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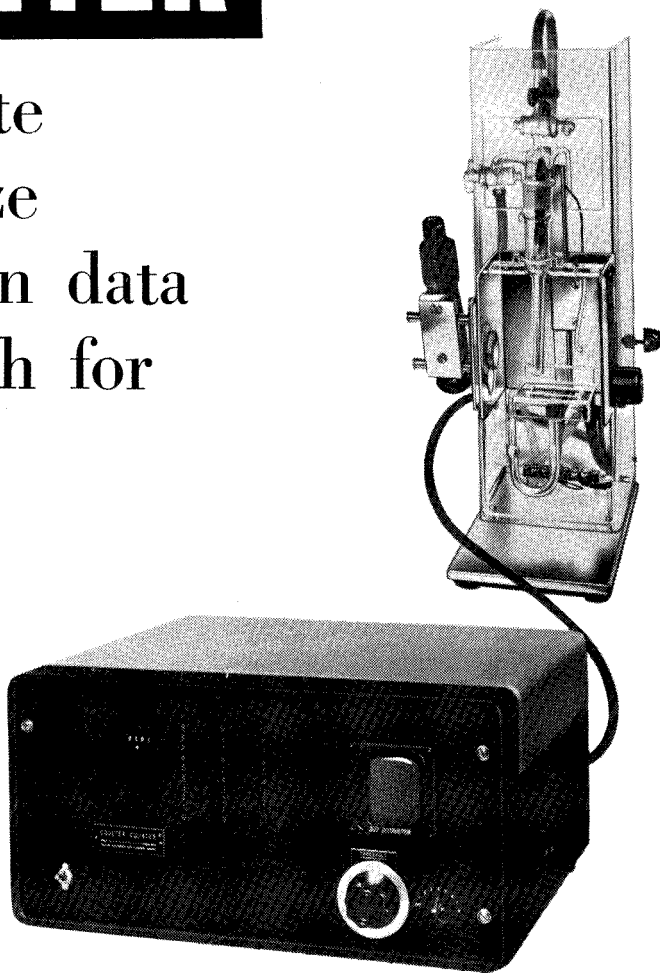
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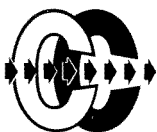
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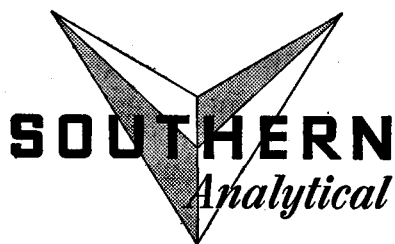
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STUDY OF THE REDUCTION WAVES OF THE ISOMERS OF NITROPHENOL BY MEANS OF THE ALTERNATING CURRENT POLAROGRAPH

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(Received 2 May 1960; Accepted 30 October 1960)

Summary—In a study of the a.c. polarography of *o*-, *m*- and *p*-nitrophenols it was found that the wave heights were proportional to the concentrations of nitrophenols in potassium hydroxide and ammonium chloride-ammonium hydroxide base solutions. The reduction waves for d.c. polarograms in certain base solutions were not solely diffusion-controlled. This applied to the first wave of *p*-nitrophenol in 0.2*M* or stronger potassium hydroxide and in sodium carbonate solutions, and similarly to *m*-nitrophenol in 0.5*M* to 0.8*M* potassium hydroxide solutions and *o*-nitrophenol in solutions in the pH range 4–7. Because the a.c. polarograms are purely diffusion-controlled such polarography is preferred to d.c. polarography for the determination of nitrophenol isomers.

INTRODUCTION

THE reduction waves of the three isomers of nitrophenol (*o*-, *m*- and *p*-nitrophenol) have been studied extensively by means of the direct current polarograph. The values of the half-wave potentials in many supporting electrolytes of various pH values have been measured and the existence of two reduction waves due to the undissociated and dissociated nitrophenol was established by Shikata and Watanabe.¹ Astle and McConnel² and Oeshpande and Parthasarathy³ discussed the difference between the polarographic behaviour of *p*- and *o*-nitrophenols in acidic solution. They concluded that through hydrogen bonding *o*-nitrophenol forms intermolecular compounds which are stable during the polarographic reduction in acidic solution.

In the present paper, the authors describe the a.c. polarographic behaviour of nitrophenol isomers, keeping in mind its possible application to chemical analysis.

Since the a.c. polarograms of *o*-, *m*- and *p*-nitrophenols showed higher wave heights in alkaline solution than in acidic solution, mainly alkaline base solutions were employed for this work.

The a.c. polarograms of nitrophenol isomers in alkaline solutions were found to be solely diffusion-controlled.

EXPERIMENTAL

Apparatus

The self-recording d.c. and a.c. polarographs used were constructed in our laboratory; details have already been reported.⁴ In the present experiments, except in a few cases, addition of gelatine to the supporting electrolytes was not made. An agar-agar bridge was used for the connection between sample solution and calomel electrode.

Hydrogen gas was employed for the removal of the dissolved oxygen. The a.c. voltage superimposed on the d.c. voltage was 10 mV and the other conditions were as follows:

Capacity of the standard condenser (*C*_s) = 0.2 μ F.

Standard resistance (*R*_s) = 0.5 K Ω .

Mercury drop rate (*m*) = 2.79 mg/sec.

Mercury drop time (*t*) = 4 sec (in 1*N* KOH solution and at -1.0 V).

RESULTS

(1) *p*-Nitrophenol

(i) *A.c. and d.c. polarograms in sodium carbonate and sodium phosphate solutions.*

Fig. 1 shows the a.c. (a) and d.c. (d) polarograms of *p*-nitrophenol in 0.25*M* sodium carbonate solution. These polarograms indicate the existence of two reduction waves.

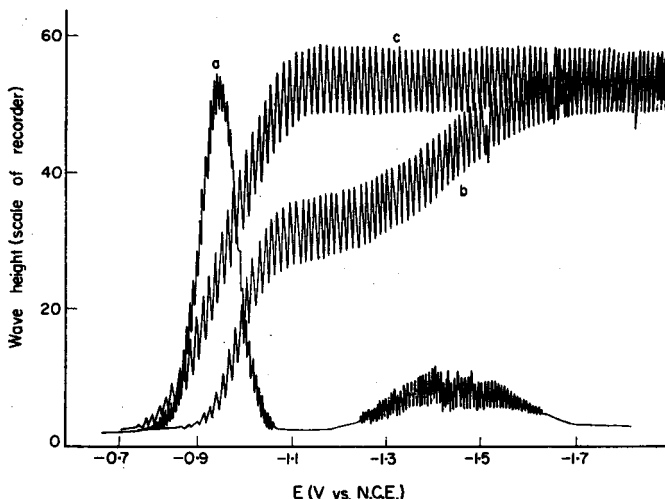


FIG. 1.—d.c. and a.c. polarograms of 1*mM* *p*-nitrophenol
 (a) a.c. polarogram in 0.25*M* sodium carbonate solution
 (scale, 20 = 0.4 mV)
 (b) d.c. polarogram in 0.25*M* sodium carbonate solution with 0.001 % gelatine
 (scale, 20 = 12 μ A)
 (c) d.c. polarogram in 1.8 % sodium borate solution with 0.001 % gelatine
 (scale, 20 = 12 μ A)
 Temp. 25°

The first wave has its peak potential at -0.94 V v. NCE and the second wave that at -1.42 V v. NCE in the a.c. polarogram. In the d.c. polarogram (with 0.001 % gelatine) the half-wave potential of the first wave is at -0.99 V v. NCE and its total wave height is almost equal to that of the single wave height of the d.c. polarogram (c) in 1.8 % sodium borate solution (pH 9.8) with 0.001 % gelatine. Table I shows the

TABLE I.—RELATIONSHIP BETWEEN THE FIRST "WAVE HEIGHTS" IN D.C. AND A.C. POLAROGRAMS AND THE CONCENTRATION OF SODIUM CARBONATE

Concentration of Na ₂ CO ₃ , <i>M</i>		0.5	0.25	0.1
The first "wave height"	d.c., μ A	19.8	17.4	15.6
	a.c., mV	1.04	1.02	1.00

relationship between the first "wave heights" in d.c. and a.c. polarograms and the concentration of sodium carbonate.

According to Table I, the first "wave height" of the d.c. polarogram increases with the concentration of the supporting electrolyte, but that of the a.c. polarogram remains almost constant. Similar results were found in the case of 0.35*M* sodium phosphate

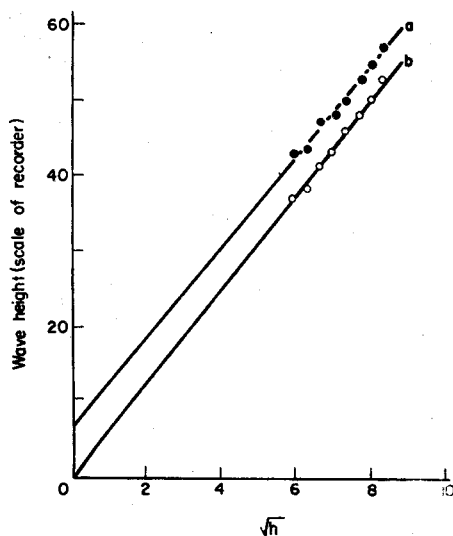
TABLE II.—RELATIONSHIP BETWEEN THE “WAVE HEIGHTS” OF A.C. AND D.C. POLAROGRAMS AND pH IN SODIUM PHOSPHATE SOLUTION

pH	12.8	12.6	12.3	12.0	11.5
The first “wave height” a.c., mV	1.04	1.04	0.99	0.97	0.88
d.c., μA	15.0	15.0	15.2	17.8	21.0

solution. However, Table II shows the “wave heights” obtained for a.c. and d.c. polarograms using sodium phosphate solution of different pH values.

In the above experiment the pH value was changed by addition of disodium orthophosphate to trisodium orthophosphate, but the total concentration of phosphate was held constant (0.35M). As shown in Table II, the height of the first wave of the a.c. polarogram increases with pH, but that of the d.c. polarogram decreases.

Fig. 2 shows the relationship between the height of the first wave of the d.c. polarogram of *p*-nitrophenol in 0.50M sodium carbonate solution and \sqrt{h} . The line (a) does not pass through the origin. The control line (b) which refers to the “wave height” of 1mM lead nitrate in 0.2N potassium hydroxide solution, passes through the origin. It is considered that the first waves of d.c. polarograms of *p*-nitrophenol

FIG. 2.—Relationship between wave height of the d.c. polarogram and \sqrt{h} .

(a) 1mM *p*-nitrophenol in 0.5M sodium carbonate solution
(scale, 20 = 12 μA)

(b) 1mM cadmium sulphate in 0.5N NH_4OH –0.5M NH_4Cl solution
(scale, 20 = 12 μA)

Temp. 25°

in sodium carbonate or trisodium orthophosphate solutions include the kinetic current are not solely diffusion-controlled.

(ii) *A.c. and d.c. polarograms in potassium hydroxide solution*: The a.c. and d.c. polarograms of *p*-nitrophenol show two reduction waves in potassium hydroxide solution as in the case of sodium carbonate or trisodium orthophosphate solution.

TABLE III.—HALF-WAVE POTENTIAL AND PEAK POTENTIAL OF *p*-NITROPHENOL IN POTASSIUM HYDROXIDE SOLUTION

Concentration of KOH, <i>N</i>		1	0.1
Peak potential, a.c. V	First wave	-0.915	-0.94
	Second wave	-1.45	-1.64
Half-wave potential, d.c. V	First wave	-0.97	-0.96
	Second wave	-1.53	-1.53

Table III gives the half-wave potentials and the peak potentials for *p*-nitrophenol in 1*N* and 0.1*N* potassium hydroxide respectively.

In Fig. 3, the polarograms (a) and (b) show the a.c. polarograms in 1*N* and 0.2*N* potassium hydroxide solutions and (a') and (b') show the d.c. polarograms in these solutions. From a comparison between them, it is found that the first "wave height"

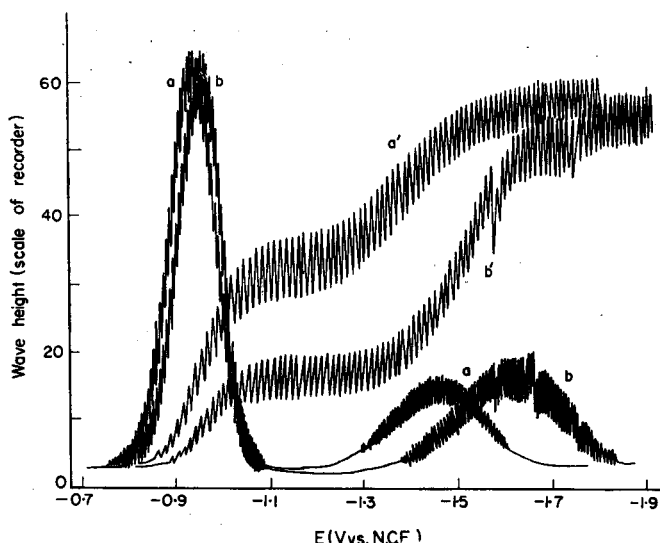


FIG. 3.—a.c. and d.c. polarogram of 1*mM* *p*-nitrophenol in potassium hydroxide solution
 (a) a.c. polarogram in 1*N* KOH (scale, 20 = 0.4 mV)
 (a') d.c. polarogram in 1*N* KOH (scale, 20 = 12 μ A)
 (b) a.c. polarogram in 0.2*N* KOH (scale, 20 = 0.4 mV)
 (b') d.c. polarogram in 0.2*N* KOH (scale, 20 = 12 μ A)
 Temp. 25°

is smaller than the second "wave height" in the d.c. polarograms but in the a.c. polarograms the first "wave height" is much greater than the second "wave height". The effect is more noticeable in more dilute potassium hydroxide solution. The first "wave height" in the d.c. polarograms increases with the concentration of potassium hydroxide, as with sodium carbonate or trisodium orthophosphate solutions (see Fig. 4). The first wave for the a.c. polarograms is unaffected by the concentration of potassium hydroxide (see Table IV).

The first "wave height" in the d.c. polarograms also increases with concentration

TABLE IV.—THE CHANGE OF THE FIRST-WAVE HEIGHT OF A.C. AND D.C. POLAROGRAMS WITH THE CONCENTRATION OF POTASSIUM HYDROXIDE

Concentration of KOH, <i>N</i>	0.2	0.7	1.0
The first "wave height" a.c., mV	1.20	—	1.22
d.c., μA	10.7	13.5	16.4

of salts such as potassium nitrate, sodium chloride, potassium bromide, added to 0.2*N* potassium hydroxide solution, but the "wave height" for the a.c. polarograms shows no change. The addition of 0.001% gelatine has little effect on the first and second "wave heights" of the d.c. polarogram but suppresses the maximum phenomenon of the second wave.

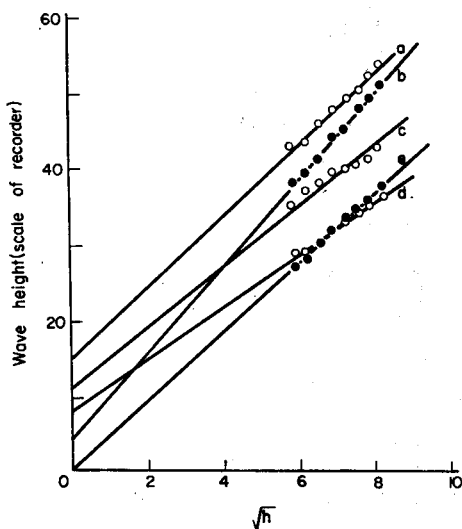


FIG. 4.—Relationship between wave height of d.c. polarogram and \sqrt{h} (1*mM* *p*-nitrophenol in KOH of various concentrations)

- (a) in 0.2*N* KOH + 0.2*M* NaCl
- (b) in 0.2*N* KOH
- (c) in 1*M* KOH
- (d) in 0.1*N* KOH + 0.9*M* NaCl
- (e) in 0.1*N* KOH
(scale, 20 = 12 μA) Temp. 25°

Fig. 4 shows the relationship between the first "wave heights" of the d.c. polarograms of 1*mM* *p*-nitrophenol in potassium hydroxide solution and \sqrt{h} . The line (e), which refers to the d.c. polarogram in 0.1*N* potassium hydroxide solution, passes through the origin, so that the first wave of *p*-nitrophenol is solely diffusion-controlled in this solution. However, if 0.9*M* sodium chloride is added to 0.1*N* potassium hydroxide the line (d) deviates from the origin, showing the addition of the kinetic current to the diffusion current. This also applies to the d.c. polarograms in KOH solutions of higher concentration than 0.1*N*. From the relatively small change of the first "wave height" in a.c. polarograms it is evident that a.c. polarography is free from kinetic current.

(2) *m*-Nitrophenol (in 1% methyl alcohol)

A.c. and d.c. polarograms in potassium hydroxide solution: Fig. 5 shows the a.c. and d.c. polarograms of 1mM *m*-nitrophenol in potassium hydroxide solution. In 0.2*N* potassium hydroxide solution the d.c. polarogram (a) does not show the first and second waves distinctly, but the a.c. polarogram (a') shows two distinct reduction waves (the first peak at -0.82 V, the second peak at -1.24 V v. NCE). However, in 1*N* potassium hydroxide solution, the a.c. and d.c. polarograms show the single wave (a.c. peak potential at -0.78 V, d.c. half-wave potential at -0.79 V). The wave height of the d.c. polarogram of *m*-nitrophenol is about two thirds that of *p*-nitrophenol

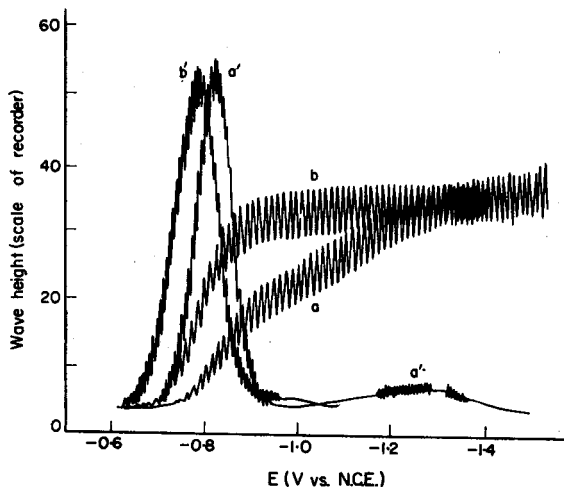


FIG. 5.—d.c. and a.c. polarograms of 1mM *m*-nitrophenol
 (a) d.c. polarogram in 0.2*N* KOH (scale, 20 = 12 μ A)
 (a') a.c. polarogram in 0.2*N* KOH (scale, 20 = 0.4 mV)
 (b) d.c. polarogram in 1*N* KOH (scale, 20 = 12 μ A)
 (b') a.c. polarogram in 1*N* KOH (scale, 20 = 0.4 mV)
 Temp. 25°

under similar conditions, but the a.c. peak height of *m*-nitrophenol is equal to that of *p*-nitrophenol and does not change with the concentration of potassium hydroxide solution.

Also it was found that the d.c. polarogram of *m*-nitrophenol in 0.1*N* potassium hydroxide solution shows a single wave instead of two reduction waves when about 0.6*M* solutions of such salts as sodium chloride, or potassium nitrate are present.

Fig. 6 shows the relationship between the wave height of 1 mM *m*-nitrophenol in 0.5*N* ammonium hydroxide solution and \sqrt{h} . The line (a) passes the origin, but other lines (b), (c), (d) such as those in 0.5*N* ammonium hydroxide and 0.4*M* sodium chloride solution, 0.8*N* or 0.5*N* potassium hydroxide solutions, do not pass through the origin, so that they are contaminated with the kinetic current. As a check the polarography of 1mM cadmium sulphate in 0.5*M* ammonium chloride-ammonium hydroxide solution was examined soon after the above experiment and it was confirmed that the line for wave height plotted against \sqrt{h} passed through the origin.

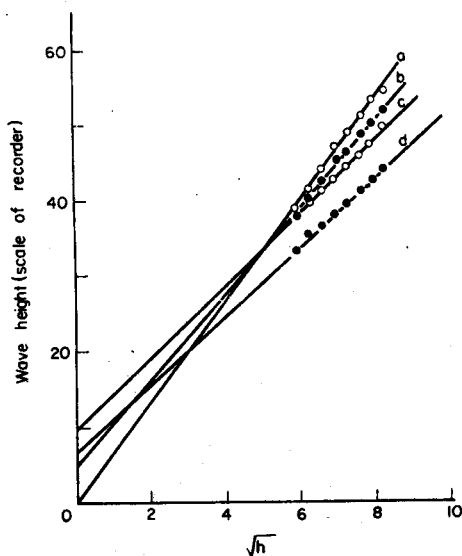


FIG. 6.—Relationship between the wave height of the d.c. polarogram of *m*-nitrophenol and \sqrt{h} .

- (a) 1mM *m*-nitrophenol in 0.5N NH_4OH (scale, 20 = 8 μA)
 (b) 1mM *m*-nitrophenol in 0.5N NH_4OH + 0.4M NaCl (scale, 20 = 8 μA)
 (c) 0.5mM *m*-nitrophenol in 0.8N KOH (scale, 20 = 4 μA)
 (d) 1mM *m*-nitrophenol in 0.5N KOH (scale, 20 = 8 μA)
 Temp. 25°

(3) *o*-Nitrophenol (in 1% methyl alcohol)

(i) *A.c. and d.c. polarograms in potassium hydroxide solution:* Fig. 7 shows the a.c. and d.c. polarograms of 1mM *o*-nitrophenol in 1N and 0.1N potassium hydroxide solutions. In 1N potassium hydroxide solution the d.c. polarogram (a') is obviously a single wave (half-wave potential at -0.89 V) with a height almost equal to the total "wave height" of the d.c. polarogram of 1mM *p*-nitrophenol in 1N potassium hydroxide solution. The a.c. polarogram (a) of *o*-nitrophenol shows a lower peak height (at -0.92 V) than does either *p*- or *m*-nitrophenol, and for a concentration of less than 0.5N potassium hydroxide the a.c. polarogram (b) of *o*-nitrophenol shows two distinct reduction waves (the first peak at -0.88 V, the second peak at 1.01 V), while the d.c. polarogram (b') shows still only a single wave (half-wave potential at -0.87 V).

(ii) *Relationship between wave height of d.c. polarograms in potassium hydroxide solution and \sqrt{h} :* Fig. 8 shows the relationship between the "wave height" of d.c. polarograms of 1mM *o*-nitrophenol in 0.2N potassium hydroxide or 0.5M ammonium chloride-ammonium hydroxide solution and \sqrt{h} . The lines (a) and (b) pass through the origin as indicated in Fig. 8 and it is confirmed that their limiting currents are evidently diffusion-controlled.

The d.c. polarogram of 1mM *o*-nitrophenol shows a lower "wave height" in acetic acid-sodium acetate solution (pH 4 ~ 6, the total amount of acetate ion being 0.5M) than in 0.2N potassium hydroxide solution. The relationship between the "wave heights" and \sqrt{h} is given in curves (c), (d) and (e) in Fig. 8, which do not pass through the origin. However, at pH 9 the curve passes through the origin and the "wave

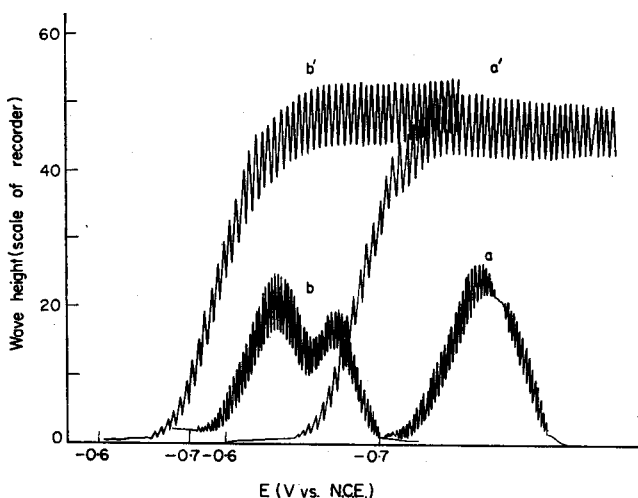


FIG. 7.—a.c. and d.c. polarogram of $1mM$ *o*-nitrophenol
 (a) a.c. polarogram in $1N$ KOH (scale, $20 = 0.4$ mV)
 (a') d.c. polarogram in $1N$ KOH (scale, $20 = 12 \mu A$)
 (b) a.c. polarogram in $0.1N$ KOH (scale, $20 = 0.4$ mV)
 (b') d.c. polarogram in $0.1N$ KOH (scale, $20 = 12 \mu A$)
 Temp. 25°

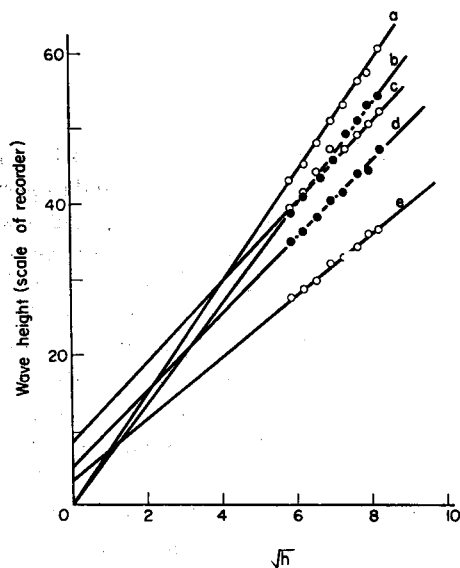


FIG. 8.—Relationship between wave height and \sqrt{h} ($1mM$ *o*-nitrophenol)
 (a) in $0.2N$ KOH (scale, $20 = 12 \mu A$)
 (b) in $0.5N$ $NH_4OH + 0.5M$ NH_4Cl (pH 9)
 (c) in NaAc + HAc (pH 7) (scale, $20 = 8 \mu A$)
 (d) in NaAc + HAc (pH 4) (scale, $20 = 8 \mu A$)
 (e) in NaAc + HAc (pH 6) (scale, $20 = 12 \mu A$)
 Temp. 25°

height" is near that obtained in 0.2*N* potassium hydroxide solution. Therefore it is evident that the d.c. polarogram of *o*-nitrophenol is contaminated with the kinetic current in the range pH 4 ~ 7, but free of the kinetic current and solely controlled by diffusion at a pH above 9.

