical Analysis**, in three volumes (in Hungarian). L. ERDEY. Akadémiai Kiadó, Budapest, 1960. pp. 346 + 739 + 383. 355 Hungarian Forint.

This book comprises all of the fundamental methods of gravimetric analysis, taking into consideration also the latest results in physical chemistry, in structural inorganic chemistry, in colloid science and in organic chemistry. The book is particularly opportune in connection with the rapid development of nuclear chemistry. This is because gravimetric analysis, regarded as micropreparative chemistry and "the science of separations," has found an extremely important field of application in nuclear chemistry.

The author discusses all of the methods critically and selects those which have particular practical importance. Results of control measurements made for critical treatment are included in tables. Most of the precipitates were investigated by means of differential thermogravimetric methods developed by the author and his co-workers.

In *Volume I*, after the introductory chapter, the author deals in detail with the successive operations of gravimetric analysis: sampling, preparation of sample, weighing, solution, fusion (the theory of high-temperature reactions is also presented), ashing and destruction of organic substances, precipitation, filtration and washing, thermal treatment of precipitates (TG, DTA and DTG methods), drying and ignition of the precipitate and weighing of the residue, calculation of errors. In the third chapter methods of separation are dealt with: fractional precipitation, organic reagents (a short but concise summary is given on the theory of complex compounds), selective dissolution, extraction (with a thorough theoretical treatment), ion-exchange resins and ion-exchange chromatography, adsorption-, partition- and paper chromatography, separation of volatile substances, indirect analysis (with an extensive mathematical treatment) and electrogravimetry (with all of its theoretical and practical problems). This Volume includes also gravimetric methods for the determination of water in solids.

In *Volume II* methods for the determination of metals are included. In some special cases micro and semimicro methods are mentioned too. Discussion of the cations follows the order of the analytical groups. The construction of each chapter is as follows: a Table (including all of the forms used for determination and the most important data for precipitation and thermal treatment), references to the methods, the forms of occurrence of the metal, preparation of the sample, detailed discussion of the procedures, thermoanalytical curves, and the accuracy of the methods. In addition, the selection of the most convenient method, the elimination of interferences, the solubility and morphology of the precipitates, the selectivity, and, finally, the methods for separation are presented. The total analysis of some raw materials and products of technological importance is discussed.

In *Volume III* are given methods for the anions. The analysis of substances containing Cl, Br, I, F, CN, SCN, S, N, P, C, Si and B, in the presence of the most frequently occurring and interfering components, is discussed, and the solution of many practical problems is presented. There is a very good summary of methods for the determination of S and Cl in organic compounds.

The appendix contains useful instructions for the handling and calculation of results.

The book is very valuable both from the theoretical and practical points of view, and, equally, both to trained experts and to beginners in analytical practice. It is an outstanding and extremely important contribution to the literature of analytical chemistry. Its translation into English and German is in progress.

E. KÖRÖS

## NOTICES

(Material for this section should be sent directly to the Associate Editor)

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### ARGENTINA

*Sunday-Saturday 16-22 September 1962: Eighth Latin-American Congress of Chemistry*, on the occasion of the *Fiftieth Anniversary of Asociación Química Argentina*. Buenos Aires (see also *Talanta*, 1961, 8, 909).

During the congress there will be delivered a series of general lectures by distinguished chemists, including:

Professor Dr. ING. F. FEIGEL  
(Brazil)

*Progress in the Spot Test Reactions of Organic Substances.*

The Section on Analytical Chemistry and Applied Analytical Chemistry has arranged special working sessions in *Catalytic Reactions induced in Analytical Chemistry* and *Optical Instrument Methods*. Latin American chemists interested in these sessions are asked to advise the Congress Organising Committee as soon as possible so that they may be placed in contact with the session organisers.

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### SOUTH AFRICA

*Monday-Wednesday 2-11 July 1962: Golden Jubilee Convention: South African Chemical Institute*. Johannesburg, Pretoria and Vereeniging areas.

The programme will include symposia on catalysis, reaction kinetics, crystal structure, chromatography, natural products, inorganic chemistry, analytical chemistry, biochemistry and chemical education.

Further information may be obtained from: Secretary, South African Chemical Institute, P.O. Box 3361, Johannesburg, South Africa.

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### UNITED KINGDOM

*Wednesday 7 March 1962: Annual General Meeting* followed by the **Bernard Dyer Memorial Lecture: Research and the National Economy**: Dr. D. W. HILL: *Society for Analytical Chemistry*. Midland Hotel, Manchester. 4.30 p.m.