(iii) *Relationship between the "wave height" in a.c. polarograms and concentration of o-, m-, and p-nitrophenol:* Fig. 9 shows the calibration curves for *o*-, *m*-, and *p*-nitrophenols in 0.2*N* and 2*N* potassium hydroxide solutions in the a.c. polarograms. The curves pass through the origin, and show a linear relationship between the concentrations of nitrophenol isomers and their "wave heights."

DISCUSSION

p-Nitrophenol is reduced on the electrode surface to *p*-aminophenol. *o*-Nitrophenol gives the same magnitude of wave height as *p*-nitrophenol at a pH above 9, so that it should be reduced to *o*-aminophenol in a parallel way to *p*-nitrophenol. But at a pH below 9, *o*-nitrophenol gives a low wave height so that the electrode reduction is apparently not so complete.³ The present study shows that the reduction is not solely diffusion-controlled.

m-Nitrophenol shows a lower "wave height" than *p*-nitrophenol, which can be reduced completely to *p*-aminophenol. The present study shows that the reduction wave of *m*-nitrophenol is solely diffusion-controlled in 0.5*N* or 0.8*N* potassium hydroxide, and in 0.5*M* ammonium hydroxide and 0.4*M* sodium chloride solutions.

The d.c. polarograms of *p*-nitrophenol show two reduction waves in 0.2*N* ~ 1*N*

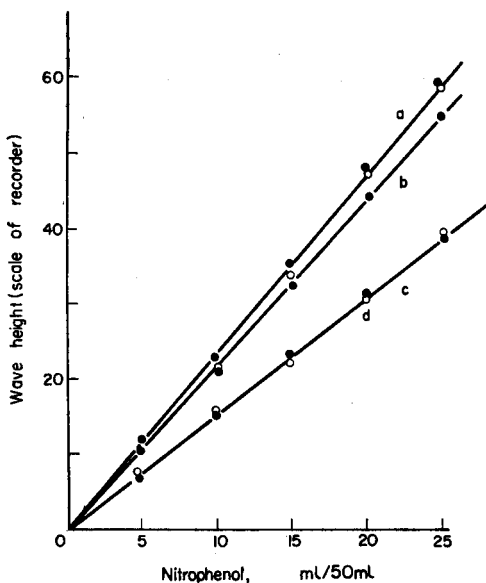


Fig. 9.—Calibration curves of nitrophenol isomers by a.c. polarography

- (a) 2.5 *mM* *m*-, and 2 *mM* *p*-nitrophenols in 0.2*N* KOH
(scale, 20 = 0.4 mV)
(b) 2 *mM* *p*-nitrophenol in 2*N* KOH (scale, 20 = 0.4 mV)
(c) 2 *mM* *m*-nitrophenol in 2*N* KOH (scale, 20 = 0.4 mV)
(d) 2 *mM* *o*-nitrophenol in 0.5*N* NH₄OH-0.5*M* NH₄Cl
(scale, 20 = 0.2 mV)

Temp. 25°

แผนกห้องสมุด กรมวิทยาศาสตร์
กระทรวงอุตสาหกรรม

potassium hydroxide solution and its first wave includes the kinetic current. Therefore it is considered that it is impossible to interpret the electrode reaction correctly since the reduction wave includes the kinetic current. Since the kinetic current refers to the relative rate of equilibration, it is concluded that in these solutions the isomers exist in different states, which are in mutual equilibrium.

From the viewpoint of analytical chemistry, a.c. polarography is more easily adapted for the polarographic determination of nitrophenol isomers than d.c. polarography, because the former is free from the kinetic current. There is a good linear relationship between the concentrations of the isomers and wave heights, which does not change with the concentration of supporting electrolytes such as potassium hydroxide.

Zusammenfassung—Die Wellenhöhe in Wechselstrompolarogrammen von *o*-, *m*- und *p*-Nitrophenol in Kaliumhydroxyd oder Ammoniumchlorid-Ammoniaklösung sind nahezu proportional der Konzentration. Verschiedene Reduktionswellen im Gleichstrompolarogramm sind durch kinetische Ströme stark gestört. Da dies in der Wechselstrompolarographie nicht der Fall ist, kann letztere sehr vorteilhaft zur Analyse von Gemischen der Nitrophenolisomere herangezogen werden.

Résumé—Les hauteurs de vague des polarogrammes en courant alternatif des *o*-, *m*- et *p*-nitrophénols sont exactement proportionnelles à leur concentration en solution de potasse ou ammoniac-chlorure d'ammonium. Plusieurs parmi ces vagues de réduction dans les polarogrammes en courant continu sont gênées par le courant cinétique. Celui-ci n'apparaît pas normalement en polarographie à courant alternatif; cette dernière méthode est beaucoup plus pratique pour le dosage des isomères du nitrophénol.

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THE SEPARATION OF SUB-MICROGRAM AMOUNTS OF URANIUM FROM MILLIGRAM AMOUNTS OF IRON, ALUMINIUM AND PLUTONIUM

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Summary—A separation procedure has been developed to facilitate the fluorimetric determination of sub-microgram quantities of uranium in the presence of milligram amounts of iron, aluminium and plutonium. The sample is mixed with a strong hydrochloric acid solution containing hydriodic acid and passed through a column of anion-exchange resin. Only the uranium is retained on the resin and it can subsequently be eluted with dilute hydrochloric acid.

INTRODUCTION

THE separation described was developed to meet a requirement for the determination of the uranium content of solutions containing 0.05–1.0 μg of uranium per ml in 1–2M nitric acid containing 0.02–0.03M iron, 0.01M aluminium and 0.001–0.005M plutonium. The uranium content of such solutions can be determined by direct fluorimetry¹ but two factors militate against this approach. Firstly, the concentration of the major components of the solution is sufficient to cause considerable quenching of the uranium fluorescence² and correction for this tends to be inaccurate at the low concentrations of uranium involved. Secondly, the presence of plutonium limits the size of the sample aliquot which can be handled without resort to glove-box working, and this in turn limits the attainable sensitivity of the procedure.

For the above reasons, a procedure for separating the uranium from the interfering ions was desirable. The method selected is based upon the fact that if the sample is made 10–11M in hydrochloric acid in the presence of a suitable reducing agent the contaminants will be present as iron^{II}, aluminium^{III} and plutonium^{III}, all of which will pass unadsorbed through an anion-exchange resin column under these conditions, whereas uranium^{VI} will be retained by the resin and can subsequently be eluted with dilute hydrochloric acid.³ Hydriodic acid proved to be a suitable reducing agent, and this system, with minor modifications to improve de-contamination from iron, yielded pure solutions of uranium ideally suited for fluorimetric analysis.

EXPERIMENTAL

Reagents

Test solution: Preliminary experiments were carried out using a synthetically prepared stock solution having the composition: 0.1 μg of uranium/ml, with 0.004M plutonium, 0.03M iron^{II}, 0.015M iron^{III} and 0.01M aluminium in 1.5M nitric acid.

11M Hydrochloric acid/7% hydriodic acid: This eluent was chosen, since earlier experience had shown that it gave efficient conversion of plutonium to the tervalent state and effectively separated plutonium from uranium on the resin column. It was necessary to remove iodine from commercial hydriodic acid before incorporating it in the eluent. This was achieved by passing the commercial solution through a column (20 cm \times 0.6 cm) of Deacidite FF in the chloride form. The life of the column could be prolonged by first removing the bulk of the iodine, by shaking the hydriodic acid with

several g of resin in a beaker. The 11M hydrochloric acid/7% hydriodic acid was prepared freshly shortly before use.

Ion-exchange columns

Columns were prepared in glass vessels, approximately 10 cm in length and of 0.4-cm outer diameter, fitted with a reservoir of some 10-ml capacity at the top and with a tap at the bottom. The resin, Deacidite FF, was air-dried and ground to pass 60–80 mesh, and 0.5 g was packed into each column. The resin was conditioned to the chloride form and treated with 11M hydrochloric acid immediately before the addition of each sample. Use of the hydrochloric acid/hydriodic acid eluent resulted in the formation of iodine which was taken on the resin. This could be removed with some difficulty by washing the resin with sodium hydroxide but, in general, replacement of the resin as necessary was preferred.

Fluorimetric analysis

The uranium eluate, usually 4 ml, was divided into two equal portions, each of which was evaporated to dryness in 1-ml lots in a platinum capsule under an infrared heater. To one of these capsules was added 0.2 μg of uranium from a standard solution to serve as an internal calibration. Each capsule was then fused in an oven at $850 \pm 20^\circ$ with 0.6 g of flux (90% sodium bicarbonate/10% sodium fluoride) for 5 min. After cooling for 5 min, the fluorescence of each capsule was read in a Harwell Type 1080A fluorimeter.

Separation procedure

To test the effectiveness of the separation procedure, several experiments were performed as follows. One ml of the test solution was pipetted into 2 ml of 11M hydrochloric acid/7% hydriodic acid contained in the column reservoir. The solutions were mixed and allowed to flow through the column at a rate of 0.4 ml/min. The column was washed with a further 1 ml of the mixed acids and the uranium eluted with varying volumes (1–4 ml) of 0.1M hydrochloric acid. The uranium content of the eluates was determined fluorimetrically.

RESULTS AND DISCUSSION

The eluates were contaminated with iron, which caused quenching of the uranium fluorescence, and precluded accurate determination of the amount of uranium recovered. Recoveries were therefore established by the use of a uranium-233 tracer.

TABLE I.—RECOVERY OF 0.1 μg OF URANIUM-233 IN THE ABSENCE OF OTHER CATIONS

Volume of eluate (0.1M HCl) collected, ml	Total amount of uranium eluted, μg
1	0.056
2	0.088
3	0.094
4	0.099

TABLE II.—RECOVERY OF 0.1 μg OF URANIUM-233 FROM TEST SOLUTION

Experiment No.	1	2	3	4	5	6
Uranium recovered, μg	0.096	0.090	0.075	0.080	0.10	0.084

α -Counting of the hydrochloric acid eluates showed a good recovery of the uranium-233, both alone and in the presence of the test solution, and also indicated that 4 ml

of 0.1M hydrochloric acid adequately eluted the uranium. Typical results are given in Tables I and II. The aluminium content of the eluates was shown by the aluminon method⁴ to be less than 5 μg .

The presence of iron in the uranium eluates is due to incomplete reduction, since iron^{II} is not adsorbed on anion-exchange resins from chloride solutions.⁵ 11M Hydrochloric acid/7% hydroxylamine hydrochloride, 11M hydrochloric acid/7% hydrazine hydrochloride and 9M hydrochloric acid/7% ascorbic acid were tried as alternatives to 11M hydrochloric acid/7% hydriodic acid in attempts to improve the efficiency of the reduction of iron^{III}, but without success. Evidently efficient reduction to iron^{II} occurs only at lower chloride concentrations where complexing of the iron^{III} by chloride is less complete. Maximum removal of iron should be obtained by incorporating an intermediate column wash, using the reducing agent in hydrochloric acid of concentration as low as possible consistent with maintaining the uranium completely in the resin phase. It was demonstrated that a 2-ml wash with 4M hydrochloric acid/7% hydriodic acid removed iron almost completely from the column

TABLE III.—APPLICATION OF METHOD TO 1 ML OF TEST SOLUTION

Uranium recovered, μg	0.08, 0.09, 0.13, 0.14, 0.11, 0.13, 0.10 0.11, 0.08, 0.08
Column blank, as μg of uranium	0.01, 0.006, 0.009, 0.008

without prejudicing the good recovery of uranium. Subsequent elution of uranium yielded solutions of sufficient purity to eliminate quenching in the fluorimetric analyses which followed.

The following procedure has been used successfully both on aliquots of the test solution and on a considerable number of sample solutions:

Procedure

Add 1 ml of the relevant solution to 2 ml of 11M hydrochloric acid/7% hydriodic acid in the column reservoir. Mix the solutions and allow them to flow through the column at 0.4 ml/min. Wash the column with 1 ml of 11M hydrochloric acid/7% hydriodic acid followed by 2 ml of 4M hydrochloric acid/7% hydriodic acid at the same flow rate. Elute the uranium from the column with 4 ml of 0.1M hydrochloric acid, again at 0.4 ml/min, and subject the eluate to fluorimetric analysis by the standard procedure. Perform occasional blank determinations on the column using the above procedure in the absence of uranium.

Table III shows a number of results obtained using the test solution; evidently 0.02 μg of uranium per ml represents a reasonable lower limit for the method.

α -Counting of the uranium eluates showed that the plutonium content was in all cases less than 0.4 μg , representing a decontamination over the column of better than 2000.

A number of samples were received in which the foreign ion concentrations were appreciably lower than those quoted for the test solution. Such samples were analysed by direct fluorimetry and corrected for quenching effects¹ as well as by the ion-exchange procedure. The results are shown in Table IV and indicate satisfactory agreement in all cases.

Clearly the method will separate uranium from other elements in addition to

iron, aluminium and plutonium, the criterion for separation being that the element, or a lower valency state thereof, does not form chloride complexes which can be adsorbed on the anion-exchange resin. The most serious interference is likely to be due to complexing anions. Such interference has not been systematically studied, but it has been noted during the present work that sulphate at a concentration of 0.05M produces no interference.

TABLE IV.—COMPARISON OF DIRECT FLUORIMETRY AND ION EXCHANGE/FLUORIMETRY

Sample No.	Uranium concentration by ion-exchange method, $\mu\text{g/ml}$	Uranium concentration by direct method, $\mu\text{g/ml}$
1	0.65	0.60
2	0.30	0.27
3	0.06	0.05
4	0.10	0.06
5	0.64	0.67
6	0.02	0.02

Acknowledgement—Some of the results given in Table IV were obtained by Messrs. E. B. Astridge and W. Dobbins.

Zusammenfassung—Eine Trennungsmethode wurde entwickelt um die fluorimetrische Bestimmung von Submikrogrammengen Uran in Gegenwart von Milligrammengen Eisen, Aluminium und Plutonium zu erleichtern. Die Probe wird mit einer Jodwasserstoff enthaltenden, starken Salzsäure gemischt und durch eine Anionenaustauschersäule geschickt. Das Uran wird in der Säule zurückgehalten und anschliessend mit verdünnter Salzsäure eluiert.

Résumé—Les auteurs ont mis au point une méthode de séparation pour faciliter le dosage fluorimétrique de quantités inférieures au microgramme d'uranium en présence de quantités de l'ordre du milligramme de fer, d'aluminium et de plutonium. L'échantillon est mélangé avec une solution d'acide chlorhydrique concentré contenant de l'acide iodhydrique et on le fait passer sur une colonne de résine échangeuse d'anions. Seul l'uranium est retenu sur la résine, il peut être ensuite élué par de l'acide chlorhydrique dilué.

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THE DETERMINATION OF OXYGEN, HYDROGEN, NITROGEN AND CARBON IN METALS

A REVIEW

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Summary—A review of the methods for determining oxygen, hydrogen, nitrogen and carbon is presented. Recent developments in apparatus and techniques which have contributed materially to more precise and high speed analyses are discussed. Inert gas fusion is reviewed, together with recent advances that have contributed towards making this apparatus a very flexible and excellent control tool. Since a large number of metals require a bath or flux in which to alloy the sample, a critical review is presented of the platinum bath, platinum flux, and intermittent bath injection methods. Recommendations for further development are for methods which are capable of analysing high purity metals containing less than 10 ppm, and for methods where the amount of sample is limited. Also new methods or techniques should be investigated for the determination of nitrogen in metals, especially in the refractory metals and alloys.

MOST metals contain measurable amounts of carbon, oxygen, hydrogen and nitrogen which have been introduced through processing *i.e.*, melting, rolling, annealing, etching, *etc.* In order to meet specifications for a given application, it is necessary to establish the order of magnitude of these impurities. Since the materials vary greatly in their impurity level, the selection of the most suitable analytical method is of prime importance. The apparatus selected should, under ideal circumstances, be based on the following criteria:

1. Sensitivity
2. Range
3. Adaptation to impurity
4. Availability of apparatus
5. Speed of analysis
6. Cost.

Several methods have been proposed and used for measuring the gas content of metals. Most of these methods are limited to the determination of oxygen only.

Solution method

This method¹ is based on the solution of the metal to leave the insoluble metal oxide. Cunningham and Price² investigated this technique for the determination of oxygen in iron, and encountered some difficulty because of the formation of insoluble iron compounds. Samples weighing 5–10 g were agitated in a solution of iron^{II} iodide. Further separations and determinations of the silicon, manganese, iron and aluminium content of the residue were required before a calculation could be made. The method is most adaptable to samples of high oxygen content and provides results which give an estimate of the metallic composition of the oxide.

Evolution method

This method is based on the vaporisation of the metal at 800° in a stream of chlorine. The residual metal oxide is weighed. The method is adaptable to metals of relatively high oxygen content. Lilliendahl, Wroughton and Gregory³ applied this technique to the determination of oxygen in zirconium. The method is subject to many corrections rendered necessary by side reactions such as that between carbon and metal oxide. Also, contamination of the oxide by other metal oxides requires a correction based on an initial impurity analysis. The precision is only about 0.02% based on a 2-g sample. This method still has some applications but, in general, it has been replaced by more precise techniques.

Bromination method

In this method⁴ the metal sample is heated with graphite, in a stream of helium or argon and bromine. In this manner, the oxygen is converted to carbon monoxide. The bromine and volatile metal bromides are removed in dry-ice traps. The carbon monoxide is oxidised to carbon dioxide, absorbed in Ascarite and weighed. This method is adaptable to the determination of oxygen in metals in the range of 100 to 5000 ppm.

Emission spectrometric method

The metal sample is excited in an inert atmosphere of argon with a d.c. carbon arc.⁵ The method is rapid, and has been found to give results comparable with those from the vacuum fusion method when applied to the determination of oxygen in refractory metals. Further extension of this method through refinements in technique and apparatus may result in its application to determine low concentrations.

Isotope dilution method

The sample is heated with a measured amount of ¹⁸O introduced as an isotope-enriched metal powder. The sample and the enriched alloy are heated in a graphite crucible to establish an equilibrium of oxygen-16/oxygen-18. At the point of equilibrium, the oxygen-16/oxygen-18 ratio is identical in all compounds and phases. The new diluted ratio is measured with a mass spectrometer. The method offers one main advantage over fusion methods in that a complete removal of the oxygen is not necessary. The technique⁶ is in limited use for metals because it requires a good high vacuum apparatus for establishing the equilibrium in addition to a mass spectrometer for analysis. However, since stable isotopes are available for nitrogen as well as for oxygen, the method offers several unique applications. The best lower limit approximates to 10 ppm.

Activation method

This method⁷ is based on surrounding the sample with lithium fluoride during irradiation by neutrons generated from a pile. The neutron reaction ${}^6\text{Li}(n,\alpha){}^3\text{H}$ produces a source of tritons, ³H. These tritons activate the oxygen nuclei in the sample to produce ¹⁸F by the secondary reaction ${}^{16}\text{O}({}^3\text{H},n){}^{18}\text{F}$. The ¹⁸F decays by positron emission. The positrons are accompanied by annihilation γ -radiations which

are used to complete the analysis by γ -scintillation spectrometry. The general use of this method is restricted because of the requirement of a strong neutron source. The method is not suitable for the determination of trace quantities of oxygen, hydrogen and nitrogen, since these elements have a low probability of neutron absorption or a very short half-life for the radioactivity. Metals have been analysed for oxygen by this technique in the range of 10 ppm and above.

Infrared absorption method

The presence of dissolved oxygen in a semi-conductor may affect infrared absorption. Kaiser, Keck and Lange⁸ found that there was an absorption band at $9\ \mu$ in silicon which corresponded to the asymmetric silicon-oxygen stretching bond vibration. Similarly, there is an absorption band at $11.7\ \mu$ corresponding to oxygen in germanium.⁹ These are the only two semi-conductors that have been studied by this method. The method was calibrated by vacuum fusion. This technique has been applied to samples containing 20 ppm of oxygen or less, with good sensitivity in the low concentrations. It has been applied to single crystal material.

Inert gas fusion

The metal sample may be melted in a graphite crucible, in an inert atmosphere of argon. The oxygen in the sample is converted to carbon monoxide, which is oxidised to carbon dioxide. The carbon dioxide formed may be absorbed in Ascarite and weighed, or even better, may be absorbed in dilute barium hydroxide. The change in conductivity of the barium hydroxide solution is measured as a function of the oxygen content. A calibration curve is established by fusing a known amount of an oxygen standard and measuring the resistance change. From this curve, the oxygen content of the sample can be determined. The method is applicable to samples containing oxygen from 10 ppm upwards, but it is more generally used for oxygen in excess of 50 ppm. The procedure is rapid, and very suitable for control work.

Vacuum fusion method

On fusing the metal sample in a graphite crucible, in vacuum, the oxygen in the sample is converted to carbon monoxide, and hydrogen and nitrogen are evolved. Provisions are made for determining the gas composition. This is the most versatile tool, since it can measure and analyse the total gas. Also, it currently is the most sensitive. This feature makes it possible to analyse high purity materials or samples when the amount available is limited. The most satisfactory working range is from 10 to 2000 ppm. Some investigations have been carried out at 10 ppm and below through special refinements in technique.

Hot extraction method

In many instances the measurement of the hydrogen content of the metal is of sole importance. This measurement is most readily made by hot extraction. The principle of the method is based on extracting the hydrogen from the metal by heating in vacuum at about 1200° . The hydrogen evolved is collected and measured. For samples which give small amounts of other gases in addition to hydrogen, provisions

are made for their separation from the hydrogen. The analysis time is generally of the order of 30 min per sample.

Determination of carbon

Most metals contain measurable amounts of carbon and oxygen, and when heated evolve either carbon dioxide, carbon monoxide or both, depending on the temperature. This reaction should be given the utmost attention in fundamental studies of materials used in electronic devices. Since the presence of carbon in metals can be detrimental in some applications, and very necessary in others, it becomes of prime importance to make a quantitative measurement of the carbon content as well as of the oxygen.

The principle of the measurement of carbon depends on the combustion of the metal sample in oxygen, with the separation and measurement of the carbon dioxide. The carbon dioxide may be measured by absorption in Ascarite and weighing, volumetric absorption in caustic potash to measure the amount of carbon dioxide absorbed, or absorption in caustic potash and measuring the change in conductivity, or separation by freezing out in liquid nitrogen. In the last case, the carbon dioxide is frozen out in liquid nitrogen, the excess oxygen is removed to vacuum pump, and the carbon dioxide pressure is measured in a known volume. Currently, the conductivity method is most widely used because of its speed, range and sensitivity. The low pressure combustion method is most applicable to the determination of carbon of a few ppm, or when a limited amount of sample is available.

Recent developments

Among the methods described above, vacuum fusion, inert gas fusion, hydrogen by hot extraction, and conductimetric carbon analyses are currently being widely used. As a result of the efforts of several gas metal groups which have carried out co-operative analyses, the range, sensitivity and accuracy of these methods have been constantly improved.

Inert gas fusion

While inert gas fusion is not new,¹⁰ the method has developed into an excellent high speed analytical tool for determining oxygen in metals. Smiley^{11,12} carried out the fusion in a graphite crucible, in an atmosphere of argon. The argon acts as a carrier gas. The carbon monoxide formed from the fusion is oxidised to carbon dioxide. The carbon dioxide is frozen out in the capillary trap with liquid nitrogen, the argon is removed by a vacuum pump, and the carbon dioxide pressure is measured in the gas phase, in a known volume. This procedure requires about 12 min per determination. The Leco Co.* modified and improved this technique by combining inert fusion with a conductimetric method for measuring the carbon dioxide. The apparatus is shown schematically in Fig. 1. The carbon dioxide is absorbed in dilute barium hydroxide, and the change in conductivity is measured. This method offered a new and rapid approach to determining oxygen in metals. The analysis time is about 8 min.

Recently, experimental work has shown that the application of this method can be extended beyond the recommended scope.

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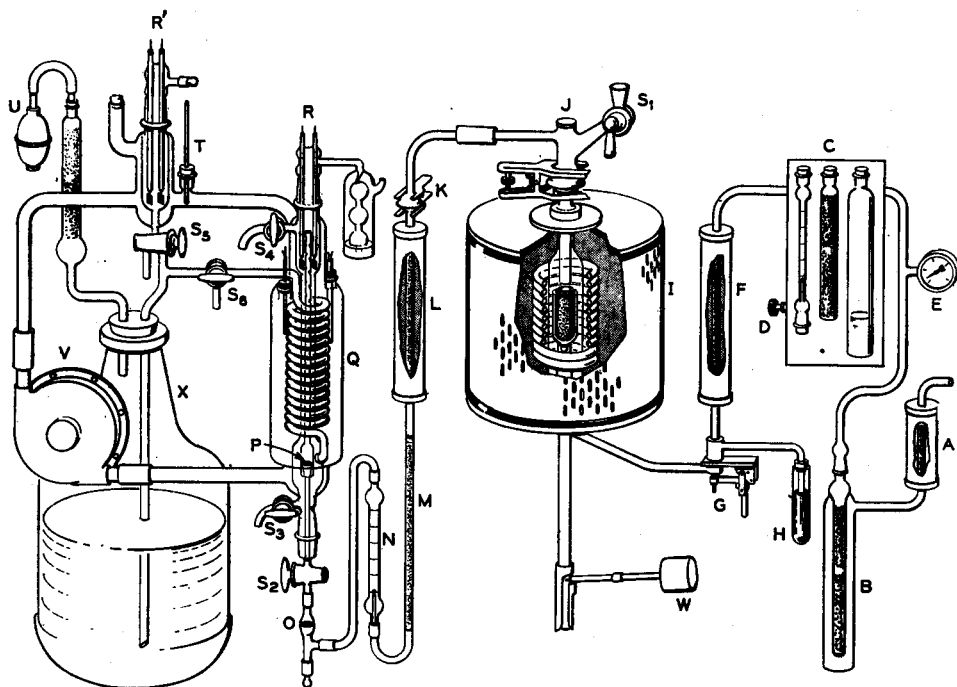


FIG. 1.—Inert gas fusion apparatus
 A—Copper oxide
 B—Magnesium perchlorate—Ascarite
 C—Sulphuric acid, magnesium perchlorate, Ascarite and flow meter
 D—Needle valve
 E—Pressure gauge
 F—Titanium metal
 G—Quick disconnect
 H—Mercury pressure release
 I—Induction furnace quartz tube, containing graphite crucible floating in lamp block
 J—Optical flat
 K—Ball joint
 L—Iodine pentoxide
 M—Sodium thiosulphate
 N—Flow-meter
 O—Porous frit and mercury trap
 P—Porous frit
 Q—Water jacket, thermostated
 R—Measuring cell
 R'—Reference cell
 S—S₂, S₃, S₄, S₅, S₆, two-way and S₆ three-way stop-cocks
 T—Thermometer
 U—Aspirator bulb
 V—Circulating pump
 W—Weight
 X—Carboy containing barium hydroxide

1. *Calibration.* It has been customary to set up a standard calibration curve by fusing 2–4 mg of silver oxide in the graphite crucible and measuring the change in conductivity due to the carbon dioxide. Because of the inherent problems in handling such small amounts of silver oxide, the use of potassium hydrogen phthalate¹³ offers a new, faster and accurate manner in which to prepare oxygen standards. In order to prepare these standards, several concentrations of potassium hydrogen phthalate are prepared in distilled water. A measured amount (0.2 ml) is transferred with a microsyringe* to tin cups having a volume >0.2 ml. These cups are placed in holes in a metal block and evaporated to dryness at a temperature not to exceed 100°. After evaporation to dryness, the tin cups are flattened with a spatula and rolled into a compact form. In this way, standards containing 10 to 2000 μg of oxygen can be readily prepared and stored for future use. In Fig. 2 is shown a typical calibration curve up to 1600 μg of oxygen, where the barium hydroxide concentration is 15 g/18

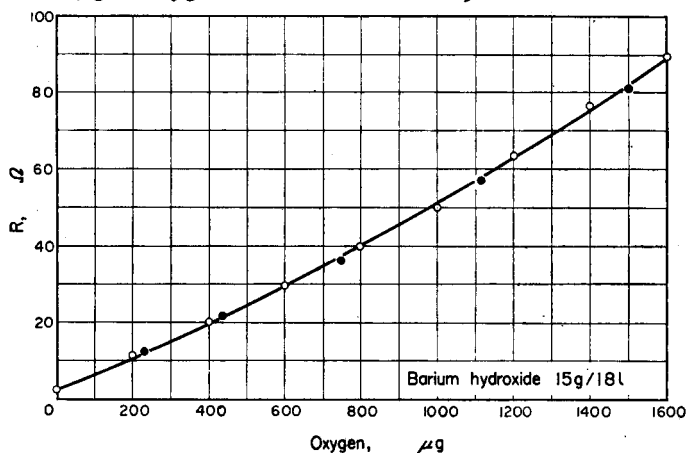


FIG. 2.—Standard calibration curve
 ○ Potassium hydrogen phthalate
 ● Silver oxide

litres. Each point on the curve represents an average of two to five determinations. The points obtained with potassium hydrogen phthalate are in good agreement with those obtained with silver oxide. Over this entire range, 0–1600 μg of oxygen, there is a deviation from a straight line relationship. This deviation is negligible over any 400- μg portion of the curve.

2. *Extending the application and range.* Initially, it was recommended that the method be applied to determinations in the range of 100–400 μg of oxygen. This was accomplished simply by adjusting the sample size. It is evident from Fig. 2, that any 400- μg portion of the curve is equally good. Therefore, it is advisable to run the sample first, then establish a calibration point on each side of the sample. A straight line drawn between these points (400- μg range) will introduce a negligible error.

In some instances where the oxygen content is high *e.g.*, ferrites, it is still not possible to reduce the sample size sufficiently to fall in a good working range. However, these high oxygen materials can be readily analysed by inert fusion, by substituting an Ascarite absorption tube for the conductivity cell. Samples weighing about 50 mg will give a weight gain of 40 mg of carbon dioxide, since one oxygen is picked up from the

* Microsyringe—0.25 ml micrometer adjustment—Scientific Glass Apparatus.

iodine pentoxide in the oxidation of the carbon monoxide to carbon dioxide. In carrying out reductions on ferrites, it is necessary to drop the sample into the crucible at ambient temperature, then switch on the induction heater to bring the temperature to 1650°. The reduction takes place at a sufficiently high temperature to favour the formation of carbon monoxide, yet slowly enough to prevent overloading the oxidising reagent and blowing the sample out of the crucible.

Currently, several gas metal studies have required the measurement of oxygen below 50 ppm. This has been found to be especially true in working with materials for electronic devices. When small amounts of oxygen are being determined, the barium hydroxide can be diluted. The barium hydroxide solution used for this work contains only 5 g/18 litres. A resistance change of 1 Ω is equivalent to only 1 or 2 ppm. In this manner, it is now possible to determine oxygen rapidly in metals below 50 ppm with a standard deviation of about 3 ppm.

One outstanding advantage of this method is that the fusion is carried out in an inert atmosphere. The argon gas suppresses the vapour pressure of the metals and prevents excessive deposition on the walls of the furnace. This opens an entirely new field of study by making it possible to determine the gas content of metals which have a high vapour pressure, heretofore not amenable to vacuum fusion. For example, metal oxides of aluminium and zinc can be quantitatively analysed.

Hot extraction method

It has been found that hydrogen present in metals may have a marked effect on the ductility. Also, "hydrogen embrittlement" has been associated with failure of metal parts. Surface blistering and blow holes have also been found to be related to the hydrogen content.

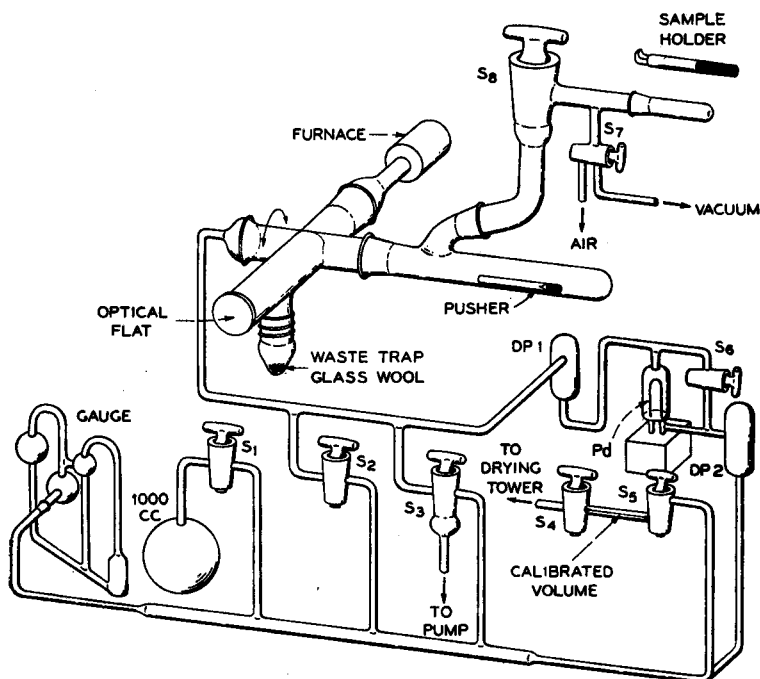


FIG. 3.—Hydrogen extraction apparatus.

Since many of the metals lose their hydrogen on standing, especially in vacuum, it is necessary to analyse these samples as rapidly as possible. This factor necessitates the injection of the sample into the apparatus for immediate analysis. Most units for measuring hydrogen have a vacuum lock which permits the immediate injection of the sample into the pre-conditioned analytical station. In Fig. 3 one unit is shown which is now commercially available.* One feature of this apparatus is the introduction of the sample for analysis through a vacuum lock. The sample is placed in the glass boat, which is inserted through the tapered joint. The cap is replaced and is made vacuum tight with Apiezon wax, W. The air about the sample is evacuated by opening stopcock S7 to vacuum. After the evacuation, S7 is closed and S8 is opened to the apparatus. The sample boat is pushed by means of a glass-enclosed metal slug through the hole in the stopcock. By rotation of the magnet, the sample is dropped without danger of contamination from the grease on the stopcock. A second magnetic pusher propels the sample into the furnace area. The furnace is rotated on a ball and tapered joint to inject the samples into the hot zone, and to reject them to the waste trap after analysis. In this way several samples can be analysed consecutively. During the hot extraction of the hydrogen, small amounts of carbon monoxide, carbon dioxide and nitrogen are evolved. The hydrogen is rapidly separated from these gases by diffusion

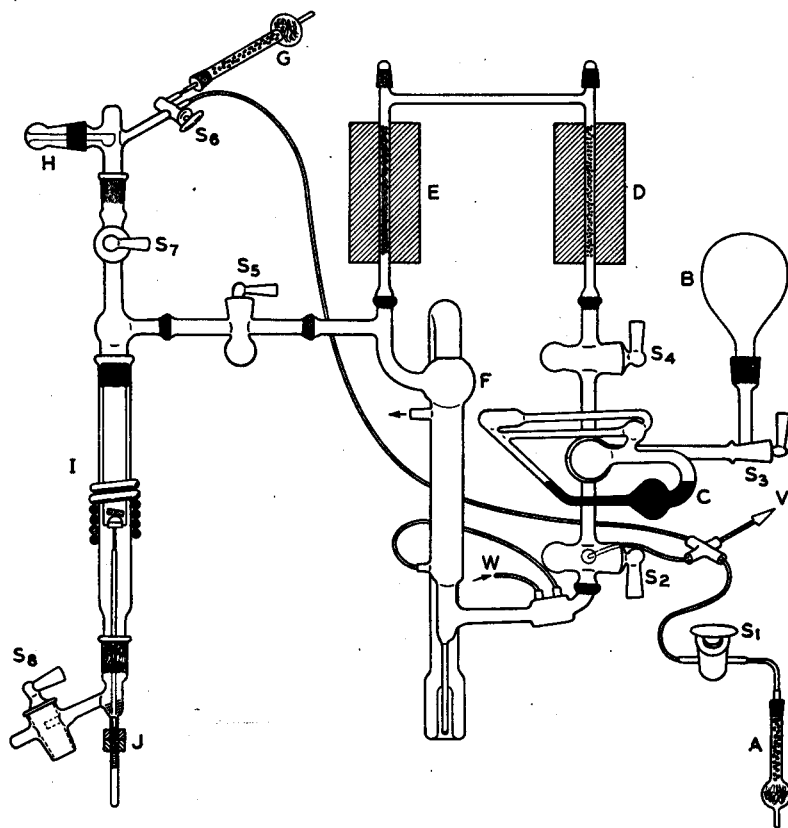


FIG. 4.—Hydrogen extraction apparatus.

* Fisher Scientific Co., Fisher-Serfass Hydrogen Analyzer

through a palladium valve or lamp. The hydrogen is collected with a diffusion pump, and is measured in a known volume by means of a Lippincott type of pressure gauge. The analysis requires about 10–30 min with a sensitivity of about 0.1 ppm.

Another apparatus* for determining hydrogen, shown in Fig. 4, employs a vacuum lock and a special stopcock with metal insert and guide tube for admitting the sample free from contamination into a vertical furnace. Also, the crucible has a false bottom operated up and down by means of a solenoid. This simple and unique feature makes it easily possible to reject a sample from the crucible after analysis. In this way, several samples can be analysed consecutively. In some instances, gases like O_2 , N_2 , CO and CO_2 may be evolved along with the hydrogen. In this apparatus, the total gas evolved is measured. Provisions have been made for circulating the gas mixture over copper oxide and magnesium perchlorate when it is considered necessary. The total gas is re-measured, and the difference is due to the hydrogen.

Vacuum fusion

The vacuum fusion method for analysis of the total gas content of metal samples is widely used, since it can be applied to almost all kinds of materials. Since the development of the high temperature all-glass fusion furnace, no major change in the equipment has developed. Most laboratories use equipment similar to the one manufactured by National Research Corporation.†

In the past five years, through the co-operative efforts of many laboratories and gas-metal panels associated with A.S.T.M. and the technical branches of the armed services, considerable progress has been made in developing better techniques and understanding of fusion analyses. The most outstanding advances are as follows:

1. Application of the platinum bath and platinum flux techniques.
2. Intermittent bath injection.
3. A study of the sorption of gas by films deposited on the furnace walls during fusion analyses.

1. *Application of the platinum bath and platinum flux techniques.* Many metals and alloys, especially the refractory ones with high melting points, require a flux to remove the gas quantitatively. Initially, platinum was used as a bath into which samples were dropped for analysis.^{12,14,15,16} Through co-operative analyses it was soon realised that the platinum bath technique could give trouble after several analyses, due to the formation of graphite flakes in the platinum melt.¹⁷ It was found that this prevented proper alloying of the sample and quantitative recovery of gas. Since the oxygen content of platinum is relatively low (about 10 ppm) as compared with the gas content of the samples, fusion analyses can be carried out by injecting the sample and the platinum simultaneously. This method is referred to as the flux technique. The platinum flux technique offers several advantages. The platinum metal has a low vapour pressure which minimises the amount of metal evaporating to the furnace walls. This factor makes it possible to carry out fusions at high temperatures. By adding the flux with the sample, the analysis time is greatly reduced. Also, the danger of developing viscous and semi-fluid fusion baths is eliminated. For the best results, the platinum : sample ratio should be about 10 : 1, and both should be injected simultaneously. The platinum is used in rod, sheet or wire form. The last two forms

* Hydrogen Analyzer—Manufactured by Laboratory Equipment Co., St. Joseph, Michigan, U.S.A.

† National Research Corporation, Cambridge, Massachusetts, U.S.A.

can be wrapped tightly about the sample. In some analyses, tin has been added in small amounts, and has been found to be of some advantage, even though it contributes to the blank. The method is widely used for determining oxygen in refractory metals and alloys. The determination of nitrogen in refractory metals appears to be quantitative when platinum is used. Further study is required through co-operative laboratory analyses to establish if the removal of nitrogen is quantitative, by comparing the values with those obtained by the Kjeldahl method. The platinum is readily recovered from the fusion melt, and most laboratories return the fused ingots to the platinum manufacturer for reclaiming.

2. *Intermittent bath injection.* The use of iron as a fusion bath has been widely accepted by most laboratories for many years. One disadvantage of using iron is that it has a relatively high gas content. In view of this it is necessary to outgas the iron thoroughly, and then to determine a blank before dropping in a sample. These steps are time consuming. In many instances, variable results were obtained when this type of bath was used. McDonald, Fagel and Balis¹⁸ showed that satisfactory recovery of gas could be obtained from a fluid iron bath. Since it was necessary to heat the iron bath to 1800° for metals having a high melting point, carbon dissolved in the iron to such an extent that the melt became viscous. This resulted in poor alloying of the sample and recovery of gas. Sloman and Harvey¹⁹ recognised this problem, and made a point of keeping the bath temperature as low as possible and completing the reduction of the oxide within 20 min. Smith²⁰ showed that the iron bath is semi-solid within 2 hr at 1800° due to the formation of large graphite flakes. The greatest concentration of these flakes is nearest the top, which makes it difficult for the sample to alloy properly. The higher the temperature, the more rapid is the solution of carbon. When considerable carbon has dissolved in the ingot, gas evolved from the sample can be trapped in the semi-fluid melt below the viscous layer. The addition of tin appeared to be advantageous to minimise the loss of gas due to "gettering" by the evaporated metal films on the furnace wall. Beach and Guldner²¹ showed that the periodic addition of iron and tin was a real advantage. The periodic addition of iron* was made after every other sample. The gas from the iron was removed to pump before the samples were analysed. The function of the tin is two-fold: firstly to increase the fluidity of the bath, and secondly to act as a mechanical stirrer. Due to the high vapour pressure of the tin at fusion temperature, the tin will boil off, stirring the molten bath. This technique minimises the danger of gas being entrapped in the iron bath. Without doubt, the iron bath used in this manner is the most satisfactory and most widely applicable fusion bath. It is applicable to all of the high melting point and refractory type metals.

3. *Sorption of gas by metal films deposited on the furnace walls.* It is inherent in vacuum fusion analyses that carbon and metal vapours deposit on the glass walls of the furnace. It is certain that many investigators have felt that some of the gas evolved from the sample was re-adsorbed on these films. In the earlier years of vacuum fusion these losses would probably have been negligible since the gas levels were comparatively high; hence no comprehensive study was carried out. Recently, the emphasis in many fields of study, especially in the use of metals in the electronic field, has been on high purity metals. With the advent of purifying the metals by zone refining, melting in vacuum or in controlled atmospheres, the gas content is often

* Ferrovac Iron—Crucible Steel Co., Syracuse, New York, U.S.A.

only a few ppm. Therefore, it becomes imperative to investigate all sources of error.

McDonald, Fagel and Balis¹⁸ admitted carbon monoxide gas in their study of the iron bath when applied to the determination of oxygen in zirconium. Beach and Guldner²² carried out a comprehensive and systematic study of gas absorption by starting out with the carbon film followed by a superimposed metal film. All conditions were adjusted to simulate fusion analyses. The results show that hydrogen was lost to the carbon film. However, it was found that when a metal was fused in the graphite crucible, the metal vapour depositing over the carbon reduced the hydrogen loss by a factor of 2. Iron, platinum, platinum-titanium and germanium films, when exposed to carbon monoxide and nitrogen from 2 to 150 mm³ sorbed less than 2 mm³ of gas. Nickel was unusual, since the errors for carbon monoxide recovery were both positive and negative, especially when small amounts were added. Nitrogen and hydrogen losses were about the same as for the other metals. Aluminium and manganese sorbed so much carbon monoxide that fusion analyses of these metals would be prohibitive. Only by using extremely large bath:sample ratios would it be possible to analyse such metals. Certainly, it is recommended that similar work should be carried out on other metals, especially when the impurity level is only a few ppm.

CONCLUSION

It is gratifying to note that most laboratories are providing for the analysis of gases in metals. Vacuum fusion offers the most widely used apparatus since it is capable of measuring oxygen, hydrogen and nitrogen in most metals. This method is currently the most sensitive.

Inert fusion offers an excellent means for the rapid determination of oxygen in metals, especially where the level is 50 ppm or more. Inert fusion has found wide application to the determination of oxygen in the refractory metals. The results are in good agreement with those obtained by vacuum fusion. One main advantage is that about 4 samples can be analysed per hr.

The conductimetric method for carbon is now widely used since a determination can be made in about 8 min. The sensitivity of the method can be changed by simply changing the concentration of the barium hydroxide.

The most satisfactory method for the determination of hydrogen in metals is by hot extraction. All samples are introduced to the analysis station through a vacuum lock. The analysis time is about 30 min per sample.

Since the current interest has been in high purity material, further research should be sponsored in exploring such methods as neutron activation, spectroscopy and isotope dilution to determine if these methods could be applied to metals having an impurity level below 10 ppm. Every effort should be made to encourage and support a programme for providing gas-metal standards of different impurity levels. Co-operative efforts of several gas-metal committees are working to achieve this goal.

Zusammenfassung—Eine Übersicht über die Bestimmung von Sauerstoff, Wasserstoff, Kohlenstoff und Stickstoff wird gegeben. Jüngste Entwicklung in Hinblick auf Apparate und Technik, soweit sie erhöhte Genauigkeit oder grössere Schnelligkeit erbrachten, werden besonders hervorgehoben. Schmelzen in inerte Gasatmosphäre wird behandelt, sowie Neuerungen, die die verwendeten Apparate verbessern und universeller anwendbar machen. Da viele Metalle Schmelzen oder Legieren erfordern, werden das Platinbad und die Platinschmelze besonders eingehend behandelt. Vorschläge für Verbesserungen und weitere Entwicklung werden gemacht, besonders für hochreine

Métalles und Fälle wo nur geringe Probenmengen zur Verfügung stehen. Es wird angeregt, Methoden zu entwickeln und zu untersuchen, die die Bestimmung von Stickstoff in Metallen ermöglichen.

Résumé—L'auteur passe en revue les méthodes de dosage de l'oxygène, de l'hydrogène, de l'azote et du carbone. Il discute les récents développements d'appareillage et de technique qui ont contribué à effectuer des analyses plus précises et plus rapides. La fusion dans un gaz inerte est passée en revue ainsi que les progrès récents qui ont contribué à faire de cet appareillage un instrument de contrôle très souple et excellent. Comme un grand nombre de métaux nécessite un bain ou un fondant pour former un alliage avec l'échantillon, l'auteur fait une revue critique des bains de platine, des fondants de platine et de l'injection intermittente de bains. Des recommandations sont faites pour des développements ultérieurs des méthodes capables d'analyser des métaux de haute pureté contenant moins de 10 ppm., et où la quantité d'échantillon est limitée. Aussi, de nouvelles méthodes ou techniques devraient être étudiées pour le dosage d'azote dans les métaux, particulièrement les métaux réfractaires et les alliages.

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THE PHOTOMETRIC DETERMINATION OF ZINC WITH XYLENOL ORANGE

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Summary—The use of Xylenol Orange as a reagent for the photometric determination of zinc is described. With this reagent, zinc forms a red complex at $\text{pH} > 4$, the optimal pH being 5.8–6.2. It was found that under these conditions only one complex, of molar ratio $\text{Zn}:\text{XO} = 1:1$, is formed. From Job's curve, the stability constant has been determined ($K \approx 1.4 \times 10^6$). In the region 0–100 μg of zinc/50 ml the Lambert-Beer law holds. This reaction has been applied to the determination of zinc in bronze after a prior separation with an ion-exchanger.

XYLENOL Orange has been described by Körbl and Přibíl^{1,2} who found it to be an excellent complexometric indicator in an acidic medium. As a photometric reagent it has recently been used by Cheng for the determination of zirconium,³ hafnium,⁴ iron⁵ and bismuth.⁶ These determinations, when carried out in a relatively strongly acid medium, exhibit high selectivity. In spite of the fact that the reactions of other elements do not exhibit this selectivity in a weakly acid medium, the reaction of zinc has been studied, since there are not sufficient suitable reactions for the photometric determination of this element. In the light of the possibility of the separation of zinc from interfering elements using an ion-exchanger, the lower selectivity of the reaction is not a serious disadvantage.

EXPERIMENTAL

Reagents

Xylenol Orange (Lachema): 0.001M solution in 10 % ethanol.

Standard zinc solution: Prepared from zinc sulphate in such a way that 1 ml of the solution contained 100 or 10 μg of zinc. The actual strength was determined complexometrically.

Buffer solution: Prepared from 0.2M acetic acid and 0.2M sodium acetate.

The solutions of the other elements were prepared from salts of the highest possible purity, strengths being determined complexometrically.

Apparatus

All the measurements were made on a Pulfrich photometer with an Elpho adaptor. The absorption curve was obtained with a Beckman DU spectrophotometer. For the measurement of pH a Multoscope II pH -meter was used.

The effect of pH

Five-ml portions of standard zinc solution (50 μg) were pipetted into a series of 50-ml volumetric flasks, and 20 ml of buffer solutions of appropriate pH and 2 ml of 0.001M Xylenol Orange solution were added to each flask. The solutions were diluted to the mark with water. A similar series of solutions was prepared without the addition of zinc. The extinction was measured, using 2-cm cuvettes, a tungsten lamp and an S57 filter against water. The results obtained are shown in Fig. 1

The red complex of the reagent with zinc is formed at pH 4.0. The reagent alone, which is yellow at pH < 5 , turns to orange with an increase of pH, and at pH > 7 has nearly the same colour as the zinc complex. The greatest difference of extinction

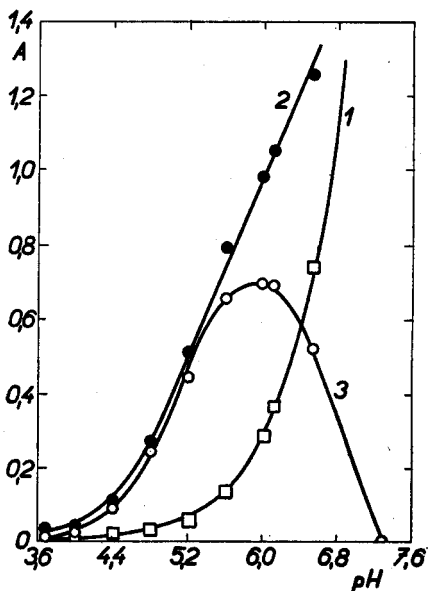


FIG. 1.—Dependence of the extinction of Xylenol Orange and its zinc complex on pH (574 $m\mu$).
1—Xylenol Orange.

2—Xylenol Orange with addition of 50 μg of zinc.

3—Difference between curves 1 and 2.

is obtained at pH 5.8–6.2. This is obviously the optimum value for the determination of zinc, and it is necessary to remain within the given limits.

Absorption curves

The absorption curves of Xylenol Orange and its zinc complex at pH 6.0 ± 0.1 are presented in Fig. 2.

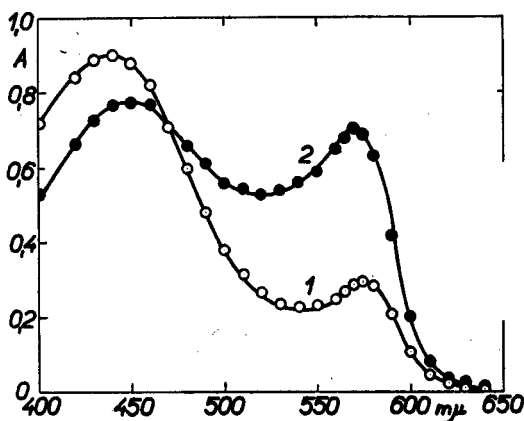


FIG. 2.—Dependence of the extinction of Xylenol Orange and its zinc complex on wavelength (pH 6.0 ± 0.1).