*Thursday 8 March 1962: Annual General Meeting: Society for Analytical Chemistry, Midlands Section*. Regent House, Birmingham, 3. 6.30 p.m.

*Monday 12 March 1962: Recent Advances in Infrared Spectroscopy*: Dr. L. G. BELLAMY: *Royal Institute of Chemistry, Leeds Area Section*. Bradford Institute of Technology.

*Friday 16 March 1962: Fluorescence*: Dr. R. J. OTTER and Dr. C. A. PARKER: *Society for Analytical Chemistry, Physical Methods Group and Western Section, and Royal Institute of Chemistry, South Wales Section*. University College, Singleton Park, Swansea.

*Friday 23 March 1962: The History of Food Technology*: Mr. T. McLACHLAN: *Society for Analytical Chemistry, Scottish Section*. Royal College of Science and Technology, George Street, Glasgow. 7.15 p.m.

*Wednesday 28 March 1962: Discussion Meeting: Society for Analytical Chemistry, Microchemistry Group. The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

*Thursday 29 March 1962: Applications of Radio-Isotopes in Analysis*: Dr. D. GIBBONS: *Society for Analytical Chemistry, Midlands Section*. Technical College, Nottingham. 7.00 p.m.

*Thursday 29 March 1962: Steric Hindrance in Analytical Chemistry*: Professor H. M. N. H. IRVING: *Society of Chemical Industry, Liverpool Section, and Royal Institute of Chemistry, Liverpool Section and College Chemical and Physical Society, Carlett Park College of Further Education, Eastham, Wirral*. 7.00 p.m.

*Wednesday-Saturday 28-31 March 1962: Conference on Molecular Spectroscopy: Institute of Petroleum, Hydrocarbon Research Group*. William Beveridge Hall, Senate House, University of London, W.C.1. (see also *Talanta*, 1962, 9, 93).

Monday–Friday 9–13 April 1962: **Feigl Anniversary Symposium: Society for Analytical Chemistry, Midlands Section**, under the patronage of *I.U.P.A.C.* University, Edgbaston, Birmingham, 15 (see also *Talanta*, 1961, 8, 561, 765 and 911).

The following additions and minor alterations to the scientific programme have been made:

- I. P. ALIMARIN and O. M. PETRUKHIN (Moscow State University, U.S.S.R.) *Extraction of Inner Complex Compounds of Rare Elements with N-Benzoylphenylhydroxylamine. Contribution to Organic Spot Test Analysis.*
- J. R. AMARAL (Ministry of Agriculture, Rio de Janeiro, Brazil) *Studies on S-Benzylthiouonium Salts and p-Bromophenacyl Esters for Identification of Organic Acids. Spot-Testing for Transuranic Elements.*
- J. BERGER (Danish School of Pharmacy, Denmark) *Spectrophotometric Determination of Traces of Silver. Utilisation de l'extraction pour le dosage des traces par diverses méthodes instrumentales. Atomic Absorption Spectroscopy in Metallurgical Analysis.*
- F. CLANET (Atomic Energy Commission, Paris, France) *Steric Hindrance in Analytical Chemistry with Special Reference to Analogues of 8-Hydroxyquinoline. Tetrazolium Salts in Qualitative Colorimetric Analysis.*
- R. M. DAGNALL and T. S. WEST (University of Birmingham, U.K.) *Physical-Chemical Investigation of New Complexans and their Analytical Applications. (to be arranged).*
- L. DUCRET (C.N.E.T. Laboratory, Paris, France) *Trace Analysis by Spectrochemical Methods.*
- W. T. ELWELL and J. F. GIDLEY (Imperial Metal Industries Ltd.) *Luminescence of Piazselenols: A New Fluorimetric Reagent for Selenium.*
- H. M. N. H. IRVING (University of Leeds, U.K.) *New Spectrophotometric Methods for the Determination of Rhenium based on its Complexing. Increase of Limit of Identification using Collectors.*
- C. A. JOHNSON (Boots Pure Drug Co., Nottingham, U.K.) *Biographer of Professor Fritz Feigl.*
- R. P. LASTOVFKII (Institute of Chemical Reagents, Moscow, U.S.S.R.) *Survey of Methods for the Identification of Carboxylic Acids and Esters. Semi-Quantitative Analysis by Spot Reactions: A Review and New Reagents. Hydrogen Peroxide as an Analytical Reagent.*
- A. G. LLACER (University of Rosario, Argentina) *Separation and Identification of Some Anions on the Microgram Scale.*
- R. L. MITCHELL (Macaulay Institute of Soil Research, Aberdeen, U.K.) *Recent Developments in X-Ray Fluorescence Analysis.*
- C. A. PARKER and L. G. HARVEY (Admiralty Materials Laboratory, Holton Heath, Poole, U.K.)
- D. I. RYABCHIPKOBV and L. V. BORISOVA (Moscow State University, U.S.S.R.)
- E. SCHULEK, Zs. REMPÖRT-HORVATH, A. LASZTITY and E. KÖRÖS (L. Eötvös University, Budapest, Hungary)
- H. SUTER (Celanese Chemical Co., Clarkwood, Texas, U.S.A.)
- S. VIEBEL (Polytechnic Institute, Copenhagen, Denmark)
- H. WEISZ (University of Freiburg-Breisgau, Germany)
- C. WHALLEY (Laporte Chemicals Ltd., Luton, U.K.)
- C. L. WILSON and F. HABA (Queen's University, Belfast, N. Ireland)
- H. N. WILSON and R. J. OTTER (I.C.I. Ltd., Billingham Division, U.K.)