1—Xylenol Orange

2—Xylenol Orange with addition of 60 μg of zinc.

The reagent alone exhibits two maxima: a higher one at $440\text{ m}\mu$, and a lower one at $575\text{ m}\mu$. These maxima correspond to the yellow and red components of the colour of the solution.

The zinc complex ($60\text{ }\mu\text{g}$ of zinc) exhibits a maximum at $570\text{ m}\mu$, a second maximum at $450\text{ m}\mu$ corresponds to the yellow component of excess of reagent. For a low zinc content ($10\text{ }\mu\text{g}$) the maxima agree with the reagent alone.

The amount of Xylenol Orange

Portions of 6.5 ml of standard zinc solution ($65\text{ }\mu\text{g} = 0.001\text{ mole}$ of zinc) were pipetted into a series of 50-ml volumetric flasks, followed by 10 ml of acetate buffer (pH 6) and from 0.2-ml to 5-ml amounts of $0.001M$ reagent solution. The solutions were diluted to the mark with water. A series of blank solutions (without the addition of zinc) were also prepared. The corresponding pairs of solutions were measured against each other, and the results are shown in Fig. 3.

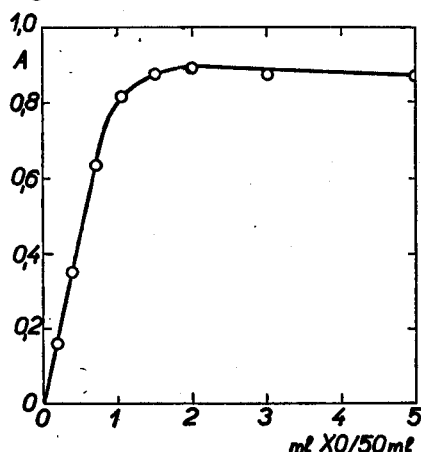


Fig. 3.—Dependence of the extinction on the amount of Xylenol Orange. ($65\text{ }\mu\text{g}$ of zinc, pH 6.0 ± 0.1 , $574\text{ m}\mu$.)

From this, it is obvious that for $65\text{ }\mu\text{g}$ of zinc about 2 ml of $0.001M$ reagent solution are sufficient. By extrapolation, the point of intersection obtained corresponds with a complex of the molar ratio $\text{Zn} : \text{XO} = 1 : 1$. This is further supported by applying Job's method (see later.)

Calibration curve

Portions of $0\text{--}10\text{ ml}$ of standard zinc solution ($0\text{--}100\text{ }\mu\text{g}$ of zinc) were pipetted into a series of 50-ml volumetric flasks, 10 ml of buffer (pH 6) and 3 ml of $0.001M$ reagent solution were added and the solutions were diluted to the mark. The extinctions were measured under these conditions, and the curve is presented in Fig. 4.

This curve is in good agreement with the Lambert-Beer law throughout the full range of concentration used.

Composition of the complex and stability constant

Job's method of continuous variation was used to investigate the composition of the complex. The initial concentration of the zinc solution and the reagent was $5 \times 10^{-4}M$. The measurements were carried out at pH 6.0 for three wavelengths. The results are given in Fig. 5.

The curves exhibit maxima at the molar ratio $\text{Zn} : \text{XO} = 1 : 1$, confirming the formation of this complex alone under the given conditions. From curve 1 (Fig. 5)

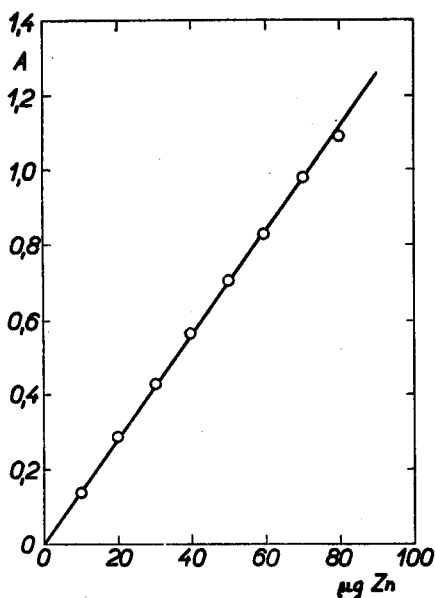


FIG. 4.—Calibration curve. (pH 6.0 ± 0.1 , $574 \text{ m}\mu$, 2-cm cuvettes.)

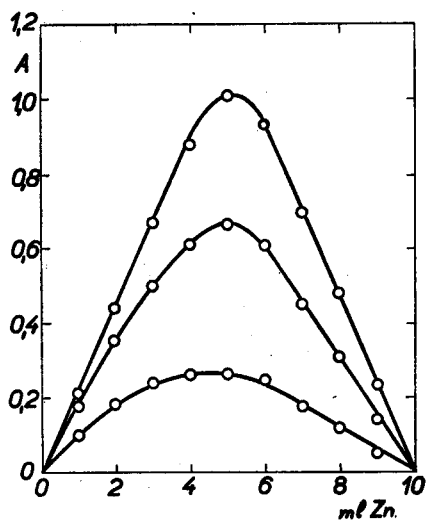


FIG. 5.—Job's curves for the zinc-Xylenol Orange complex (pH 6.0 ± 0.1).
Top— $574 \text{ m}\mu$; middle— $530 \text{ m}\mu$; bottom— $492 \text{ m}\mu$.

the approximate value of the stability constant of the complex has been determined as $k \approx 1.4 \times 10^6$. This is of the same order as the stability of the complex with hafnium.⁴

Determination of zinc in bronzes

The method has been applied to the determination of 0.01 — 0.50% of zinc in copper alloys (bronzes). For the separation of zinc from other elements a strongly basic ion-exchanger was used.*

* Strongly basic ion-exchanger (Research Institute of Synthetical Resins, Pardubice, Czechoslovakia.)

The sample is dissolved in nitric acid and evaporated to small volume. The solution is filtered into a volumetric flask and made to the mark with water. From a suitable aliquot of this solution, copper and lead are separated electrolytically. The solution is again transferred to a volumetric flask, and an aliquot corresponding to about 20–40 mg of the sample is evaporated to dryness. The residue is dissolved in 5 ml of 2N hydrochloric acid, and separated on a column of the ion-exchanger in the chloride form (5 ml, grain size 0.1–0.2 mm, rate of flow 1 ml/min). The column is washed with 50 ml of 2N hydrochloric acid, and zinc is eluted with 25 ml of 0.1N hydrochloric acid. The eluate is evaporated to dryness. The residue is dissolved in water and transferred to a 50-ml volumetric flask. The remainder of the procedure is as described for preparing the calibration curve. The extinction is measured against a blank solution which has been carried through the above procedure.

DISCUSSION

From the results obtained it is obvious that Xylenol Orange can be used for the comparatively selective photometric determination of zinc when suitable conditions are observed. The optimum value of the pH is 6.0 ± 0.1 , at which value the greatest difference between the extinction of the zinc complex and that of the reagent is obtained. The value of pH mentioned is best achieved with an acetate buffer. A wavelength of about 570 m μ is the most suitable for measuring the extinction. The difference in extinction between the complex and the reagent is maximal in this wavelength region. The stability of the colour is stable under the given conditions for at least 3 hours.

A difficulty in the practical application of the method is its small selectivity if directly applied. Xylenol Orange, in a weakly acidic medium, reacts with a range of elements such as Cu, Al, Fe, Ni, Mn, Pb. All these elements can, however, be separated by electrolysis followed by the use of an ion-exchanger.

Preliminary experiments showed that at pH 6.0 the copper complex exhibits the same absorption maximum as that of zinc. The lead complex, under the same conditions, exhibits a maximum at about 530 m μ . At 575 m μ the extinction of the copper complex, under the same conditions, corresponds to about 56%, and of the lead complex to about 30% of the extinction measured for the zinc complex. Thus the determination of zinc in the presence of these metals suffers serious interference, even at the 10- μ g level, and their separation is essential.

When using the method for the determination of zinc in bronzes at the 0.05% level, the standard deviation in 8 determinations was $\pm 0.009\%$; at the 0.16% level of zinc, it was $\pm 0.015\%$.

Acknowledgement—It is our pleasant duty to thank Mr. B. Kysil, SONP Kladno, for the measurement of the absorption curve.

Zusammenfassung—Eine photometrische Methode zur Bestimmung von Zink mit Xylenolorange wird beschrieben. Der rote Komplex wird oberhalb pH 4 geformt, der beste pH-Bereich ist 5.8–6.2. Unter den beschriebenen Bedingungen wird ein 1:1 Komplex geformt. Aus einer Job-Kurve wurde die Stabilitätskonstante des Komplexes zu etwa 1.4×10^6 bestimmt. Im Bereich 0–100 μ g Zn/50 ml ist Beer's Gesetz erfüllt. Die Methode wurde zur Bestimmung von Zink in Bronzen herangezogen. Eine Trennung unter Verwendung eines Anionenaustauschers geht dem Photometrieren voraus.

Résumé—Les auteurs décrivent l'utilisation de xylenol orange comme réactif pour le dosage photométrique du zinc. Le zinc forme un complexe rouge à pH > 4. La condition la meilleure pour le dosage est à pH 5,8–6,2. Dans les conditions décrites, un complexe se forme, de rapport molaire Zn/XO = 1/1. D'après la courbe de Job, la constante de stabilité a été déterminée: $K \sim 1,4 \cdot 10^6$. Dans le domaine 0–100 μ g de Zn pour 50 ml, la loi de Lambert-Beer est suivie. La réaction a été appliquée au dosage du zinc dans le bronze après une séparation préliminaire sur un échangeur d'ions.

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THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—VI*

THE DETERMINATION OF TANTALUM AND NIOBIUM

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Summary—A method is described for the determination of tantalum and niobium in beryllium or beryllium oxide. These two elements are precipitated with cupferron, using zirconium as a collector. A further separation from other elements is obtained by passing a mixed chloride-fluoride solution through a column containing a strongly basic anion-exchange resin. Niobium and tantalum are selectively eluted from the column and finally determined spectrophotometrically, niobium with hydroquinone and tantalum with pyrogallol. For niobium, the method is accurate to $\pm 5\%$ or $10\ \mu\text{g}$, whichever is greater, and for tantalum it is accurate to $\pm 10\%$ or $30\ \mu\text{g}$, whichever is greater. No interference was caused by the presence of 10-mg amounts of 68 elements.

INTRODUCTION

A METHOD for the determination of niobium and tantalum is presented which is specific within the limits investigated. No interference was caused by 10-mg amounts of 68 elements.

The method is based on the precipitation of niobium and tantalum from a mixed hydrochloric-sulphuric acid solution with cupferron using zirconium as a collector. A hydrochloric-hydrofluoric acid solution, containing the niobium and tantalum and other elements quantitatively or partly precipitated with cupferron (antimony, bismuth, copper, gallium, hafnium, iron, molybdenum, palladium, tin, titanium, vanadium, tungsten, and zirconium), is passed through a column containing Dowex-1X8 anion-exchange resin. Niobium and tantalum and a portion of the tin are retained, all other elements passing unadsorbed into the eluate. Niobium is subsequently eluted with a mixture of hydrofluoric acid and ammonium chloride. Tantalum is eluted with a mixture of ammonium fluoride and ammonium chloride. The ion-exchange separation of niobium and tantalum, from each other and from other elements, is a modification of work published by Krause and Moore¹ and Hague *et al.*² The two elements are again precipitated with cupferron using zirconium as a collector. Niobium is finally determined spectrophotometrically with hydroquinone in a concentrated sulphuric acid medium.³ The absorbance, measured at 395 or 490 $m\mu$, is a linear function of the niobium concentration, at least from 0 to 4 μg of niobium per ml, and is stable for at least 24 hr. Tantalum is determined spectrophotometrically with pyrogallol in a mixed ammonium citrate-ammonium oxalate-sulphuric acid medium.³ The absorbance, measured at 398 or 420 $m\mu$, is a linear function of the tantalum concentration, at least from 0 to 12 μg of tantalum per ml, and is stable for at least 24 hr.

* Part V, see *Talanta*, 1961, 8, 104.

EXPERIMENTAL

Apparatus

Beckman DU and Cary Model 14 spectrophotometers with 5-cm cells.

Ion-exchange columns: Polyethylene or polystyrene, 1-cm internal diameter, 15-cm long, containing 10 cm of Dowex-1, 200-400 mesh, 8% crosslinkage.

Reagents

Distilled water used throughout.

Standard niobium solution: Fuse 0.1431 g of niobium pentoxide with 5 g of potassium bisulphate. Dissolve the fused mass with 100 ml of 4% ammonium oxalate and dilute the clear solution to 1 litre. Dilute this solution to obtain a solution containing 10 μg of niobium per ml.

Standard tantalum solution: Fuse 0.1221 g of tantalum pentoxide with 5 g of potassium bisulphate. Dissolve the fused mass with 100 ml of ammonium citrate-ammonium oxalate solution (see below) and dilute the clear solution to 1 litre. Dilute this solution to obtain a solution containing 10 μg of tantalum per ml.

Zirconium sulphate solution: Dissolve 0.1 g of zirconium metal in dilute hydrofluoric acid, add 5 ml of sulphuric acid, evaporate to sulphur trioxide fumes and dilute to 100 ml. One ml contains 1 mg of zirconium.

Boric acid

Hydrofluoric acid, 29M:

Hydrochloric acid, 12M, 6M and 1M.

Sulphuric acid, 18M, 9M, 6M and 0.45M.

Nitric acid, 16M.

Cupferron 6% (w/v) aqueous solution, freshly prepared.

Potassium bisulphate

Ammonium hydroxide, 15M.

Sodium bisulphate

Eluent No. 1: Dilute 250 ml of hydrochloric acid and 200 ml of hydrofluoric acid to 1 litre with water.

Eluent No. 2: Dissolve 140 g of ammonium chloride in water, add 40 ml of hydrofluoric acid and dilute to 1 litre.

Eluent No. 3: Adjust the pH of Eluent No. 2 with ammonium hydroxide to 5.7 ± 0.2 .

Hydrogen peroxide, 30%.

Hydroquinone solution: Dissolve 50 g of hydroquinone in 18M sulphuric acid and dilute to 1 litre with the same acid. Prepare fresh as needed.

Tin^{II} chloride solution: Dissolve 10 g of tin^{II} chloride in 40 ml of 6M hydrochloric acid and dilute to 100 ml with the same acid.

Ammonium citrate-ammonium oxalate mixture: Dissolve 3 g of ammonium citrate and 3 g of ammonium oxalate in 100 ml of 0.45M sulphuric acid.

Ammonium oxalate: 4% (w/v) aqueous solution.

Pyrogallol: Some commercially available material results in a cloudy solution when the tantalum complex is formed. It is quite important that the solution whose absorbance is to be measured is clear.

Procedure

Transfer a sample containing 20 to 200 μg of niobium and/or 25 to 300 μg of tantalum to a 600-ml beaker. Dissolve beryllium oxide in hot 6 M sulphuric acid (25 ml for 1 g of beryllium oxide, 50 ml for 3 g). Dissolve beryllium metal by suspending the sample in water and gradually adding hydrochloric acid (10 ml for a 1-g sample). When the reaction ceases, add, if necessary, a few drops of 30% hydrogen peroxide to dissolve any remaining particles of unoxidised metal. Heat to destroy the excess peroxide. Inasmuch as niobium and tantalum are to be precipitated and ignited, they need not be completely dissolved by this treatment. If the sample was dissolved in 6M sulphuric acid, add 10 ml of hydrochloric acid. If the sample was dissolved in hydrochloric acid, add 25 ml of 6M sulphuric acid. Dilute to about 150 ml.

Add 10 ml of zirconium sulphate solution and a little filter pulp. Cool the sample solution, the 6% cupferron solution, and a wash solution of 1M hydrochloric acid containing a little cupferron to

10–15°. Add 15 ml of cupferron solution.⁴ Filter, using Whatman No. 40 filter paper, and wash the precipitate 10 to 15 times with the wash solution. Ignite the precipitate in a platinum crucible and fuse the residue in about 2 g of sodium bisulphate. Sodium bisulphate is used in this case rather than the potassium salt because of the tendency for potassium fluotantalate to precipitate. Dissolve the melt in a polyethylene beaker with 50 ml of Eluent No. 1. Pass this solution through the anion-exchange column and wash with 50 ml of the same eluent, discarding the eluate. Pass 60 ml of Eluent No. 2 through the column. Collect the eluate, containing the niobium and possibly a small amount of tin, in a polyethylene beaker. Replace this beaker with another polyethylene beaker and elute tantalum with 60 ml of Eluent No. 3.

To each of the two eluates add 8 g of boric acid dissolved in about 100 ml of hot water. Add 20 ml of 12*M* hydrochloric acid and transfer the solutions to 400-ml beakers. Dilute to approximately 250 ml. Add 10 ml of zirconium sulphate solution, followed by some filter pulp and 15 ml of cupferron solution. Perform the precipitations below 15° as before. Filter and wash the precipitate 15 times with 1*M* hydrochloric acid containing a little cupferron. Proceed with the treatment of the niobium and tantalum precipitates as follows.

Niobium: Ignite the precipitate in a platinum crucible. Fuse the residue in 1 g of potassium bisulphate and dissolve the melt with 50 ml of 4% ammonium oxalate solution.

Transfer the solution or an aliquot containing about 200 μg of niobium to a 100-ml beaker. Add 10 ml of 9*M* sulphuric acid. If an aliquot is taken, add sufficient potassium bisulphate to provide 1 g of this salt. Add 5 ml of 16*M* nitric acid and 3 ml of 12*M* hydrochloric acid. Evaporate the solution to sulphur trioxide fumes. Add 2 or 3 drops of hydrogen peroxide and 1 ml of water and again evaporate to fumes. Repeat the addition of hydrogen peroxide until there is no further evidence of organic material when the sample is evaporated to sulphur trioxide fumes. Wash down the sides of the beaker with water and again evaporate to fumes. Repeat the water rinse and evaporation step several times. It is essential that organic material is completely destroyed and that nitric acid is completely removed.

Cool, add 1 drop of tin^{II} chloride solution, 25 ml of hydroquinone solution and transfer to a 50-ml volumetric flask, using hydroquinone solution for washing purposes. Dilute to the mark with hydroquinone solution and mix. Allow to stand for 10 min and measure the absorbance in 5-cm cells at 490 $m\mu$ using a reagent blank carried through the entire procedure as a reference. Determine the niobium concentration by reference to a calibration curve obtained by treating aliquots of the standard niobium solution as described in the previous paragraph. A blank and standard should be carried through the entire procedure.

Tantalum: Ignite the cupferron precipitate in a Vycor or quartz crucible. A platinum crucible is not used here because of the interference of platinum in the determination of tantalum with pyrogallol.⁵ Fuse the residue with 0.5 g of potassium bisulphate and dissolve the melt with 15 ml of ammonium citrate-ammonium oxalate solution. Transfer the solution, or an aliquot containing about 300 μg of tantalum, to a 25-ml volumetric flask. If an aliquot is taken, add sufficient potassium bisulphate to provide 0.5 g of the salt. Add 3.0 ± 0.1 g of pyrogallol and swirl until a clear solution results. Dilute to the mark with ammonium citrate-ammonium oxalate solution. Mix, allow to stand for 10 min, and measure the absorbance in 5-cm cells at 398 or 420 $m\mu$ depending upon the instrumentation available, using a reagent blank carried through all steps of the procedure in the reference cell. Determine the tantalum concentration by reference to a calibration curve prepared by adding pyrogallol to aliquots of the standard tantalum solution and diluting to 25 ml with ammonium citrate-ammonium oxalate solution. A blank and standard should be carried through the entire procedure.

DISCUSSION AND RESULTS

Measurement of the niobium-hydroquinone complex

The absorbance of the niobium-hydroquinone complex, although a maximum at 395 $m\mu$, is usually measured at 490 $m\mu$, presumably because of (a) the lack of adequate instrumentation, (b) the high blank at 395 $m\mu$ (when measured in 5-cm cells using sulphuric acid as a reference, the blank is about 0.6 at 395 $m\mu$ compared to about 0.3 at 490 $m\mu$), and (c) the fact that niobium seriously interferes at 395 $m\mu$ whereas little interference is apparent when the absorbance is measured at 490 $m\mu$. The absorbance,

measured at either wavelength, is a linear function of the niobium concentration, at least from 0 to 4 μg of niobium per ml, and is constant for at least 24 hr. The absorbance of a solution containing 2 μg of niobium per ml, in 5-cm cells, is approximately 0.5 at 490 $\text{m}\mu$ and 1.1 at 395 $\text{m}\mu$ (using a reagent blank in the reference cell). A two-fold increase in sensitivity may be obtained by making absorbance measurements using 10-cm cells. Using the procedure described for the formation of the niobium-hydroquinone complex, the absorbance of 1 mg of tantalum is equivalent to approximately 5 μg of niobium at 490 $\text{m}\mu$ and approximately 105 μg at 395 $\text{m}\mu$.

Measurement of the tantalum-pyrogallol complex

The absorbance of the tantalum-pyrogallol complex is a maximum at 398 $\text{m}\mu$. However, the absorbance of the complex is frequently measured at 420 $\text{m}\mu$, presumably because of the lack of adequate instrumentation. The absorbance measured at either wavelength, is a linear function of the tantalum concentration, at least from 0 to 12 μg of tantalum per ml, and is constant for at least 24 hr. The absorbance of a solution containing 12 μg of tantalum per ml, using 5-cm cells, is approximately 0.9 at 398 $\text{m}\mu$ and 0.8 at 420 $\text{m}\mu$. The absorbance is unaffected by the use of 1.5 g of potassium bisulphate rather than the 0.5 g called for in the procedure. The amount of pyrogallol should be controlled at 3.0 ± 0.1 g. The use of greater or less pyrogallol causes a change in absorbance amounting to about 10% per g between 2 and 4 g. Although an increase in the amount of pyrogallol used would result in an increased absorbance, the coloured solution becomes turbid when the amount is slightly greater than 4 g.

Using the procedure described for the formation of the tantalum-pyrogallol complex, the absorbance of 1 mg of niobium is equivalent to that of 4 μg of tantalum, at both 398 and 420 $\text{m}\mu$.

Effect of other elements

In testing the effect of other elements on the determination of niobium and tantalum by the above procedure, the elements were added to a solution containing the appropriate amounts of beryllium sulphate, sulphuric and hydrochloric acids, before the precipitation with cupferron preceding the ion-exchange separation.

No interference was caused by the presence of 10-mg amounts of Al, Sb^{III}, As^{III}, Ba, Bi, B, Br, Cd, Ca, Ce^{IV}, Cs, Cr^{III}, Co, Cu^{II}, Dy, Er, Eu, F, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Hg^{II}, Mo^{VI}, Nd, Ni, Nb (for Ta determination), Pd^{IV}, P(as PO_4^{3-}), Pt^{IV}, K, Pr, Re, Rh, Rb, Sm, Sc, Se^{IV}, Si, Na, Sr, Ta (for Nb determination), Te^{IV}, Tb, Tl, Th, Tm, Sn^{IV}, Ti^{IV}, W^{VI}, U^{VI}, V^{VI}, Yb, Y, Zn or Zr.

It should be noted that the preliminary precipitation with cupferron separates niobium and tantalum from all but antimony, bismuth, copper, gallium, hafnium, iron, molybdenum, palladium, tin, titanium, vanadium, tungsten and zirconium.

The subsequent anion-exchange step provides two solutions. One contains niobium and part of the tin originally present in the sample, the other contains only tantalum. Tin does not interfere with the niobium determination, being used as a reagent in the final spectrophotometric determination with hydroquinone.

Application of the method

A 10-g sample of beryllium oxide analysed for niobium and tantalum using this procedure was found to contain less than 1 ppm of niobium and less than 3 ppm of

TABLE I. RECOVERY OF NIOBIUM AND TANTALUM ADDED TO BERYLLIUM OXIDE

BeO, g	Nb added, μg	Nb found, μg	Ta added, μg	Ta found, μg
2	15	21.0	—	—
5	50	54.2	—	—
5	100	97.3	—	—
5	225	218.0	200	208.3
5	200	—	500	519.3
5	—	—	50	43.0
5	—	—	150	158.9
5	—	—	250	245.3
5	—	—	400	382.7
5	200	—	400	390.2
5	2000	—	250	254.4
5	250	247.6	2000	—

tantalum. The recovery of niobium and tantalum added to this sample of beryllium oxide is shown in Table I.

No niobium or tantalum was found in 3-g portions of New Brunswick Laboratory standard samples of beryllium metal (85, 86, 87, 88) and beryllium oxide (72-1, 72-2, 72-3, 72-4, 72-5), indicating the concentration of niobium in these samples to be less than 3.3 ppm and that of tantalum less than 10 ppm.

Zusammenfassung—Eine Methode zur Bestimmung von Tantal und Niob in Beryllium und dessen Oxyd wird beschrieben. Die beiden Elemente werden mittels Cupferron gefällt unter Verwendung von Zirkonium als Collector. Eine Trennung von weiteren Ionen wird erzielt, indem man die Lösung, die Fluss- und Salzsäure enthält, durch einen starken Anionenaustauscher schickt. Niob und Tantal werden selektiv eluiert und schliesslich photometrisch bestimmt; Niob mit Hydrochinon und Tantal mit Pyrogallol. Die Methode ist genau auf 5% oder 10 μg Niob und 10% oder 30 μg Tantal, was immer der grössere Wert ist. Keine Störung wird versucht durch Anwesenheit von 10-mg Mengen von 68 geprüften Fremdelementen.

Résumé—Les auteurs décrivent une méthode de dosage du tantale et du niobium dans le béryllium ou l'oxyde de béryllium. Ces deux éléments sont précipités par du cupferron, le zirconium étant utilisé comme collecteur. Une séparation ultérieure des autres éléments est réalisée en faisant passer une solution de chlorure et fluorure mélangés sur une colonne contenant une résine échangeuse d'anions fortement basique. Le niobium et le tantale sont élués sélectivement et sont dosés finalement par spectrophotométrie, le niobium avec de l'hydroquinone et le tantale avec du pyrogallol. Pour le niobium, la méthode est précise à ±5% ou 10 μg et pour le tantale à ±10% ou 30 μg. La présence de quantités de l'ordre de 10 mg de 68 éléments ne gêne pas le dosage.

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THE ANION-EXCHANGE SEPARATION OF TIN, ANTIMONY, LEAD AND COPPER

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Summary—The selective adsorption of anionic complexes of tin, antimony, lead and copper on an anion-exchange resin is used for their quantitative separation from each other. The method is subsequently adapted to the analysis of alloys.

INTRODUCTION

THE widespread employment of alloys containing varying amounts of tin, lead, copper and antimony, together with the tediousness of established methods for their analysis, have prompted the search for a stepwise anion-exchange separation of these metals.

Conditions for the adsorption on anion-exchange resins, from various media, have been determined for most of the above metals¹ and single components have also been separated from others,^{2,3} but no complete stepwise separation of this metal system, allowing the successive determination of its components, has been described.

DISCUSSION

The separation of metals on anion-exchange resins is based on the selective adsorption of their anionic complexes on the resin, this being a function of the nature of the complex-forming ligand, the composition of the medium employed, *etc.* Adsorption curves from a base electrolyte of the type HL usually exhibit maxima, due to the formation, at high acidities, of an uncharged species, $H_s ML_n$. This complex does not, to any appreciable extent, enter the resin; its formation, therefore, is accompanied by a decrease in the concentration of metal in the resin phase. The heights and relative positions of these maxima vary from metal to metal, according to the stability of the metal-ligand complexes, their dimensions, *etc.*

From published adsorption curves¹ it appears that many elements may be separated, singly or in groups, employing hydrochloric acid and an anion-exchange resin; the co-employment of other eluents greatly widens the applicability of the method.

It was decided to use these curves as a starting point, rather than employ the recent half-theoretical approach of building adsorption curves,⁴ since the presence of numerous adverse factors, such as probable side reactions and the un-ideal systems incurred, made this appear impracticable.

From a consideration of data published by Kraus and Nelson¹ for adsorption on Dowex-1 resin, several possibilities of separation for the Sn-Sb-Cu-Pb system seemed feasible. Table 1 contains pertinent distribution coefficient data for varying concentrations of hydrochloric acid, while similar data for 1N hydrofluoric acid, in

the presence of varying concentrations of hydrochloric acid, are summarised in Table II.

TABLE I.—ADSORPTION OF Sn^{IV}, Sb^V, Sb^{III}, Cu^{II} and Pb^{II} FROM HYDROCHLORIC ACID (D = DISTRIBUTION COEFFICIENT)

HCl, N	12	7	2.4	1.5
log D:				
Sn ^{IV}	3.3	2	3	2.8
Sb ^V	5.4	4.8	1.7	0
Sb ^{III}	1.2	2	2	3.3
Cu ^{II}	1	1	0	0
Pb ^{II}	0	0	1	1.1

TABLE II.—ADSORPTION OF Sn^{IV}, Sb^V and Sb^{III} FROM MIXTURES OF HYDROCHLORIC ACID AND 1N HYDROFLUORIC ACID (D = DISTRIBUTION COEFFICIENT)

1N HF—HCl; HCl, N	0.3	1	6
log D:			
Sn ^{IV}	1.8	1	3
Sb ^V	2.8	2	2.5
Sb ^{III}	0.3	1	2

Because of the similarity of the resins, it seemed permissible to employ these data as starting points for a separation employing Amberlite IRA-400. This was borne out by the similarity of adsorption data for copper, obtained experimentally on both resins. The proposed sequence of elution steps, based on these data, is summarised in Fig. 1;

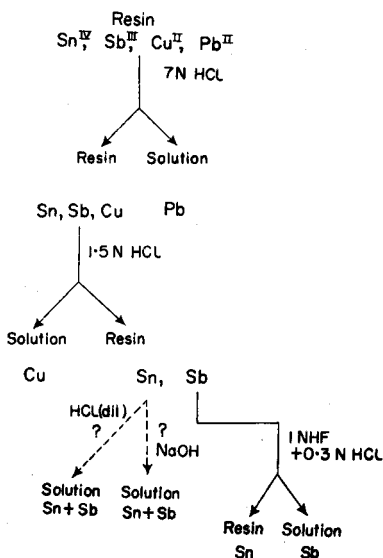


FIG. 1.—Scheme for the successive elution of Pb^{II}, Cu^{II}, Sb^{III} and Sn^{IV}.

for each successive elution step, eluents were chosen in which D for the element to be eluted was low and that of the others, to be retained in the column, high.

Column length, size of the resin particles and minimum volume of eluent necessary for each quantitative elution were computed theoretically,⁵ and found suitable for the practical carrying out of the separation. The sample size chosen initially was small (*ca.* 1 mg for each metal), with a view to exploiting fully the speed and convenience of micro methods. Subsequent considerations limited the sample size further, the final method being applicable to samples containing up to 400 μg of each metal. It was found that the precision obtainable was limited chiefly by the methods employed for the determination of the single components ($\pm 1\%$ maximum relative error) and not by the efficiency of the separation, which was better than this error limit.

Following the theoretical computations, the minimum volume of eluent necessary for the quantitative elution of 1 mg of each element was determined experimentally. The amount of elution of each element, as caused by the passage, through the column, of the eluents employed for the elements eluted previously, was also determined. The data of the elution curves obtained are condensed in Fig. 2. Inspection of this figure might indicate the feasibility of a successive separation of the four elements, based on the elution curves of the single metals. An experimental attempt to separate the elements, by passing volumes of eluents sufficient for their elution when present singly,

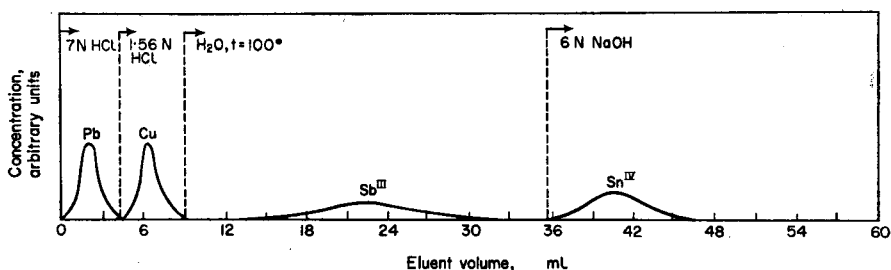


FIG. 2.—Elution curves for Pb^{II} , Cu^{II} , Sb^{III} and Sn^{IV} (present singly).

was, however, unsuccessful; as may be seen from Table III, only tin was eluted quantitatively; antimony remained in the column, while the elution of copper and lead was incomplete.

TABLE III.—ATTEMPTED SEPARATION OF A MIXTURE OF Sn^{IV} , Sb^{III} , Cu^{II} and Pb^{II}

Element	Eluent employed	Eluent volume, ml	Element in mixture, mg	Element eluted, mg	% eluted
Pb	7N HCl	4.0	0.500	0.150	30
Cu	1.56N HCl	4.0	0.500	0.389	78
Sb	H_2O at 100°	25.0	0.500	0	0
Sn	6N NaOH	10.0	1.000	0.995	100

It is apparent that in the presence of more than one element and as a result of their mutual interaction, the elution curves are displaced in the direction of larger eluent volumes required for quantitative separation. The extent of this displacement was determined experimentally; the results are given, in Fig. 3 for the elution of lead, in Figs. 4 and 5 for the elution of copper, and condensed in Fig. 6. As is apparent

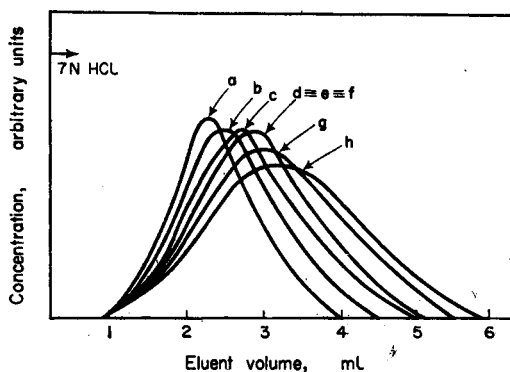


FIG. 3.—Elution curves for Pb^{II} from columns loaded with:
 a. 0.2 mg of Pb^{II} ;
 b. 0.2 mg of Pb^{II} , 1 mg of Cu^{II} ;
 c. 0.2 mg of Pb^{II} , 1 mg of Cu^{II} , 1 mg of Sb^{III} ;
 d. 0.2 mg of Pb^{II} , 1 mg of Cu^{II} , 1 mg of Sb^{III} , 0.4 mg of Sn^{IV} ;
 e. 0.05 mg of Pb^{II} , 0.4 mg of Sn^{IV} ;
 f. 0.05 mg of Pb^{II} , 0.5 mg of Sn^{IV} ;
 g. 0.4 mg of Pb^{II} , 0.4 mg of Sn^{IV} ;
 h. 0.05 mg of Pb^{II} , 2 mg of Sn^{IV} .

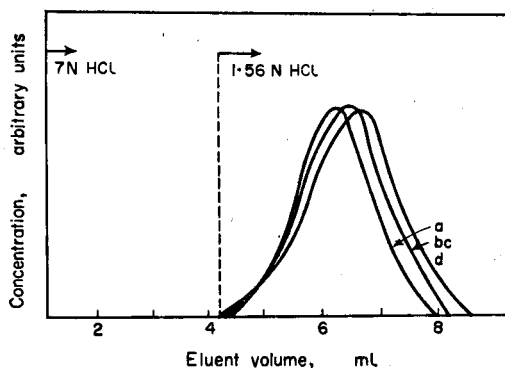


FIG. 4.—Elution curves for Cu^{II} from columns loaded with:
 a. 1 mg of Cu^{II} ;
 b. 1 mg of Cu^{II} , 0.2 mg of Pb^{II} ;
 c. 1 mg of Cu^{II} , 0.2 mg of Pb^{II} , 1 mg of Sb^{III} ;
 d. 1 mg of Cu^{II} , 0.2 mg of Pb^{II} , 1 mg of Sb^{III} , 0.4 mg of Sn^{IV} .

from Fig. 6 the efficiency of the separation can be upheld only by severely limiting the amount of tin present in the sample mixture, the upper limit being $400\mu g$ (see Fig. 6c; at this concentration of tin, there is minimum overlapping).

The elution of antimony, employing boiling water as eluent, is seriously disturbed by the presence of tin. Even 6N sodium hydroxide solution, which should elute both tin and antimony simultaneously, elutes tin quantitatively and does not elute antimony, which remains in the column and is not eluted by either hot water or 6N sodium hydroxide even after the tin has been removed quantitatively. No adequate explanation of this surprising retention of antimony has been found; it might be supposed that it is due to the formation, in the presence of tin, in sodium hydroxide solution or water, of some antimony compound which is tenaciously held by the resin.

As may be seen from Table II, a solution 0.3N in hydrochloric acid and 1N in hydrofluoric acid should elute antimony, leaving tin in the column. The tin may

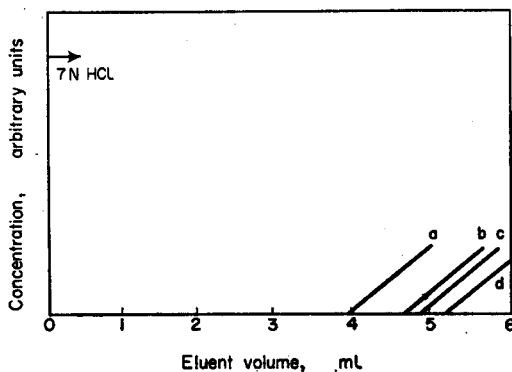


FIG. 5.—Elution curves for Cu^{II} from columns loaded with:
 a. 1 mg of Cu^{II} ;
 b. 1 mg of Cu^{II} , 0.4 mg of Sn^{IV} ;
 c. 1 mg of Cu^{II} , 0.5 mg of Sn^{IV} ;
 d. 1 mg of Cu^{II} , 2 mg of Sn^{IV} .

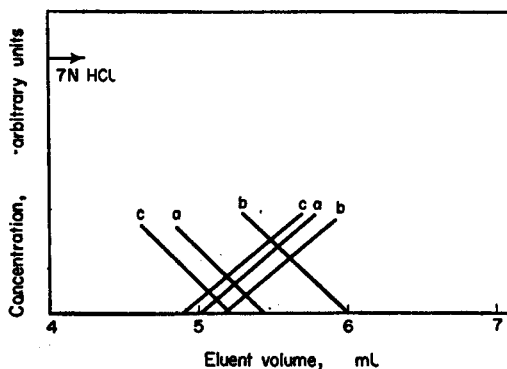


FIG. 6.—Overlapping of Pb^{II} and Cu^{II} elution curves, for varying amounts of Sn^{IV} present:
 a. Condensation of data presented in Fig. 3f and Fig. 5c;
 b. Condensation of data presented in Fig. 3h and Fig. 5d;
 c. Condensation of data presented in Fig. 3e and Fig. 5b.

subsequently be eluted with 6*N* sodium hydroxide solution. The pertinent elution curves for 1 mg of each element were experimentally determined and are given in Figs. 7 and 8. The use of hydrofluoric acid demands the employment of corrosion-proof apparatus, the construction of which is described below (Fig. 9).

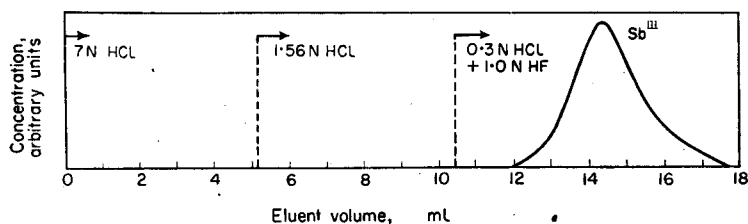
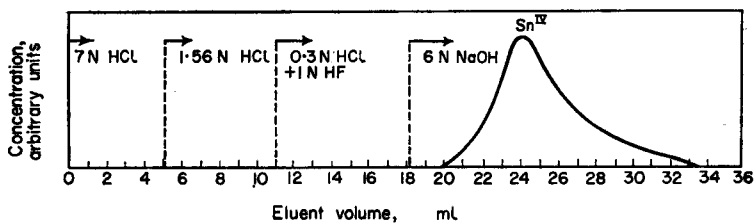
The separation of the four elements is feasible, as may be seen from Fig. 10 which contains the condensed facts of Figs. 3b, 4d, 5b, 7 and 8. Synthetic mixtures of varying proportions of the constituents were absorbed on the resin and the metals eluted successively by passing 5.2 ml of 7*N* hydrochloric acid for the lead, 5.2 ml of 1.56*N* hydrochloric acid for the copper, 7.7 ml of 1*N* hydrofluoric acid 1*N* in hydrochloric acid for the antimony and, finally, 10 ml of 6*N* sodium hydroxide solution for the tin. Each metal was determined in its eluate by methods specified in the experimental part of this paper. Blank determinations were carried out in each case, but were found significant for tin only, where they were properly deducted. The results obtained are given in Table IV.

The method was adapted to the analysis of tin- and lead-base alloys, which were dissolved in concentrated hydrochloric acid and either hydrogen peroxide or bromine

TABLE IV.—THE SEPARATION AND DETERMINATION OF Sn^{IV} , Sb^{III} , Cu^{II} AND Pb^{II} FROM THEIR MIXTURES

Metal content of sample, μg				Metal recovery after separation, μg							
Pb	Cu	Sb	Sn	Pb	Relative error, %	Cu	Relative error, %	Sb	Relative error, %	Sn	Relative error, %
		40.0	400.0					40.3	+0.3	397.0	-0.8
200.0			400.0	198.0	-1.0					406.0	+1.3
400.0		40.0		396.0	-1.0			39.7	-0.8		
40.0		40.0	400.0	39.5	-1.2			39.7	-0.8	395.0	-1.2
100.0	60.0	40.0	400.0	98.9	-1.1	59.0	-2.0	39.5	-1.2	397.0	-0.8

water or potassium chlorate, the solution obtained containing copper^{II}, lead^{II}, antimony^V and tin^{IV}, hydrochloric acid and excess oxidising agent. Antimony may be reduced by various reagents such as sodium sulphite,⁶ tin^{II} chloride,⁷ chromium^{II}

FIG. 7.—Elution curve for Sb^{III} .FIG. 8.—Elution curve for Sn^{IV} .

chloride,⁸ titanium^{III} chloride⁹ or mercury metal.¹⁰ It was considered inadvisable to introduce new cations, or anions which might complex the metals, into the system; hydrogen peroxide was, therefore, employed as oxidising agent and sodium sulphite as reducing agent. After reduction, the solution is ready for adsorption on the resin column, and elution by the method evolved. Table V contains the analysis of the alloys employed to test the method (according to A.S.T.M. methods), together with representative results obtained by the proposed procedure.

As may be seen, good results ($\pm 2\%$ maximum relative error) may be obtained with this method; in view of the speed with which an analysis can be carried out (four parallel analyses may be completed in 2 hr) this seems satisfactory. The percentage composition of the alloys to which this method is applicable may vary considerably.

TABLE V.—ANALYSIS OF TIN- AND LEAD-BASE ALLOYS*

Analysis of alloy, %				Experimental results by proposed procedure, %					
Pb	Cu	Sb	Sn	Pb	Relative error	Sb	Relative error	Sn	Relative error
36.5		6.22	63.6	36.1	-1.1	6.16	-1.0	63.0	-0.9
94.7		5.00	93.8	93.2	-1.5	4.96	-0.9	93.0	-0.9
50.4	0.92	7.40	42.1	49.8	-1.3	7.34	-0.8	41.7	-1.0

* Copper was not determined after its separation; the amount present in the standard alloys available was too low for satisfactory determination by the spectrophotometric method employed.

EXPERIMENTAL

Apparatus

Polarographic determinations were carried out with a Type E Leeds Northrup Electro-Chemograph, spectrophotometric measurements with a Unicam SP 500-spectrophotometer, and potentiometric titrations with a Fisher Titrimeter.

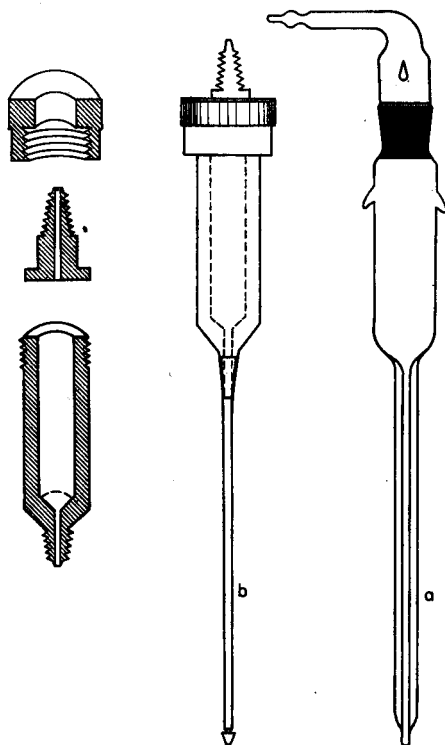


FIG. 9.—Construction details of columns employed.

Adsorption columns: The anion-exchange resin employed was 100–140 mesh Amberlite IRA-400, washed and decanted. The columns employed were 200 mm long, with an internal diameter of 3 mm. The eluents were passed through the column at the rate of 3 ml per min. Two kinds of columns were used in this work (Fig. 9): one constructed from glass only (Fig. 9a) and the other made of Plexiglass and Tygon tubing (Fig. 9b). The upper part of the latter column contains three Plexiglass parts; a section of 0.3-mm internal diameter and 200 mm long Tygon tubing is attached; this contains a small

conus of hard plastic material at its end, to serve as a support for some thin Plexiglass shavings on which the resin filling rests. Four such columns are connected, by means of individual pressure taps and a manifold, to a pressure source, such as an oxygen or nitrogen gas container. This arrangement allows the regulation of pressure for each column separately, without affecting the other three. After passing 4 ml of 7*N* hydrochloric acid through each column, the apparatus is ready for use.

Reagents

Standard copper, antimony tin and lead chloride stock solutions: Prepared by dissolving appropriate amounts of the pure metals in mixtures of hydrochloric acid and hydrogen peroxide, removing excess peroxide by boiling and making up to volume with hydrochloric acid (antimony was reduced to the trivalent state by adding small amounts of sodium sulphite to the solution and boiling, before the final dilution). From these, by appropriate dilution with 1:1 hydrochloric acid, the solutions employed in the experiments described, containing the single metal ions or their mixtures, were prepared.

Standard potassium bromate solution: Prepared by dissolving the pure, dried salt in water and checked against the standard antimony^{III} solution.

All other reagents were of reagent grade.

Procedures

The methods employed for the determination of the single components (after collection of the pertinent eluate fraction) are:

1. Lead was determined polarographically, a method based on the reduction of plumbite ion in 1*N* sodium hydroxide solution being employed.¹¹ The lowest limit for this determination was 10 mg of lead per litre, within the limits of error allowed.

2. Antimony was determined by potentiometric titration with potassium bromate.¹² This method gave rapid and accurate results, provided the oxide film formed on the platinum electrode^{13,14} was removed by immersing the electrode for 15 min in a reducing solution (0.01*M* iron^{II} sulphate, 0.05*M* in sulphuric acid) after each titration. The hydrofluoric acid present in the eluate slowly attacks the glass parts of the electrodes, making their replacement advisable after *ca.* 50 titrations. One mg of antimony per litre could still be easily determined, with a relative error not exceeding $\pm 1\%$.

3. Tin was determined polarographically in a supporting electrolyte 3*N* in sodium chloride and 1*N* in hydrochloric acid, with 0.001% Triton X-100 present as maximum suppressor. The composition of the supporting electrolyte was dictated by the eluent employed for tin (6*N* sodium hydroxide solution). Seven mg of tin per litre could still be determined with a relative error not exceeding $\pm 1\%$.

4. Copper was determined spectrophotometrically, employing ferrocyanide.¹⁵

Based on the above, the following procedure is suggested for the separation of lead, copper, antimony and tin:

0.1 ml of the sample, containing up to 400 μg of each metal and 7*N* in hydrochloric acid, is introduced on top of the resin column, followed by two successive portions of 0.2 ml each of 7*N* hydrochloric acid. The following eluents are now passed through the column at the rate of 3 ml per min: 5.2 ml of 7*N* hydrochloric acid (lead fraction), 5.2 ml of 1.56*N* hydrochloric acid (copper fraction), 7.7 ml of 1*N* hydrofluoric acid, 0.3*N* in hydrochloric acid (antimony fraction), 1 ml of 7*N* hydrochloric acid (to be discarded; this serves to remove hydrofluoric acid from the column), and 10 ml of 6*N* sodium hydroxide solution (tin fraction).

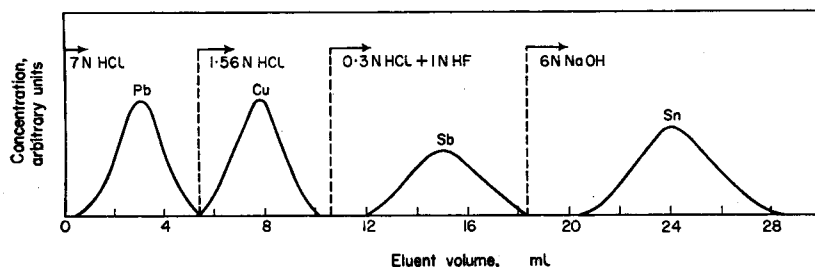


FIG. 10.—The separation of the four elements.

The eluents are passed through the column in the order given, each fraction being collected separately and analysed by the methods specified above.

For the analysis of alloys, 0.1–0.3 g of the alloy are dissolved in 15 ml of concentrated hydrochloric acid, with the dropwise addition of 3 ml of 30% hydrogen peroxide and heating. After complete dissolution, excess hydrogen peroxide is removed by boiling, the solution is cooled and 0.3 g of sodium sulphite are added. Two short glass capillaries are introduced, the solution is boiled to remove sulphur dioxide and is made up to 25 ml with concentrated hydrochloric acid. An aliquot of this solution is now introduced on top of the resin column and eluted according to the procedure suggested above.

Zusammenfassung—Die selektive Sorption der negativ geladenen Komplexionen von Zinn, Antimon, Blei und Kupfer an einem Anionenaustauscher wurde herangezogen um die Metalle voneinander quantitativ zu trennen. Die Methode wurde zur Analyse von Legierungen verwendet.

Résumé—La fixation sélective des complexes anioniques de l'étain, de l'antimoine, du plomb et du cuivre sur une résine échangeuse d'anions a été utilisée pour leur séparation quantitative. La méthode a été ensuite adaptée à l'analyse des alliages.

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THE SELECTIVE DETERMINATION OF ACTIVE HYDROGEN WITH DISPERSED SODIUM

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Summary—Sodium in the dispersed state has been found to be a selective reagent for the determination of active hydrogen in acids, alcohols, phenols, amides and sulphonamides. The pressure change in a constant-volume system caused by the evolution of gaseous hydrogen is measured after a sample is treated with an excess of dispersed sodium. Under the same conditions, amines, aldehydes, ketones, esters and 1-acetylenes do not produce any hydrogen.

THE many methods available^{1,2,4,7,9-11} for the determination of active hydrogen in organic compounds share the characteristic that each technique determines the total active hydrogen present without regard to the particular type of compound represented. Such a lack of selectivity is a distinct drawback to active hydrogen analysis.

In the procedure developed here, three methods of determination are used to separate the compounds containing active hydrogen into three classes of reactivity. The first two methods use a dispersion of metallic sodium in an inert medium as the reagent, while the third method can be any of the conventional, undifferentiating procedures.