The following lecturers have unfortunately had to withdraw from the symposium: G. V. M. DUYNCHAERTS, H. FREISER and I. M. KOLTHOFF. The paper to be delivered by A. C. Menzies will be read by R. Lockyer.

The following speakers have been invited to contribute to the discussion on *Teaching of Analytical Chemistry*:

L. ERDEY	H. MALISSA	L. OTTENDORFER
H. WEISZ	P. W. WEST	C. L. WILSON
		J. ZYKA

The seventeenth Annual General Meeting of the Biological Methods Group of the Society for Analytical Chemistry was held on Thursday 14 December 1961 at *The Feathers*, Tudor Street, London, E.C.4. Mr. W. A. Broom presided.

The following were elected Officers of the Group for the forthcoming year:

*Chairman:* Mr. J. S. Simpson

*Vice-Chairman:* Mr. W. A. Broom

*Hon. Secretary and Treasurer:* Mr. K. L. Smith, Standards Department, Boots Pure Drug Co., Ltd. Nottingham, England.

The Annual General Meeting of the *Western Section, Society for Analytical Chemistry*, was held at University College, Cardiff, on Friday, 12 January, 1962.

The following were elected Officers of the Section for the forthcoming year:—

*Chairman:* Dr. F. H. POLLARD

*Vice-Chairman:* Mr. E. A. HONTOIR

*Hon. Secretary and Treasurer:* Dr. T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

#### UNITED STATES OF AMERICA

*Thursday 15 February 1962: Trace Analysis Utilising Gas Chromatography:* Dr. D. A. MAKAY: *Metropolitan Microchemical Society.*

*Friday–Saturday 2–3 March 1962: Third Conference on Experimental Aspects of NMR Spectroscopy.* Mellon Institute, Pittsburgh, Pa.

*Monday–Friday 5–9 March 1962: Thirteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:* *Analytical Chemistry Group of Pittsburgh Section, American Chemical Society and Spectroscopy Society of Pittsburgh.* Penn-Sheraton Hotel.

*Thursday 15 March 1962: An Approach to the Microdetermination of Carbon and Hydrogen:* Dr. H. F. HABER: *Metropolitan Chemical Society.*

*Tuesday–Thursday 20–29 March 1962: American Chemical Society, 141st National Meeting.* Washington D.C.

*Wednesday–Friday 13–15 June 1962: Analytical Automation and Data Processing: Annual Summer Symposium of Division of Analytical Chemistry, American Chemical Society and Analytical Chemistry.* College Park, Maryland.