The most reactive group of compounds containing active hydrogen is that comprising the acids, alcohols and some phenols, which can be determined by adding an excess of a standardised dispersion of sodium to a weighed sample dissolved in xylene, and converting the excess sodium to sodium ethoxide with an excess of ethyl alcohol. The sodium ethoxide is titrated with a standard acetic acid solution, and the amount of sodium consumed by the organic acid or active phenol is found by difference. The details of this procedure have been published.⁶

The sum of the active hydrogen due to the most reactive group of compounds and the group of intermediate reactivity, including acetylated amines, sulphonamides and the remainder of the phenols, can be determined by the procedure described in detail in the experimental part of this paper.

The sum of all types of active hydrogen can be determined by any of the conventional procedures, such as the Zerewitinoff method or the lithium aluminium hydride method. By difference one can ascertain the amount of active hydrogen contained in the least reactive group, which includes aldehydes, ketones, amines, esters and 1-acetylenes.

In the procedure described here for the determination of the sum of the highest and intermediate reactivity groups, an excess of dispersed sodium is allowed to react with either a pure liquid sample or a solution of a solid sample in an inert solvent, and the evolved hydrogen is determined by measuring the pressure change when the reaction is carried out in a constant-volume system.

EXPERIMENTAL

Reagents

Commercially available reagent-grade chemicals were used when possible. Solvents were purified by refluxing over sodium, followed by distillation. Samples were the best grade available and were used without further treatment in most cases.

Dispersed sodium: The dispersions of sodium were prepared using the apparatus described by U.S. Industrial Chemicals Co.,⁸ modified by passing the stirrer shaft through a ball bearing instead of through the Oilite bushing, and omitting the thermometer. Periodic replacement of the ball bearing was necessary, as the condensing solvent vapours gradually removed the grease. Two hundred and fifty ml of xylene, 10 drops of oleic acid and approximately 2 g of sodium were added to a 500-ml three-necked creased flask, which was then mounted in the apparatus and allowed to heat. When the sodium had melted, the mixture was stirred at about 12,000 rpm for 10 min. The resulting dispersion was allowed to cool, with care being taken not to agitate the mixture during cooling, in order to prevent coagulation. Dry, oxygen-free nitrogen was passed over the contents of the flask throughout these operations.

When cool, the dispersions were diluted with 500 ml of either xylene or dioxan, and a second 10 drops of oleic acid were added. The diluted dispersion was refluxed overnight while protected from moisture with a Drierite drying tube.

A freshly shaken dispersion may be satisfactorily pipetted with only the normal precautions for a corrosive liquid.

Apparatus

Measurements of pressure change caused by liberated hydrogen were carried out in a cylindrical glass vessel 40 cm long and 4 cm in diameter, topped by a 34/28 standard taper joint with a long tube sealed in it. The inner tube extends to within a few cm of the bottom, to accommodate a 1-ml ampoule which is supported by a brass plate held to the bottom of the inner tube by means of four springs attached to hooks on the outer side of the tube. The tube extends 25 cm above the joint to accommodate a pointed iron striker which is held in place by an external magnet. A side arm near the top of the vessel leads to a vacuum line, an outlet to the air, and a mercury manometer. The vessel is mounted in a constant-temperature bath. A magnetic stirrer placed below the water bath permitted the sodium to be kept in suspension.

Procedure

The measurements were carried out by sealing a weighed sample in an ampoule, mounting it in the apparatus containing 100 ml of dispersed sodium, applying vacuum to the system until solvent ebullition commenced, and closing the system. In 20 min to 1 hr a constant pressure reading may be obtained on the manometer, at which time the striker is allowed to fall, breaking the ampoule and initiating the reaction. When constant pressure is again attained, the result is noted.

Calibration

Seven samples of Baker and Adamson reagent-grade methanol and six samples of Matheson, Coleman and Bell Spectroquality methanol were measured by the foregoing procedure and assumed to contain 1.00 active hydrogen. From the weights of the samples and their corresponding pressure changes the volume of the system was calculated. Blanks were determined and found to produce 4 mm pressure change.

Calculation

The weight of the sample and the corresponding pressure change, corrected for the blank, along with the temperature, molecular weight and volume of the system, were used to calculate the number of active hydrogens present per molecule.

Choice of conditions

Experiments under a variety of conditions showed that solid samples did not react satisfactorily, probably because the inner parts of the solid did not come into contact with the sodium. Liquid samples were found to react satisfactorily, and solids were determined successfully if dissolved in

dioxan. The dispersion was found to be most suitable when prepared in a mixture of 2 parts of dioxan to 1 part of xylene by volume. Apparently the solvent power of dioxan for the salt-like products formed was necessary to prevent these products from coating the sodium particles before reaction was complete. Dispersions in dioxan alone were not used, as it was felt that finely divided sodium floating to the top of the dispersion medium upon standing created a situation too hazardous for routine determinations.

RESULTS AND DISCUSSION

Table I shows the number of active hydrogens found for a variety of compounds and the average error for the determinations, calculated as the difference between the pressure change found and the pressure change expected for the sample if it contained an integral number of active hydrogens.

TABLE I. VALUES OF ACTIVE HYDROGEN DETERMINED

Compound	Number of Determinations	Average amount taken, <i>m moles</i>	Average active hydrogen	Average error of pressure change (absolute value)
Ethanol	1	4.306	0.98	2.2
t-Butyl alcohol	2	3.867	1.00	2.8
Acetic acid	3	6.029	0.999	2.2
n-Butyric acid	2	4.609	0.99	1.0
Benzoic acid	2	2.040	0.85	9.1
Salicylic acid	2	2.087	1.04	2.4
Resorcinol	8	1.413	1.62	13.0
Aniline	1	3.599	0.09	9.2
n-Butylamine	6	3.368	0.06	5.6
2,4-Dimethylphenol	2	2.688	1.10	7.6
o-Nitrophenol	7	0.979	0.68	9.1
4-Chloro-3-methylphenol	2	1.711	0.89	9.0
2,4-Dinitrophenol	2	0.960	0.92	2.2
Cyclohexanone	4	2.973	0.18	15.9
1-Hexyne	1	3.488	0.003	0.3
n-Butyraldehyde	1	5.327	0.03	4.2
Ethyl acetate	2	3.698	0.04	4.9
Acetone	2	4.640	0.03	3.2
Benzonitrile	1	3.021	0.000	0.6
Azobenzene	1	0.368	0.000	2.2
Bromobenzene	1	3.351	0.000	0.1
Acetanilide	2	0.796	0.87	3.0
Sulphanilamide	3	0.693	0.91	4.9

As a measure of the precision of the method of obtaining the pressure change, the methanol values used to calibrate the volume of the system were re-calculated on the basis of the average volume, and the error in pressure change was found for each sample. The sum of the squares of these errors divided by one less than the number of measurements was used to establish a 95% confidence limit for the error in the pressure change by use of a one-tailed chi square test. Errors in the pressure change greater than the limit found, 11.3 mm, represent errors that could not be accounted for by the pressure measuring device, a metre-stick manometer. Comparison of this value with the average error recorded for each substance in the Table shows that all of the measurements are well within the experimental error of an integral value with the

exception of resorcinol and cyclohexanone. Similar results for these two compounds have been previously reported.^{3,5} The relatively large deviation from theoretical integers with a small experimental error reported for *o*-nitrophenol and acetanilide are due to the limited solubility of the compounds. These small sample sizes caused pressure changes of about 25 mm of mercury, while larger samples of liquids or more soluble solids caused pressure changes as great as 200 mm. Since the errors in measurement were essentially constant, the relative error in the small samples, which is seen as the deviation of the number of active hydrogens from an integer, is considerably greater than for compounds for which larger samples could be used.

The essentially constant errors suggest that the largest errors are independent of the particular substance being determined. A consideration of the various sources of experimental error indicates that the primary cause of poor precision is in the reading of values on the manometer. The manometer used for this exploratory work was a 4 mm glass capillary bent in the form of a U around a metre-stick and filled with mercury. It is to be anticipated that the use of a more precise manometer with the present system will yield values having a precision of 1 to 2% for small samples and a few parts per thousand for liquids and readily soluble solids. In fact the use of a differential dibutylphthalate manometer might enable even the more difficultly soluble materials to be run with a precision of about 0.5%.

It is particularly of interest to note that aniline and *n*-butylamine do not give any appreciable reaction in this method, thus permitting the differentiation of less reactive types of active hydrogen compounds from the more reactive ones. Extensive studies were made to determine conditions under which amines would react. At the boiling point of xylene, amines were found to be still unreactive. The presence of ferric oxide or chloride, aluminium oxide or chloride, or zinc chloride did not cause amines to show reaction. Sodium dispersions in xylene, tri-*n*-butylamine, and xylene-dioxan mixtures were equally ineffective in causing amines to react.

Since a back-titration procedure using dispersed sodium can be applied to acids, alcohols and some phenols,⁶ it is possible to classify active hydrogen compounds into three reactivity types. The first class are those which can be determined by the back-titration procedure. The second class, some phenols, acetylated amines and sulphonamides are those which show reaction by the procedure presented here but not by the back-titration procedure. Finally, the class of amines, aldehydes, ketones, esters and 1-acetylenes are those which do not react with dispersed sodium but can be determined by a Zerewitinoff method.

Zusammenfassung—Natrium in fein dispergierter Form hat sich als selektives Reagens zur Bestimmung des aktiven Wasserstoffes in Amiden, Alkoholen, Phenolen und Sulfonamiden erwiesen. Die Druckänderungen in einem volumkonstanten System werden gemessen, nachdem die Probe mit dispergiertem Natrium reagiert hat. Unter diesen Bedingungen produzieren Amine, Ketone, Aldehyde, Ester und 1-Acetylene keinen Wasserstoff.

Résumé—Les auteurs ont montré que le sodium, à l'état dispersé, était un réactif sélectif pour le dosage de l'hydrogène actif dans les acides, les alcools, les phénols, les amides et les sulfonamides. La variation de pression, dans un système à volume constant, provoquée par le dégagement de l'hydrogène gazeux, est mesurée après qu'un échantillon ait été traité par un excès de sodium dispersé. Dans les mêmes conditions, les amines, les aldéhydes, les cétones, les esters et les 1-acétylènes ne produisent pas d'hydrogène.

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ISOTOPIC DILUTION ANALYSIS BY SOLVENT EXTRACTION—I

PRINCIPLE AND THEORY OF THE METHOD

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Summary—The proposed method serves for the selective determination of trace amounts of metals. The analytical procedure consists of a single extraction of the metal to be determined, in the form of a complex with an organic reagent, and measuring the radioactivity of the extract obtained. The amount of the organic reagent employed must always be less than would correspond to the stoichiometric ratio. A theoretical evaluation of the extraction is given for these conditions, from which the conclusion may be drawn that a number of metals may thus be determined with greater selectivity than in a conventional extraction with a stoichiometric excess of organic reagent. On the basis of the relation obtained, conditions have been predicted for the determination of many elements. The possibilities of the selective determination of metals in the presence of interfering metals are also discussed.

INTRODUCTION

ISOTOPIC dilution analysis is based on the determination of the change of specific activity caused by mixing a radioactive and a non-radioactive isotope of the element analysed. This method, the foundations of which were laid down by Hevesy and Hobbie¹ and by Starik² more than 25 years ago, has previously been used more often in organic analysis and in biochemistry than in the analysis of inorganic systems, where it has been used relatively seldom. Its greatest advantage over all other analytical methods is, that in order to carry out the analysis only a part of the component to be analysed need be isolated in a pure state, and only the change of the isotopic composition of this part need be determined.

The method of isotopic dilution would be of great importance for trace analysis not only for its high sensitivity, but also because the quantitative separation of the analysed component, present in such small amounts, is otherwise very difficult. The use of the dilution method has up to now been rendered difficult in these cases by the procedure employed, which necessitated the determination of specific activity. Thus, it was necessary to isolate an amount of the substance sufficient to make it possible to determine not only its radioactivity but also its amount. The sensitivity of the analysis was therefore limited by the sensitivity of the method by which the isolated amount was determined. In most of the published methods, precipitation or electrolysis were used for isolation and the isolated amount was either weighed or determined by some other analytical procedure. The amount of the element to be determined was then calculated by the relation:^{1,2}

$$x = y \left(\frac{A_1}{A_2} - 1 \right) \quad (1)$$

where y is the amount of radio-isotope used, A_1 is the specific activity of the radio-isotope, and A_2 is the specific activity of the mixture of radio-isotope and added analysed element. Specific activity is equal to the ratio of absolute activity and amount of sample measured, *i.e.*

$$A_1 = \frac{a_1}{m_1} \quad \text{and} \quad A_2 = \frac{a_2}{m_2}$$

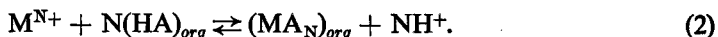
where a_1 and a_2 are the absolute activities, and m_1 and m_2 are the isolated amounts.

If we always isolate the same amounts of the substance from the solution of original activity and from the solution obtained by dilution with the non-active determined element (*i.e.* $m_1 = m_2$), then in relation (1) the specific activities may be replaced directly by relative activities, measured under the same conditions. Therefore it is not necessary to know the values m_1 and m_2 , since for calculation of the amount of the element to be determined it is sufficient to know the relative activities and the amount of radio-isotope added to the analysed solution.

Development of isotopic dilution analysis into the region of trace amounts therefore depends on the development of methods by which equal and very small amounts may always be isolated with high precision and reproducibility. In general this may be done by extraction, chromatography, electrolysis, precipitation or adsorption on surfaces of equal areas. From the results of work published up to now³⁻⁷ and from the results described a further paper,⁸ the most suitable methods are seen to be extraction and electrolysis. The use of ion-exchangers for this purpose will probably also be very advantageous.

THEORY

In order always to extract the same amount of the complex of the metal and the organic reagent from solutions containing various concentrations of this metal, it is necessary always to use a smaller amount of the organic reagent than corresponds to the stoichiometric ratio. The conditions of the extraction in this case may in general be determined from the fundamental equation of the extraction process:



The equilibrium constant of this process, K , is given by:

$$K = \frac{[MA_N]_{org}[H^+]^N}{[M^{N+}][HA]_{org}^N} \quad (3)$$

where the subscript *org* denotes the organic phase. By inserting the equilibrium concentrations of the complex MA_N and of the reagent HA in the organic phase, the concentration of the metal M in the aqueous phase and the value for K in relation (3), the value of the threshold pH may be calculated, at which always the same amount of metal can be extracted.

The equilibrium concentration of the complex MA_N is determined from the condition that more than 99.9% of the organic reagent HA has been used up in forming the complex MA_N , *i.e.*

$$[MA_N]_{org} \cdot V_{org} \geq 0,999 \frac{c_{HA}}{N} \cdot V_{org} \quad (4)$$

where V_{org} is the volume of the organic phase, and c_{HA} is the original concentration of

the reagent in the organic phase. This condition guarantees the isolation always of the same amount of metal with a precision of better than 0.1%.

The equilibrium concentration of the metal M is determined from the relation:

$$[M] \cdot V = c_M \cdot V - \frac{c_{HA}}{N} \cdot V_{org} \quad (5)$$

where V is the volume of the aqueous phase, and c_M is the original concentration of the metal in the aqueous phase.

For the equilibrium concentration of the organic reagent it is found that:

$$[HA]_{org} \cdot V_{org} < 0,001 c_{HA} \cdot V_{org} \quad (6)$$

By solving equations (3), (4), (5) and (6) the value of the threshold pH is:

$$pH \geq \frac{1}{N} \cdot \log \frac{c_{HA}}{N} - \frac{1}{N} \log \left[c_M - \frac{c_{HA} V_{org}}{NV} \right] - \frac{1}{N} \log K - \log 0,001 c_{HA} \quad (7)$$

Expression (7) is precisely valid only in the case where the dissociation of the organic reagent in the aqueous phase may be neglected, *i.e.* when $V \cdot [A^-] < [HA]_{org} \cdot V_{org}$. This condition is fulfilled for a hydrogen ion concentration

$$[H^+] > K_{HA} \cdot q_{HA}^{-1} \frac{V}{V_{org}} \quad (8)$$

where K_{HA} is the dissociation constant of the organic reagent, and q_{HA} is the distribution coefficient of the organic reagent.

For the extraction of metals by a solution of dithizone in carbon tetrachloride, the threshold hydrogen ion concentration, calculated according to equation (7), must be

higher^{9,10} than $10^{-9} \frac{V}{V_{org}} \left(K_{HA} \cdot q_{HA}^{-1} = 10^{-9} \right)$. When the threshold hydrogen ion

concentration is less than $10^{-9} \frac{V}{V_{org}}$, dithizone dissociates in the aqueous phase to such

an extent that the condition expressed by relation (4) cannot be fulfilled.

From an analysis of relation (7) it is evident that the first two terms on the right-hand side have relatively little influence on the value of the threshold pH. If, for example, the amount of organic reagent is less than half that which would correspond to the stoichiometric ratio, the sum of these two terms for $V_{org} = V$ is zero; if the amount of organic reagent is ten times lower, it is equal to $-1/N$ *etc.* A far greater influence on the value of threshold pH is exerted by the last two terms of equation (7). For the determination of microgram amounts of metals, concentrations of the organic reagent of 10^{-4} and less are used, the value of $-\log 0,001 c_{HA}$ is therefore >7 . In order to obtain a threshold pH value which is not too high, one can use for the determination of metal traces by the proposed method only complexes whose value of $-(1/N) \cdot \log K$ is sufficiently low. This condition is best fulfilled by some dithizonates, cupferrates *etc.*⁹ The limitation mentioned, on the other hand, results in an increased selectivity for the various determinations.

In Table I the K values for dithizonates of various metals, threshold pH values and suitable isotopes are listed for the determination of various elements by this method. Threshold pH values have been calculated according to relation (7) for a double

excess of metal, for $c_{\text{HA}} = 10^{-4}M$ and $V/V_{\text{org}} = 10$. The pH region for the determination of a certain metal is limited on the alkaline side partly by the formation of insoluble hydroxides and in the case of dithizonates also by the formation of insoluble secondary dithizonates.¹⁰ Hydrolysis of metals may be eliminated by the use of

TABLE I.—THE K -VALUE OF METAL DITHIZONATES AND THE PREDICTED pH VALUES OF DETERMINATION

Element	K (Reference)	$-\frac{1}{N} \log K$	pH of determination	Suitable isotope (half-life) ¹²
Pd ²⁺			to 4*	
Hg ²⁺	5.7×10^{26} (13) 7.1×10^{26} (14)	-13.4	-6 to 4*	²⁰³ Hg (46.5 d)
Pt ²⁺			to 4*	
Ag ⁺	4×10^7 (15) 9×10^8 (13)	-7.6 -8.9	0 to 7*	¹¹⁰ Ag (270 d)
Po ²⁺				
Cu ²⁺	3.6×10^9 (13) 3×10^{10} (16)	-4.8 -5.2	2.5 to 5*	
Bi ³⁺	3.5×10^9 (13)	-3.6	>4.0	RaD + RaE (25 y)
Au ³⁺			to 4*	
In ²⁺	6.9×10^4 (17)	-1.6	>6.0	¹¹⁴ In (50 d)
Zn ²⁺	5×10^3 (18)	-1.3	>6.2	⁶⁵ Zn (250 d)
Cd ²⁺	1.4×10^3 (18)	-1.1	>6.4	¹¹⁵ Cd (43 d)
Pb ²⁺	17 (18)	-0.6	>6.9	RaD + RaE (25 y)
Ni ²⁺	2.4×10^{-1} (13)	+0.3	>7.8	
Sn ²⁺	9×10^{-3} (13)	+1.0	>8	¹¹⁹ Sn (125 d)
Fe ²⁺			—	
Tl ⁺	4.6×10^{-4} (17)	+3.3	—	
Mn ²⁺			—	

* At higher pH a secondary very slightly soluble dithizonate is formed.¹⁰

complexing agents such as tartrates, cyanides, *etc.* Under these conditions the metal is present in the aqueous phase as a non-extractable complex MB_s , which is in equilibrium with free cations of the metal. The extraction constant of the process is in this case equal¹¹ to:

$$K' = \frac{[MA_N]_{\text{org}}[H^+]^N}{([M^{N+}] + [MB_s])[HA]_{\text{org}}^N} = \frac{[MA_N]_{\text{org}}[H^+]^N}{[M^{N+}](1 + K_s'[B^-]^s)[HA]_{\text{org}}^N} = \frac{K}{1 + K_s'[B^-]^s} \quad (8)$$

where

$$K_s' = \frac{[MB_s]}{[M^{N+}][B^-]^s}$$

and $[B^-]$ is the equilibrium concentration of the anion of the complexing agent.

By inserting relation (8) into relation (7) we obtain:

$$\text{pH} \geq \frac{1}{N} \log \frac{c_{\text{HA}}}{N} - \frac{1}{N} \log \left[c_{\text{M}} - \frac{c_{\text{HA}}}{N} \frac{V_{\text{org}}}{V} \right] - \frac{1}{N} \log K + \frac{1}{N} \log (1 + K_s'[B^-]^s) - \log 0.001c_{\text{HA}} \quad (9)$$

The threshold pH value is increased in the presence of a complexing agent, but on the other hand determinations may be carried out at even high pH values.

DISCUSSION

Selectivity of the method

Each organic reagent forms extractable complexes only with a certain number of metals. It is therefore evident that an extractable metal can be determined in the presence of any excess of non-extractable metals. For instance, each of the elements listed in Table I can be determined in the presence of all metals not named in this table, that is in the presence of all metals which are not extracted by dithizone.

A selective determination of a certain metal may be worked out, however, even in the presence of metals which also form extractable complexes with the reagent employed. The concentration ratio of two metals in the organic phase is easily determined from the individual K values. For instance, from the values of K for mercury and copper dithizonates (Table I):

$$\frac{[\text{HgA}_2]_{\text{org}}}{[\text{CuA}_2]_{\text{org}}} = \frac{10^{26}[\text{Hg}^{2+}]}{10^{10}[\text{Cu}^{2+}]}$$

In this case the ratio $[\text{HgA}_2]_{\text{org}}/[\text{CuA}_2]_{\text{org}}$ is independent of pH and $[\text{HA}]_{\text{org}}$. The concentration of mercury in the organic phase will therefore be 10^{16} times higher than the concentration of copper, but in the presence of excess dithizone both of these elements are extracted together.¹⁰

For silver and copper dithizonates (Table I):

$$\frac{[\text{AgA}]_{\text{org}}}{[\text{CuA}_2]_{\text{org}}} = \frac{10^8[\text{Ag}^+][\text{H}^+]}{[\text{Cu}^{2+}][\text{HA}]_{\text{org}}10^{10}}$$

In this case the charges of the elements which are to be separated are different, and the ratio $[\text{AgA}]_{\text{org}}/[\text{CuA}_2]_{\text{org}}$ depends on pH as well as on $[\text{HA}]_{\text{org}}$. In carrying out the extraction at pH = 0 by a dithizone solution of concentration $10^{-4}M$ ($[\text{HA}]_{\text{org}} < 10^{-7}M$, see relation (6)), the following holds:

$$\frac{[\text{AgA}]_{\text{org}}}{[\text{CuA}_2]_{\text{org}}} \geq 10^5 \frac{[\text{Ag}^+]}{[\text{Cu}^{2+}]}$$

It should therefore be possible to extract silver with sufficient precision even in the presence of a one hundred-fold excess of copper, but on the other hand at pH = 0, in the presence of excess dithizone, both elements are extracted together.¹⁰

From the above it is evident that the metal complex having the highest value of K can be selectively separated from the other metals which form extractable complexes with the given organic reagent. Thus, for instance, the selective separation of mercury in the form of a dithizone complex may be expected (only palladium interferes, see Table I); of iron^{III} in the form of a complex with thenoyltrifluoroacetone or acetylacetone; of gallium^{III} in the form of a complex with 8-hydroxyquinoline, *etc.*

If the K values of separated complexes are near to each other or if the K value of the interfering complex is higher than that of the determined complex, a selective separation may even then be obtained by the addition of a further complexing agent, which forms a non-extractable complex with the interfering ion.

From the values of K we see, for instance, that in the determination of bismuth by dithizone palladium, mercury, silver and copper interfere (see Table I). In the presence of cyanide ions, however, these ions do not interfere, because stable cyanide

complexes are formed. Thus, in the determination of bismuth in the presence of mercury at pH = 9 and $[\text{CN}^-] = 10^{-2} M$ from relation (3):

$$\frac{[\text{BiA}_3]_{\text{org}}}{[\text{HgA}_2]_{\text{org}}} = \frac{10^9 [\text{Bi}^{3+}] [\text{HA}]_{\text{org}} 10^{24}}{10^{26} \cdot C_{\text{Hg}} [\text{H}^+]}$$

where $C_{\text{Hg}} = [\text{Hg}^{2+}] + [\text{Hg}(\text{CN})_4^{2-}] = [\text{Hg}^{2+}](1 + K'_{\text{Hg}(\text{CN})_4^{2-}} \cdot [\text{CN}^-]^4)$
 $(K'_{\text{Hg}(\text{CN})_4^{2-}} = 10^{42})^{19}$

In the presence of cyanide ions there will be a far larger amount of bismuth in the organic phase, even in the presence of excess mercury^{II} ions. As we see from the values of K for lead and tin dithizonates, these elements will not interfere in the determination of bismuth by this method, though in the conventional extraction procedure in cyanide medium these two elements interfere,¹⁰ for like bismuth they form only very weak cyanide complexes.

Similarly, the influence of interfering metals may be eliminated by the use of precipitating agents. For example, diethyldithiocarbamate forms sparingly soluble crystalline precipitates with most metals, except zinc. If the solubility products of these precipitates are known, the influence of interfering metals can easily be determined. Thus, for the extraction of zinc in the presence of mercury and diethyldithiocarbamate:

$$\frac{[\text{ZnA}_2]_{\text{org}}}{[\text{HgA}_2]_{\text{org}}} = \frac{[\text{Zn}^{2+}]10^2}{[\text{Hg}^{2+}]10^{26}} = \frac{P_{\text{Zn}} \cdot 10^2}{P_{\text{Hg}} \cdot 10^{26}}$$

where P_{Zn} and P_{Hg} are the solubility products.

Because $P_{\text{Hg}} \ll 10^{-26} P_{\text{Zn}}$, it is possible to determine zinc even in the presence of mercury.^{20,21}

Limitations of the method

The use of the proposed method for the determination of amounts of metals larger than 1 mg is not advantageous, because physicochemical analytical methods may be used whose precision is, under these conditions, better than the precision of radio-metric methods, which is controlled by the statistical character of radioactive decay. The sensitivity of the method is limited by two factors: (a) the organic reagent employed cannot be diluted infinitely, and (b) at present there are not radio-isotopes of sufficiently high specific activity at hand for all cases. The latter limitation will doubtless be solved by the development of a procedure for the preparation of carrier-free radio-isotopes.

CONCLUSION

On the basis of the principle described, a number of selective determinations of trace amounts of metals in the form of complexes with various organic reagents can be worked out. Up to now the proposed method has been used for the selective determination of zinc in amounts of the order of 10^{-6} to 10^{-9} g/ml.⁸

As was said at the beginning of this paper, a separation of similar amounts may also be carried out using ion-exchangers. The principle of this method is as follows: to the solution, which contains a number of metals, add a complexing agent which forms with the metal to be determined the most stable neutral or negatively charged complex. If the amount of added complexing agent (for instance EDTA) is lower than

that which corresponds to the stoichiometric ratio, then by passing this solution through a cation-exchange column the same amount of metal complex can always be isolated, which fact may be used for the determination of metal traces by isotopic dilution analysis.

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Zusammenfassung—Extraktionsmethoden im Verein mit Isotopenverdünnung erlauben die selektive Bestimmung von Metallspuren. Die Analyse besteht aus einer einzigen Extraktion des Metalles als Komplex mit einem organischen Komplexbildner in eine organische Phase und anschließende Zählung der Radioaktivität der isolierten organischen Phase. Die Menge an organischem Komplexbildner muss immer kleiner sein, als stöchiometrisch nötig. Eine theoretische Behandlung und Erklärung dafür wird mitgeteilt. Es wird gezeigt, dass die Selektivität unter solchen Bedingungen höher ist, als wenn nach der üblichen Art mit Reagensüberschuss gearbeitet wird. Auf grund der Ableitungen wurden die optimalen Bedingungen für verschiedene Systeme vorausgesagt. Die Möglichkeiten in Anwesenheit von Störmetallen zu arbeiten werden ebenfalls diskutiert.

Résumé—L'analyse par dilution isotopique associée à l'extraction par solvant peut servir au dosage sélectif de traces de métaux. La méthode analytique consiste en une simple extraction du métal à doser sous forme d'un complexe avec un réactif organique, et d'une mesure de la radioactivité du produit obtenu. La quantité de réactif organique employé doit toujours être inférieure à celle correspondant au rapport stoechiométrique. Une évaluation théorique de l'extraction est donnée pour ces conditions; on peut conclure qu'un certain nombre de métaux peut être ainsi dosé avec une plus grande sélectivité que dans l'extraction conventionnelle par un excès stoechiométrique de réactif organique. En se basant sur la relation obtenue, les auteurs ont prévu les conditions de dosage d'un certain nombre d'éléments. Les possibilités de dosage en présence de métaux gênants sont aussi discutées.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH NITRILOTRIACETIC ACID

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Summary—Palladium^{II} in aqueous solution yields with nitrilotriacetic acid a complex which is suitable for the spectrophotometric determination of this element. The other platinum metals interfere when present in appreciable amounts. The influence of pH, ionic strength, and palladium and nitrilotriacetic acid concentrations are investigated. Evidence is given for the presence of a bico-ordinated palladium complex.

UNLIKE that of other metals, the behaviour of the noble metals with complexones is only slightly known. This is due to the fact that the platinum group metals either cannot form complexes with ligands of this type or can only do so in special conditions. Palladium, the least noble among the metal ions of the platinum group, is able to form complexes with ethylenediaminetetra-acetic acid (EDTA) as Hynes *et al.*,¹ Flaschka² and MacNevin and Kriege³ have pointed out. The last two authors, in a later work⁴ affirm that iridium^{IV} can also be complexed by EDTA in strongly alkaline media.

In a wide investigation, which is being carried out in this Institute^{5,6} for analytical purposes, of the behaviour of the noble metals with several ligands, a study of palladium complexes with nitrilotriacetic acid (NTA) has seemed worth while. The lack of publications on the behaviour of NTA with noble metals has to be taken into account, as well as the ability of this ligand, in some cases,⁷ to form complexes with a metal-ligand ratio other than 1:1.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman DU spectrophotometer, 1-cm silica cells being used.

Reagents

Palladium solution: Prepared by dissolving PdCl₂ in 0.1M hydrochloric acid and diluting, to give 530 μg of Pd²⁺/ml. The solution was standardised gravimetrically with dimethylglyoxime.

Nitrilotriacetic acid: This solution, after neutralisation with sodium hydroxide, was standardised with magnesium^{II} solution.

Solutions of other noble metals were prepared by diluting standard solutions prepared from IrCl₄, IrCl₃, H₂PtCl₆, RuCl₃, and Na₃RhCl₆.

RESULTS

In a hydrochloric acid medium a deep red-brown chloro complex is formed when palladium^{II} is present, becoming yellow in colour in very dilute solutions. In the violet and ultraviolet range a sharp absorption appears. On adding a small amount of NTA to these solutions, a non-visible reaction occurs, although a noticeable variation in the spectrum can be observed, as is shown in Fig. 1: the maximum is shifted towards a shorter wavelength and the absorption increases greatly; on the whole, the

spectrum appears to be altered appreciably. It is evident that palladium^{II} has been complexed by NTA. When the ligand concentration increases, the colour of the solution decreases slightly.

The palladium^{II}-NTA complexes can be formed either in acidic, neutral or alkaline media, as shown in Fig. 2. A considerable change of the absorption maximum is observed when the hydrogen ion concentration is altered. In the range pH 0-3 the absorbance increases remarkably with pH. On the other hand, in the range pH 3-11 the absorbance is constant, and it decreases above pH 11. As is shown in Fig. 3, a spectrophotometric determination can be performed by adjusting the solution to pH 3-11. The formation of the palladium-NTA complex is practically instantaneous: measurements carried out at several intervals on the same solutions have not shown any appreciable differences.

When plotting the optical density corresponding to the absorption maximum versus NTA concentration in a palladium^{II} solution at pH 7, an unusual curve is obtained. In fact, a maximum is reached (at 360 m μ) with a ratio of Pd: NTA = 1:1; with higher amounts of NTA a decrease is observed up to a ratio of 1:2. At the same time the absorption maximum is slightly shifted to a shorter wavelength. Beyond the latter ratio no noticeable variation is observed at 330 m μ , which is the wavelength of the new maximum.

A reliable interpretation of this phenomenon, which is illustrated in Fig. 4, appears to be as follows: in the presence of a low concentration of complexing agent, the 1:1 complex is firstly formed; with increasing NTA, a more co-ordinated complex is present in solution which presumably has a co-ordination number of 2. The ability of the palladium^{II} ion to co-ordinate two NTA molecules is not completely unexpected: the formation of the bico-ordinated complex depends on the relatively small volume of the ligand, particularly as compared with that of EDTA. Indeed, the only practical difference between these two complexing agents consists in the smaller dimensions of the former.

Adherence to Beer's law in the above mentioned range of pH is shown both by the monoco-ordinated and by the bico-ordinated complex. However, in the case of an analytical determination the ligand concentration must, of course, be higher than that necessary to give the 1:2 complex. A large excess of NTA does not interfere. A suitable analytical range is from 20 to 220 ppm of palladium. In Table I quantitative results are reported.

TABLE I.—DETERMINATION OF PALLADIUM WITH
NITRILOTRIACETIC ACID

Pd taken, ppm	Pd found, ppm
20	20.2
28.5	28.1
53	52.3
79.5	80.1
106	107
132.5	134.1
159	157.8
185.5	184.5
212	213.2

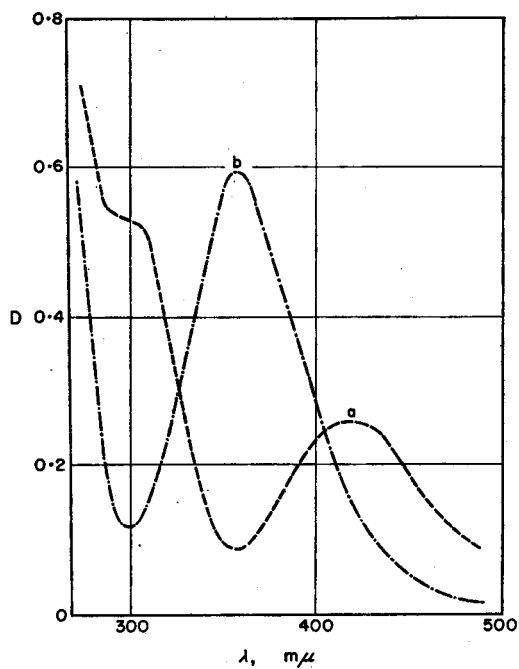


FIG. 1.—Absorbance curves for (a) palladium-chloro complex, and (b) palladium-NTA complex. (Pd = 106 ppm, pH = 7).

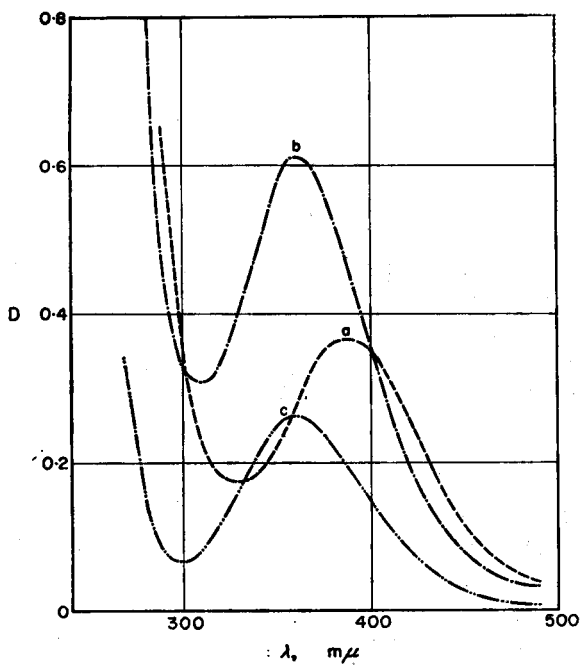


FIG. 2.—Absorbance curves for palladium-NTA complex at (a) pH 1.81, (b) pH 6.86, and (c) pH 11.93. (Pd = 106 ppm, Pd/NTA = 1:1).

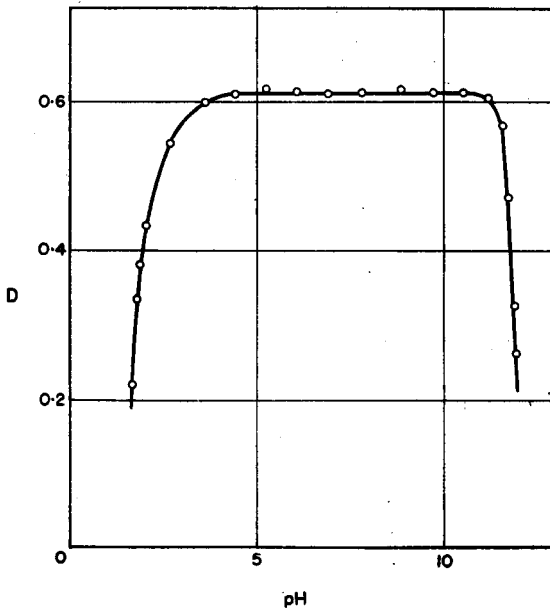


FIG. 3.—Absorbance maximum with change of pH for palladium-NTA complex (Pb = 106 ppm, Pd/NTA = 1:1).

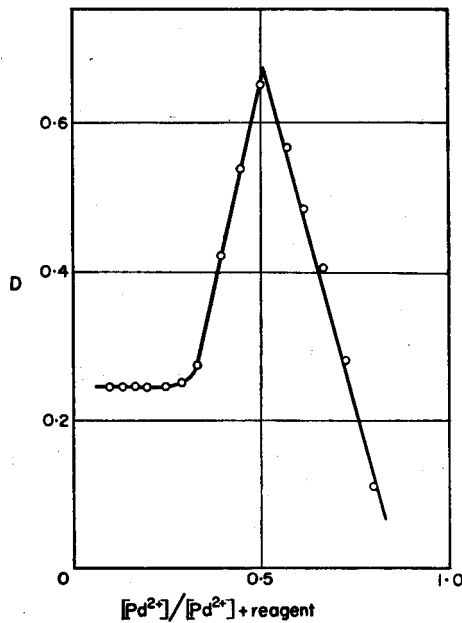


FIG. 4.—Job's method of evaluating the composition of the palladium-NTA complex.

The ionic strength has been maintained constant at about 0.1 by means of sodium perchlorate. An increase in the ionic strength does not involve any appreciable difference in the values of the maximum absorbance, as is shown by the results in Table II.

TABLE II.—EFFECT OF THE "IONIC STRENGTH" ON THE ABSORBANCE OF THE PALLADIUM-NTA COMPLEX (Pd = 106 ppm, Pd/NTA = 1:2).

Ionic strength	Optical density $\lambda = 330 \text{ m}\mu$
0.1	0.448
0.2	0.452
0.3	0.450
0.4	0.447
0.5	0.445

The use of a buffer, such as a phosphate one, to adjust the pH of the solutions in the range 5–9, is permissible. Measurements made after adjusting the solutions to the required pH range with sodium hydroxide, potassium hydroxide or with phosphate buffer yielded similar results.

Interfering ions

The metals of the platinum group interfere with the determination of palladium with NTA when they are present in appreciable amounts. The interferences were studied by observing the absorbance change taking place in a standard solution of

TABLE III.—TOLERANCE TO OTHER PLATINUM METALS

Ion	Limiting concentration, <i>ppm</i>
Ir ^{IV}	19
Rh ^{III}	89
Pt ^{IV}	9.5
Os ^{IV}	3.5
Ir ^{III}	13
Pt ^{II}	4.5
Ru ^{III}	2

palladium^{II} containing an excess of NTA, on the addition of the other metals in the form of chloride solutions. The solutions were adjusted to pH 7 ± 0.5 with sodium hydroxide, potassium hydroxide or phosphate buffer. In Table III are reported the amounts of the other metals which produce a variation of 1% in the optical density. The interference of noble metals can be easily eliminated by separating the palladium^{II}

TABLE IV.—DETERMINATION OF PALLADIUM AFTER SEPARATION FROM Ir^{IV}, Pt^{IV} and Rh^{III} WITH DIMETHYLGLYOXIME

Taken, <i>mg</i>				Pd found, <i>mg</i>
Pd	Pt	Ir	Rh	
1	1	1	1	0.98
1	2	1	1	0.97
1	2	2	1	0.98
1	2	2	2	0.98

by precipitation with dimethylglyoxime according to the method of Ayres and Berg,⁸ digesting the precipitate with *aqua regia*, and then evaporating the solution to dryness. The residue is taken up in dilute hydrochloric acid, and the solution is adjusted to pH 7 ± 0.5 after the addition of an excess of NTA. The absorbance is measured at 330 m μ . In Table IV are reported the results obtained by this method in the determination of palladium in the presence of appreciable amounts of platinum, iridium and rhodium.

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Zusammenfassung—Palladium(II) gibt mit Nitrilotriessigsäure in alkalischem Medium einen Komplex, der die photometrische Bestimmung des Metalles ermöglicht. Andere Platinmetalle stören, wenn in grösseren Mengen anwesend. Der Einfluss von pH, Konzentration der Reaktanten, sowie der Ionenstärke wurde studiert. Evidenz für einen bi-coordinierten Komplex wird erbracht.

Résumé—Le palladium (II) en solution aqueuse donne avec l'acide nitrilotriacétique un complexe qui peut être utilisé pour le dosage spectrophotométrique de cet élément. Les autres métaux de la mine du platine gênent quand ils sont en quantités appréciables. Les influences du pH, de la force ionique, des concentrations du palladium et de l'acide nitrilotriacétique ont été étudiées. Les auteurs montrent la présence d'un complexe bicoordonné du palladium.

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APPLICATIONS OF INFRARED SPECTROSCOPY—IV*

THE CAUSES OF ANOMALOUS ALKOXYL DETERMINATIONS GIVEN BY SUGARS AND POLYHYDRIC ALCOHOLS

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Summary—The volatile reaction products from Zeisel determinations on sugars and related compounds have been identified. One of the products from certain common sugars is 2,5 dimethylfuran, which interferes with the Vieböck iodometric determination of alkyl iodide, and has been shown to be a contributing cause of apparent alkoxy values. Suggestions that hexyl iodide is evolved from sugars and that vinyl iodide is a product from polyhydric alcohols have been disproved.

ZEISEL determinations on unmethylated sugars and polysaccharides have been reported^{1,2} to give small apparent alkoxy values. This implied that all carbohydrate materials would give slightly high analytical results, and made particularly difficult the interpretation of analyses of polysaccharide functions having a small but real methoxy content.

In contrast, Goldstein and Smith³ found that certain periodate oxidation products gave very high results. They proposed that the liberation of "extra" alkyl iodide from polyhydric alcohols such as glycerol was responsible. Von Rudloff⁴ had earlier reported that polyhydric alcohols gave anomalous alkoxy values. Strangely, he also obtained very unsatisfactory results for α -methyl-D-glucoside, a recommended reference standard⁵ which gives excellent results.⁶⁻⁹ Although it had been clearly established that the volatile products from ethylene glycol were ethylene + ethyl iodide, von Rudloff claimed that vinyl iodide + ethyl iodide were formed.

It is significant that the apparent methoxy values quoted for standard compounds *e.g.* glucose and sucrose, ranged from zero to 0.4% (*cf.* refs. 1 and 2). Modification of Willstätter and Utzinger's trimethylamine technique¹¹ was found¹⁻³ to give results more satisfactory (although still high) than were obtained by the more convenient Vieböck iodometric titration. Recently, in a paper¹³ which apparently repeats the published description¹⁴ of a combustion method for alkoxy determinations, Fukuda states that the method is not applicable to carbohydrates or related substances; the combustion method fails, in fact, for compounds liberating any non-acidic organic vapour in addition to alkyl iodides.

The identity of the volatile products from carbohydrate materials, and the sources of error contributing to the anomalous results, have hitherto not been clearly established. For simple sugars, Gran² showed that the apparent methoxy content was not caused by traces of contaminating alcohols *etc.* He suggested that the formation of volatile hexyl iodides was responsible, although he could not identify or isolate such products.

* Part III—D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, 8, 1.

The proposals of von Rudloff and Gran were clearly based on inadequate experimental evidence: further investigation was desirable. Following our studies^{9,15} of certain aspects of the Zeisel determination, it appeared that vapour-phase infrared spectroscopy could be applied to identify the volatile products from sugars and related compounds.

EXPERIMENTAL

Apparatus

The reagents, reaction conditions, and apparatus used for alkoxy determinations were as described.⁹ The technique for trapping volatile products, and details of the infrared method for their subsequent identification, have been given.^{16,17}

Reagents

Glucose, sucrose, mannitol—all M.A.R.

5-Hydroxymethylfurfural was prepared by Haworth's method.¹⁸

5-Methylfurfural, furan, 2-methylfuran, 2,5-dimethylfuran and compounds not described in footnotes to Table I were commercial samples which conformed, after purification where necessary, to literature description.

Procedure

Samples (30–60 mg) of the compounds listed in Tables I and II were refluxed for 1 hr with hydriodic acid (6 ml, constant-boiling, pre-conditioned⁹) using nitrogen as flow-gas (6–8 ml per min.). The mixture of volatile products was collected, after passage through Anhydrone, in a trap immersed in liquid nitrogen. The components of each mixture were subsequently identified and quantitatively determined by vapour-phase spectroscopy^{16,17}: since 2-iodohexane (b.p. 165°) was insufficiently volatile, it was identified as a pure liquid. All components were identified without difficulty; none of the mixtures was sufficiently complex for prior separation of the components by vapour-phase chromatography to be necessary.

RESULTS

Table I shows the products liberated in 1 hr from 30-mg to 60-mg samples of sugars and polysaccharide materials. The products from polyhydric alcohols are shown in Table II.

Effect of varying reaction-time and sample weights

The results obtained from experiments with glucose are shown in Table III.

Volatilisation of iodine

With 60 mg of glucose, only small amounts of iodine were released, insufficient to form a sublimate on the condenser walls: iodine did not pass the condenser. With 250-mg and 500-mg samples, however, extensive volatilisation occurred.⁹ Although most of this condensed, some iodine reached the cold trap in which the volatile products were collected. The efficiency of removal of such quantities of iodine by 10% aq. sodium antimony tartrate in the B.S. design of scrubber⁹ was therefore tested. When 100 mg of iodine were refluxed with pre-conditioned hydriodic acid, the amount of iodine passing the scrubber increased the reagent blank from 0.03 ml of 0.01*N* sodium thiosulphate to 0.06 ml (*cf.* ref. 8). When 500 mg of glucose was refluxed, the apparent methoxyl content found iodometrically was exactly equivalent to the amount of methyl iodide found by the infrared method in a duplicate run.

TABLE I

Compound*	Yield of volatile products†‡					
	n-Heptane	n-Hexane	n-Pentane	n-Butane	2,5 Dimethyl-furan	Acetone
Glucoheptose	tr	—	—	—	—	—
2-Deoxyglucose	—	tr	—	—	—	—
5-Hydroxymethylfurfural	—	tr	—	—	—	—
Glucose, hexoses	—	tr	—	—	2%	—
Fructose, sorbose	—	1%	—	—	2%	—
Rhamnose, fucose	—	1%	—	—	2%	—
Glucosamine HCl	—	tr	—	—	tr	tr
Sucrose	—	tr	—	—	2%	1%
Glucurone*	—	—	tr	—	—	—
Xylose, pentoses	—	—	tr	—	—	—
Furfural	—	—	tr	—	—	—
5-Ketogluconolactone ^b	—	—	tr	—	—	tr
Galactono- γ -lactone ^c	—	—	tr	—	—	tr
Erythrose	—	—	—	tr	—	1%
Glyceraldehyde	—	—	—	—	—	1%
Oat starch ^d	—	tr	—	—	1%	—
Waxy maize starch	—	tr	—	—	3%	tr
Glycogen ^e	—	tr	—	—	3.5%	tr
Inulin ^f	—	tr	—	—	4.5%	tr
Agar ^g	—	tr	—	—	2%	tr
Cellulose ^h	—	—	—	—	2%	tr
Araboxylin ^h	—	—	tr	—	—	—

* 30–60 mg in 6 ml of HI under reflux for 1 hr.

† expressed as % of wt. of sample taken; tr denotes $\geq 0.02\%$.

‡ In addition to the products shown, all compounds in this table gave a trace of CO₂, except for a, b and c, which gave approx. 0.75 mole of CO₂ per mole of compound.

d, Anderson and Greenwood, *J. Sci. Food Agric.*, 1955, 6, 587.

e, ex Mussel; L. Light and Co. Ltd.

f, B.D.H. Ltd.

g, ex *Nitella translucens*; Anderson and King, in preparation.

h, ex Rye flour; Aspinall and Sturgeon, *J. Chem. Soc.*, 1957, 4469.

TABLE II

Compound*	Volatile products†
Sorbitol, mannitol	CO ₂ (tr) + n-hexane (tr) + 2-iodohexane
Ribitol	CO ₂ (tr) + n-pentane (tr) + 2-iodopentane
Erythritol	CO ₂ (tr) + 2-iodobutane
Glycerol	isopropyl iodide
Ethylene glycol	ethylene + ethyl iodide
Allyl alcohol	isopropyl iodide
Vinyl ethyl ether	ethyl iodide

* Reaction details as in Table I, footnote †.

† For yields of alkyl iodides, see Discussion: tr denotes $\geq 0.02\%$.

DISCUSSION

When a carbohydrate material is suspected to have a low methoxyl content, large sample weights must be employed if the methyl iodide released is to be determined accurately. There is also a tendency for reflux periods longer than normal to be used (*cf.* ref. 2). Table III shows that *up to a certain ratio* (100 mg of sample per 6 ml of hydriodic acid) the volatile products from sugars are independent of the sample weight taken: for larger samples, different decomposition mechanisms are clearly

TABLE III

Wt. of glucose, <i>mg</i> [*]	Reflux period, <i>hr</i>	Volatile products†
20-100	1	CO ₂ (tr) + n-hexane (tr) + 2,5-dimethylfuran (2%)
20-100	4	CO ₂ (tr) + n-hexane (tr) + 2,5-dimethylfuran (4%)
250	1	CO ₂ (tr)
500	1	CO ₂ (tr) + methyl iodide (0.12%)
500	3	CO ₂ (tr) + methyl iodide (0.4%)

* treated with 6 ml of HI under reflux.

† yields expressed as in Table 1.

involved. Hexyl or other iodides are only liberated, however, when hexahydric alcohols are present. This, therefore, refutes the suggestion made by Gran.² Table III shows that methyl iodide is only formed when exceptionally large weights of sugars are reacted; the very small amount liberated (equivalent to 0.03% and 0.1% of methoxyl after 1 and 3 hours respectively) does not explain in full the anomalous results previously reported.

Alternative possible sources of error were therefore investigated. Those included (a) volatilisation of iodine, (b) formation of 2,5-dimethylfuran and of hydrocarbons and acetone, (c) retention by polysaccharides of organic solvents used in their preparation.

Volatilisation of iodine

Previous workers^{7,8} have commented on the volatilisation of small but significant quantities of iodine. In particular, Belcher⁸ showed that volatilisation could occur, although correct results were obtainable if the appropriate increased "blank" value was taken into account. This, however, indicates that iodine vapour, when liberated in quantity, is not *totally* retained by aqueous scrubbers. Our results are in agreement, but the amounts of iodine passing the scrubber are very small, even under testing conditions.