The tentative programme is as follows:

W. J. BLAEDEL	<i>Automatic Enzyme Procedures.</i>
H. FREUND	<i>Continuous Automation Systems.</i>
K. W. GARDINER	<i>An Automated Instrumental Approach to Classical Chemical Analysis.</i>
J. HEIGL and A. L. MACRITCHIE	<i>Data Handling Systems for Gas Chromatography.</i>
D. R. JOHNSON, J. W. CASSELS, E. G. BRAME and D. F. WESTNEAT	<i>Automated Infrared Analysis of Polymer Films.</i>
H. J. NOEBELS	<i>Automated and Automatic Laboratory Analytical Equipment.</i>
H. PURDUE	<i>Automatic Potentiometric Reaction Rate Method—Microdetermination of Cystine.</i>
A. SAVITZKY	<i>Some Numerical Operations on Analytical Data.</i>
B. F. SCRIBNER	<i>Experience with Direct Reading Spectrometers.</i>
R. STELZNER	<i>Some Direct Readout and Linearisation Circuits in Analytical Laboratory Instrumentation.</i>
D. THOMAS	<i>Infrared Spectral Data Retrieval by Digital Techniques.</i>
R. E. WAINERDI	<i>Automatic Activation Analysis.</i>

Further information may be obtained from Dr. LEWIS H. ROGERS, Vitro Laboratories, West Orange Laboratory, 200 Pleasant Valley Way, West Orange, N.J.

Upon his retirement from Brooklyn College, Dr. N. CHERONIS was awarded an Honorary Membership and Scroll for outstanding contributions to the *Metropolitan Microchemical Society*. The award was presented at the Society's regular monthly meeting on January 18, 1962.

## PAPERS RECEIVED

- An automatic analyser for hypophosphite with particular reference to electrodeless plating solutions  
S. GREENFIELD and R. M. COOPER. (2 December 1961).
- Colorimetric estimation of cobalt as the thiocyanate complex—Part I: Use of 2-picoline as the complexing agent in aqueous solutions: M. R. VERMA and P. K. GUPTA. (5 December 1961).
- Colorimetric estimation of cobalt as the thiocyanate complex—Part II: Use of tri-n-butyl phosphate as extractant for the complex: M. R. VERMA and P. K. GUPTA. (5 December 1961).
- Indirect derivatographic determination of calcium, strontium and barium ions in the presence of one another: L. ERDEY, G. LIPTAY, G. SVEHLA and E. PAULIK. (6 December 1961).
- An investigation by electron-spin resonance of the redox indicator Variamine Blue: L. ERDEY and R. C. PINK. (7 December 1961).
- Untersuchung der Kationensorption aus Komplexanmedium III: Chromatographische Trennung von Strontium und Barium: ZDENĚK ŠULCEK, PAVEL POVONDRA und RICHARD ŠTANGL. (15 December 1961).
- The separation and determination of chromium, tungsten, molybdenum and vanadium by partition chromatography: A. S. WITWIT, R. J. MAGEE and C. L. WILSON. (19 December 1961).
- Determination of <sup>90</sup>strontium in bone: HARRY FOREMAN and M. B. ROBERTS. (20 December 1961).

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## ERRATA—Volume 9

- Page 1, last line of summary: the formula should read  $(\text{NH}_4)_3[\text{Sc}(\text{C}_8\text{H}_8\text{O}_3)_3]$ .
- Page 9, footnote: the reference should read *Zhur. analit. Khim.*, 1959, 14(5), 574.
- Page 26, line 2: for Sajó method<sup>a</sup> read Sajó method<sup>b</sup>.
- Page 76, footnote: the reference should read *Talanta*, 1961, 8, 720.





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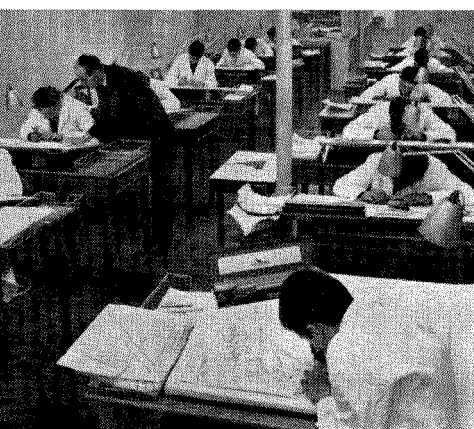
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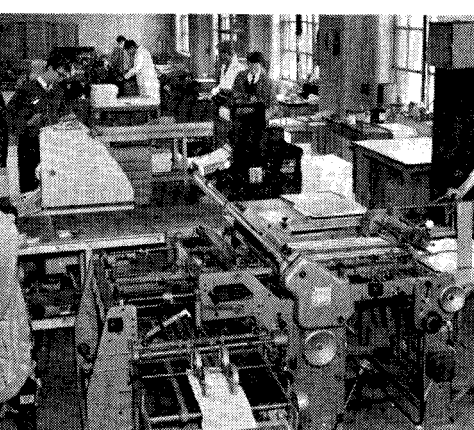
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