Volatilisation of iodine is therefore not the only possible source of error, although it may well have made a major contribution to some of the high results reported by previous workers, particularly when very large sample weights, fast flow rates and long reflux periods were used. Any tendency for errors to arise through volatilisation of iodine can be minimised by use of the solid scrubber, soda-asbestos.¹⁹

Result of formation of 2,5-dimethylfuran

The observation that 2,5-dimethylfuran is one of the volatile reaction products from certain sugars permits a new explanation of anomalous high results to be given. Soda-asbestos and the scrubbing solutions normally used in the Zeisel determination do not absorb 2,5-dimethylfuran.

When 100 mg of this compound were added to 10 ml of the conventional oxidising solution (glacial acetic acid/bromine/potassium acetate) used in the iodometric determination of alkyl iodides,¹² a reaction, clearly involving bromine, took place. A precipitate, found to be potassium bromide, was produced. When the determination was completed in the usual way, the thiosulphate titre indicated, when carried out immediately, an apparent addition of 0.9 mg of methyl iodide. If 10 min were allowed to elapse before titrating,⁶ the titre was equivalent to 1.8 mg of methyl iodide, indicating 0.4% of methoxyl. Slow liberation of iodine continued for 5 hours, when the apparent methoxyl content was 1.2%. Furan and 2-methylfuran reacted similarly, but liberated smaller quantities of iodine than 2,5-dimethylfuran. The effect of 2,5-dimethylfuran

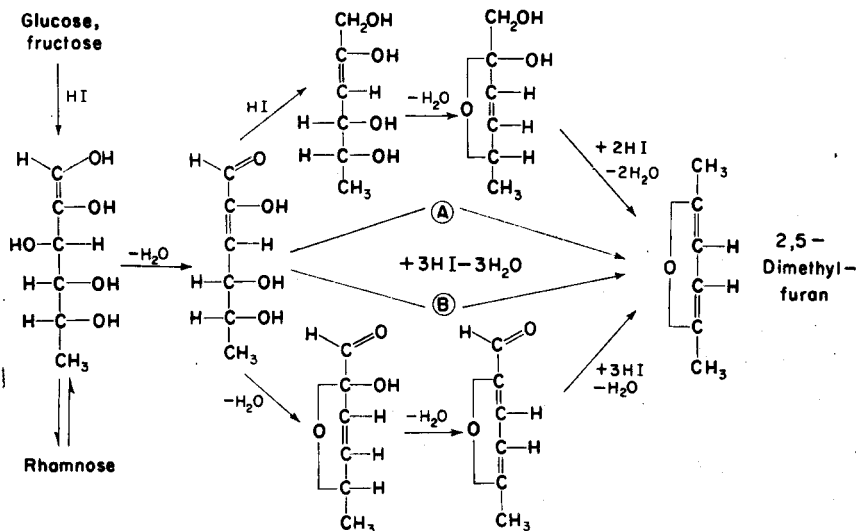


FIG. 1.

was not associated with addition of excess formic acid²⁰ or excess sodium acetate and sulphuric acid,²¹ and clearly contributes to the anomalous Zeisel reactions of sugars.

When furan is added to a cold solution of bromine in acetic acid containing potassium acetate, potassium bromide is precipitated and 2,5-diacetoxy-2,5-dihydrofuran, which is hydrolysed to malealdehyde, is produced in good yield.²² Our experiments show that both 2-methyl- and 2,5-dimethylfuran react analogously to furan, although 2,5-diacetoxy-2-methyl-5-hydrofuran was too unstable^{23,24} to be isolated from the 2-methylfuran reaction mixture. The following facts suggest that the hydrolysis products are involved in the liberation of titratable iodine: (a) iodine is released continuously for 4–5 hour, (b) the relative instabilities of the diacetoxy addition products increase in the order, furan, 2-methylfuran, 2,5-dimethylfuran, which is the order of increasing yields of iodine by these substances.

Pathway A in Fig. 1 shows a possible reaction mechanism for the unexpected formation of 2,5-dimethylfuran. When 5-methylfurfural was refluxed with hydriodic acid, extensive resinification and polymer formation occurred; negligible amounts of 2,5-dimethylfuran were produced. Pathway B is therefore not operative. From Tables I and II, it is also apparent that reaction of glucose with hydriodic acid does not involve the intermediate formation of sorbitol.

Quantitative infrared experiments showed that 100 mg of glucose refluxed with hydriodic acid (6 ml) for 1 hour liberated 2 mg of 2,5-dimethylfuran. This, it can be calculated from the results already given, would liberate iodine equivalent to an apparent methoxyl content of 0.01%. The yields of 2,5-dimethylfuran that are found explain positive errors of the magnitude reported by Adams and Castagne,¹ whose results have been duplicated in experiments using the Vieböck titration.

Result of liberation of hydrocarbons and acetone

The n-hydrocarbons liberated (see Table I) are, like 2,5-dimethylfuran, not retained by the scrubbers normally employed. Pentane, hexane and heptane did not interfere with the Vieböck determination, although a sluggish starch/iodine end-point, caused presumably by slight solvent-extraction of the iodine, was observed.

Table I shows that certain substances liberate small amounts of acetone. Morgan¹⁰ considered that acetone might interfere in Vieböck determinations. The blank values found in experiments using 100 mg of acetone were, however, negligible.

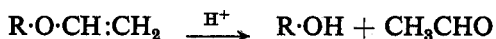
Products from polyhydric alcohols

Table II shows the volatile products given by polyhydric alcohols. Propylene was not produced from glycerol (*cf.* ref. 10). We confirm, however, that the relative amounts of ethylene and ethyl iodide produced from ethylene glycol are affected by several factors;¹⁰ we found that the concentration of phenol used as solubiliser was also critical, and this effect is under investigation. For the present purpose, one mole of ethylene glycol gives 0.4–0.6 mole of ethyl iodide.

In 1 hour, 1 mole of glycerol liberates 0.9–1.0 mole of iso-propyl iodide. The relative involatility ascribed^{7,10} to iso-propyl iodide is difficult to understand; even 2-iodobutane is sufficiently volatile for approximately 0.8 mole to be given by 1 mole of erythritol in 1 hour. 2-Iodopentane and 2-iodohexane are less volatile, but the amounts volatilised in 1 hour indicated apparent methoxyl contents of 40% for ribitol and 15% for mannitol. (*cf.* ref. 4).

Formation of vinyl iodide

Von Rudloff's proposal that vinyl iodide was formed from ethylene glycol in the Zeisel reaction was not substantiated. Allyl alcohol gives 1 mole of iso-propyl iodide, whilst vinyl ethyl ether gives 1 mole of ethyl iodide as the only volatile product (see Table II). Vinyl propionate gives no volatile products. The reaction



(which represents the essential reaction involved in the standard method²⁵ for analysis of vinyl ethers) explains our findings. Vinyl groups are converted to acetaldehyde, which immediately polymerises so that no volatile products result. Vinyl iodide is therefore not a possible volatile reaction product in Zeisel determinations.

Von Rudloff's proposal⁴ was based on the detection of formaldehyde after passage of the volatile products from the reaction of ethylene glycol with HI (*i.e.*, ethylene and ethyl iodide) through a permanganate-periodate reagent. Tests show that this oxidising reagent produces some formaldehyde from ethylene; there is therefore no need to postulate formation of vinyl iodide in order to explain the production of formaldehyde.

CONCLUSIONS

It is evident that several factors can contribute to cause anomalous results. Samples should not be larger than required to give the minimal amount of methyl iodide determinable. The reflux period should not be longer than normal; true methoxyl compounds react within 8–12 minutes,^{7,9,13,26} and it is suggested that reflux of carbohydrate materials for longer than 1 hour leads only to increased error. High results from volatilisation of iodine can be eliminated by using the soda-asbestos scrubber.^{9,19} Small positive errors of the magnitude reported by Adams and Castagne¹ are given in the Vieböck procedure; these are caused by the production of 2,5-dimethylfuran.

The larger errors reported by certain authors (*cf.* refs. 1,2) cannot be explained by the 2,5-dimethylfuran contribution alone; two suggestions can be offered. Firstly, that abnormally large samples were allowed to react for excessive periods, so creating errors through liberation of 2,5-dimethylfuran and volatilisation of iodine; and possibly also, in extreme cases, through formation of methyl iodide. Secondly, that the polysaccharide samples concerned retained small amounts of organic solvents, particularly alcohols, ethers or esters used in their preparation or isolation. Jansen²⁷ warned that pectic materials were particularly liable to give this effect; the warning has been repeated more recently²⁸ with regard to wood products. Experiments²⁹ have shown that organic solvents used to de-fat or dehydrate polysaccharide materials are retained, up to temperatures at which the materials begin to decompose, despite oven and high-vacuum drying at temperatures much higher than the boiling-point of the solvents involved (*cf.* ref. 27). Although pectic materials and plant gums gave the greatest retention, starches retained smaller but easily measurable quantities (*cf.* ref. 30).

Polysaccharide materials isolated with the aid of organic solvents should therefore be re-dissolved, dialysed and freeze-dried wherever possible, otherwise misleading results will be given in alkoxy and other analyses: care should still be taken with freeze-dried samples, which can retain solvents.³¹ When freeze-drying is not possible, the use of methanol and methoxy compounds should be avoided; analysis by one of the valid methods^{15,32} for methoxyl in presence of ethoxyl can then be used. For materials suspected to contain both methoxyl and ethoxyl groups, the use of isopropanol or acetone during preparation will allow the infrared method¹⁵ to give the true content of both alkoxy groups: methoxyl determinations may also be made in the presence of polyhydric alcohols, since none of these (see Table II) liberate methyl iodide. Indeed, examination of the spectrum of the mixture of volatile reaction products would also reveal which polyhydric alcohols, or mixtures thereof, were present, if this were not otherwise known. Valuable evidence in structural studies, in the detection of anomalous linkages, and in the examination of products obtained by periodate oxidation³ or hydrogenolysis³³ may thus be given by the infrared method, which also offers a rapid method for "difficult" analyses such as the determination of glycerol in presence of residual sugar substrates and 2,3-butanediol.³⁴

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Zusammenfassung—Die flüchtigen Reaktionsprodukte, die während der Zeiselbestimmung von Zuckern und ähnlichen Substanzen entstehen, wurden identifiziert. Ein Produkt aus gewöhnlichen Zuckern ist 2,5-Dimethylfuran, welches die Bestimmung von Alkyljodid nach Vieböck stört. Es

wurde gezeigt, dass diese Substanz dazu beiträgt, dass scheinbare Alkoxywerte erhalten werden. Die Annahmen, dass Hexyljodid gebildet wird und dass Vinyljodid als Produkte aus Polyalkoholen entstehen, wurde als unzutreffend bewiesen.

Résumé—Les produits de réaction volatiles obtenus dans les dosages de sucres et de composés apparentés par la méthode de Zeisel ont été identifiés. Un de ces produits obtenu à partir de certains sucres courants est le 2,5-diméthylfuranne, qui gêne dans le dosage de l'iodure d'alkyle par la méthode de Viebock; les auteurs ont montré que ce produit était la cause des valeurs apparentes d'alkoxyle. Les suggestions suivantes ont été réfutées: de l'iodure d'hexyle se dégage à partir des sucres, l'iodure de vinyle est un produit obtenu à partir des alcools polyhydriques.

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METALLOCHROMIC INDICATORS—X*

A NEW MIXED INDICATOR FOR CHELATOMETRIC DETERMINATION OF CALCIUM

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Summary—A new mixed indicator for chelatometric determination of calcium, prepared by mixing fluorescein complexone and phenolphthalein complexone in the ratio of 4:1, is described. It has been shown by comparison with fluorescein complexone alone that in chelatometric titrations of calcium in pure solution and in the presence of sodium salts this mixed indicator gives a sharper end-point and a more accurate recovery of calcium.

In a previous communication of this series,¹ the properties of phenolphthalein complexone have been described, the reaction of which with calcium is especially notable: at lower pH (10–11) calcium ions cause a colour change from pink to red; in more alkaline solution (pH 13–14), where the indicator is itself coloured intense purple, an almost complete discoloration takes place on addition of calcium. On titration with EDTA the original colour returns.¹ This diverse behaviour of phenolphthalein complexone toward calcium ions in different pH ranges has been explained by assuming differences in the nature of the bond between the phenolic oxygen of the indicator and the cation; it is postulated that at lower pH values the bond has an ionic character, while at higher pH it is predominantly covalent.^{2,3}

The possibility of the practical application of phenolphthalein complexone as an indicator in chelatometric titrations of calcium has not been studied in detail so far, since in preliminary experiments it did not appear promising in comparison with other more suitable "complexan-type" indicators. The end-point colour change at higher pH has not been found sufficiently sharp for practical purposes. However, interesting phenomena have been observed² when using phenolphthalein complexone in mixture with fluorescein complexone (Calcein, Fluorexon).⁴ At a suitable ratio of these dyes, the pink colour of the calcium complex of phenolphthalein complexone is screened by the intense green fluorescence of fluorescein complexone. On the other hand, at the equivalence point, the purple colour of the free phenolphthalein complexone fully obscures the residual fluorescence of fluorescein complexone. Hence, this combination represents a unique case where the disadvantages of both indicators are mutually corrected. For this reason, this combination has now been examined in detail in order to find the most advantageous ratio of the indicators; the application of the resulting mixed indicator to the chelatometric determination of calcium led to an improvement in the end-point change and to an objective increase of accuracy as compared with fluorescein complexone when used alone.

* Part IX: See *Coll. Czech. Chem. Comm.*, 1960, **25**, 1037.

EXPERIMENTAL

Reagents

EDTA solution, 0.025M: Prepared by dissolving 18.62 g of disodium dihydrogen ethylenediaminetetra-acetate in water and diluting to 2000 ml. The solution was standardised in the usual manner.

Calcium solution, 5 mg Ca²⁺/1 ml: Prepared from A.R. calcium nitrate. Its titre was checked by chelatometric titration with methylthymol blue, thymolphthalein complexone and cresolphthalein complexone, respectively, as indicators.

Fluorescein complexone (Fluorexon Lachema) and phenolphthalein complexone (Fenolftalexon Lachema) were used as 1:100 finely ground mixtures with potassium chloride.

Procedure

To a sample of calcium salt diluted with water, 2 ml of 5*N* potassium hydroxide were added. The volume was made up to 100 ml with water, indicator was added, and the solution was titrated with 0.025*M* EDTA solution to the quenching of the brilliant green fluorescence (in the case of fluorescein complexone alone) or to the simultaneous colour change from pale yellow to purple-red. All titrations were carried out in diffuse daylight.

RESULTS

Titrations with fluorescein complexone

The quality of the fluorescent end-point of this indicator, and also the accuracy of the determination of calcium in pure solution, are proportional to the amount of calcium to be titrated. With an increasing amount, the end-point is less sharp and the results of individual determinations are scattered over a larger interval. The errors in the recovery of calcium are predominantly negative and the standard deviation shows an increasing tendency.

In the presence of larger amounts of sodium (added as sodium chloride), the sharpness of the end-point is affected by the relatively strong residual fluorescence (*cf.* reference 5). The average recovery of calcium appears to be slightly high, and the reproducibility of the results obtained decreases, as deduced from the values of standard deviations.

The results of all titrations with fluorescein complexone as indicator are given in Table I.

TABLE I.—TITRATION WITH FLUORESCIN COMPLEXONE AS INDICATOR

Ca taken, <i>mg</i>	Na added, <i>mg</i>	Ca found, <i>mg</i>	Standard deviation	Number of detms.
5.00	—	5.01	±0.016	10
10.00	—	9.99	±0.039	15
24.99	—	24.97	±0.048	10
49.99	—	49.96	±0.056	10
10.00	200	10.03	±0.045	15
10.00	500	10.02	±0.073	15

Titrations with the mixed indicator

In order to establish the optimum ratio of the indicators, preliminary experiments have been made with fluorescein complexone—phenolphthalein complexone mixtures in ratios ranging from 6:1 to 1:1. The best fluorescent and colour end-point with regard to sharpness has been observed when using this mixture in a ratio of 4:1, and the titrations with this mixed indicator have given the most accurate and reproducible recoveries of calcium.

In comparison with fluorescein complexone alone, the determination with this mixed indicator gives a more regular distribution of the results around the theoretical value and the standard deviation remains practically constant, even with calcium amounts up to 50 mg. When sodium is present in a 20–50-fold excess, the end-point change remains sharp, since the disturbing influence of the residual fluorescence is negligible. Although the results show a slight tendency for higher recoveries of calcium in this case also, the accuracy of the determination is not unfavourably affected by the presence of sodium (see Table II).

TABLE II.—TITRATION WITH THE MIXED INDICATOR

Ca taken, <i>mg</i>	Na added, <i>mg</i>	Ca found, <i>mg</i>	Standard deviation	Number of detms.
5.00	—	5.01	±0.024	10
10.00	—	10.01	±0.025	15
24.99	—	24.98	±0.021	10
49.99	—	49.97	±0.027	10
10.00	200	10.00	±0.014	15
10.00	500	10.02	±0.034	15

DISCUSSION

Fluorescein complexone is one of the best chelatometric indicators for the determination of calcium. Nevertheless, further improvement has been achieved by combining it with phenolphthalein complexone. This combination has a sound theoretical basis since it provides a mutual correction of disadvantages of the two indicators. The new mixed indicator is especially suitable for the chelatometric determination of calcium in the presence of sodium salts, where fluorescein complexone alone gives only a poor fluorescent end-point change.⁵

In respect of interferences of other cations, the proposed mixed indicator has the drawbacks of both of its components. In spite of this fact, we believe that the mixed indicator will find valuable applications in those cases where the determination of calcium is preceded by its separation from other interfering elements.

It is true that one of the tendencies of modern analytical chemistry is the search for new methods of determination of a given cation even in complex mixtures. However, there also exists a simultaneous development of modern separatory methods which justify the elaboration of procedures for determining individual cations in pure solutions. In such cases, the proposed mixed indicator allows the most accurate determination of calcium known so far.

Zusammenfassung—Ein neuer Indikator für die chelatometrische Bestimmung von Calcium, hergestellt durch Zusammenmischen von Fluoresceinkomplexon und Phenolphthaleinkomplexon im Verhältnis 4:1, wurde beschrieben. In Vergleichsversuchen mit Fluoresceinkomplexone allein wurde gezeigt, dass bei der Titration von Calcium in reiner Lösung oder in Anwesenheit von Natriumsalzen, der beschriebene Mischindikator einen schärferen Endpunkt sowie genauere Resultate gibt.

Résumé—Les auteurs ont décrit un nouvel indicateur mixte pour le dosage complexométrique du calcium; cet indicateur est préparé en mélangeant du fluorescéine-complexone et du phénolphthaleine-complexone dans le rapport 4/1. Les auteurs ont montré, par comparaison avec le

fluoresceine-complexone seul, que, dans les titrages complexométriques du calcium en solution pure et en présence de sels de sodium, cet indicateur mixte donnait un point équivalent plus net et une détermination plus précise du calcium.

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NEW SELECTIVE MICROMETHODS IN THE ANALYSIS OF METALS

TITRIMETRIC DETERMINATION OF SMALL AMOUNTS OF NICKEL AT AN EQUIVALENT RATIO OF 1:24

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Summary—A new selective titrimetric method for the determination of minute amounts (75 to 250 μg) of nickel has been evolved. Nickel is precipitated as nickel dimethylglyoxime. The washed precipitate is dissolved in 20% hydrochloric acid and hydrolysed, producing an equivalent amount of hydroxylamine. The hydroxylamine content is determined in the hydrolysate by oxidation with bromine chloride, being converted to nitric acid. The equivalent weight of nickel in the method corresponds to 1/24 of the atomic weight.

THE analytical methods evolved for the determination of nickel ions on the basis of the formation of a precipitate of nickel dimethylglyoxime practically insoluble in water¹ are extremely selective. In addition to nickel^{II} ions, only palladium^{II} ions are capable of forming a precipitate with dimethylglyoxime. The former can be precipitated quantitatively in an ammoniacal solution (or one buffered by acetate), while the precipitation of the latter requires a medium slightly acidified by hydrochloric acid; palladium dimethylglyoxime is readily dissolved in ammonia. Thus it is possible to separate nickel from palladium by altering the pH value of the reaction mixture. The coloured complexes of dimethylglyoxime with iron^{II}, cobalt^{II} and copper^{II} ions are soluble in water, and they only interfere with the quantitative precipitation of nickel in very high concentrations.

Many papers² deal with the practical application and selectivity of the analytical methods based on the formation of nickel dimethylglyoxime. The majority of these methods are gravimetric ones. It is also possible to determine amounts of nickel from 0.01 to 0.1 mg by photometry,³ using the water-soluble coloured complex of dimethylglyoxime formed with nickel^{IV} ions. By using an ethanolic solution of dimethylglyoxime, nickel^{II} ions can be titrated directly, with instrumental indication of the end-point (usually by amperometry).⁴

Tougarinoff,⁵ and Furman and Flagg⁶ dissolved the filtered and washed precipitate of nickel dimethylglyoxime in acid. By boiling with acid the dimethylglyoxime was hydrolysed to the corresponding ketone and hydroxylamine, the latter being determined by oxidimetry. Tougarinoff⁵ oxidised the hydroxylamine with a solution of iron^{III} to nitrous oxide, and measured by permanganometry the amount of iron^{II} ions formed. In this method, the equivalent weight of nickel corresponds to 1/4 of the atomic weight (A/4). Furman and Flagg,⁶ on the other hand, oxidised hydroxylamine with bromate to nitric acid, and in this case the equivalent weight of nickel corresponds to 1/24 of the atomic weight (A/24). However, they reported (and this is in accordance with our own observations) that this method can only be used on a 0.1N scale. Errors of

$\pm 4-5\%$ may occur when the consumption of the standard solution is below 10 ml, satisfactory results only being obtained when the consumption of standard solution is more than 20 ml (equivalent to 5–10 mg of nickel). As a consequence, the advantage of operating with a low equivalent weight is practically lost.

In an earlier communication⁷ a method for the determination of hydroxylamine, based on its oxidation by bromine chloride, was suggested. This reaction takes place according to the equation



It was found that this oxidation also was suitable for the measurement of hydroxylamine on a 0.01*N* scale.

Because of the low solubility of nickel dimethylglyoxime, the reaction was utilised for the titrimetric determination of minute amounts of nickel, after dissolving the precipitate in hydrochloric acid, and hydrolysing dimethylglyoxime to hydroxylamine and the corresponding ketone (and to the decomposition products of the latter).

Since one nickel atom forms a precipitate with two molecules of dimethylglyoxime, and two molecules of hydroxylamine are derived from each molecule of dimethylglyoxime, and since in the oxidation of hydroxylamine by bromine chloride the change in the oxidation state of the nitrogen atom is 6 ($-I \rightarrow +V$), the equivalent weight of nickel in this method of determination is 1/24 of the atomic weight ($A/24$). Therefore 1 ml of 0.01*N* BrCl is equivalent to 24.45 μg of nickel.

The selectivity of this method is dependent on that of the formation of nickel dimethylglyoxime precipitate. It is therefore possible to determine small amounts of nickel in the presence of almost any other metal.

EXPERIMENTAL

(1) *Decomposition of hydroxylamine on boiling in a medium of 20% hydrochloric acid*

Hydroxylammonium chloride suffers a partial decomposition on boiling in a solution of 20% hydrochloric acid for more than 10 min. The content of hydroxylamine was determined by oxidation with bromine chloride. Since oxygen dissolved in the reaction mixture would interfere strongly in the iodometric measurement, because of the strongly acidic medium, 0.5–1.0 g of potassium hydrogen carbonate was added to the cooled solution, after boiling with hydrochloric acid.

(2) *Hydrolysis of dimethylglyoxime*

On boiling dimethylglyoxime on a 0.1*N* or 0.01*N* scale for 1 min, it quantitatively hydrolyses to hydroxylamine and the corresponding ketone (and to the decomposition products of the latter).

(3) *Titrimetric determination of nickel*

Reagents:

Bromate-bromide solution: 0.01*N* solution (1:2 ratio of bromate to bromide), prepared by weighing 0.2784 g of potassium bromate and 0.3967 g of potassium bromide, dissolving in distilled water and making the volume to 1000.0 ml.

Sodium thiosulphate: 0.01*N* standard solution.

Dimethylglyoxime: 1% ethanolic solution.

Nickel dimethylglyoxime: cold saturated aqueous solution.

Hydrochloric acid solution: 20% (azeotropic).

Ammonium hydroxide solution: 2*N*

Potassium iodide

Starch solution: 1% (decomposed and preserved by 0.1% salicylic acid).

All the reagents should be of analytical grade.

Method

An aliquot of the stock solution (not more than 5 ml) containing 75–250 μg of nickel, is transferred to a 25-ml beaker, and while boiling, 0.2 ml of dimethylglyoxime solution and 1 ml ammonium hydroxide solution are added dropwise. Boiling is continued for about 5 min, the solution is cooled for 10 min, and the liquid together with the precipitate is poured on to a G3 glass filter and the mother liquor is sucked off. The residual precipitate in the beaker, together with the precipitate on the filter are washed with 2×6 ml of hot nickel dimethylglyoxime solution, and then with 5 ml of water. The washed precipitate is dissolved in 6 ml of hot hydrochloric acid, the beaker and the filter are washed with a further 2×6 ml of hydrochloric acid, and the hydrochloric acid solution is collected in a 100-ml beaker. The solution is boiled for 1 min, allowed to cool for 10 min, quantitatively washed into a Schulek bromination flask, and diluted with water to 100–150 ml. In order to eliminate the interfering effect of oxygen dissolved in the reaction mixture, about 0.5 g of potassium hydrogen carbonate is added to the solution. (If a greater amount of hydrochloric acid was necessary for dissolving the precipitate, a consequently greater amount of potassium hydrogen carbonate is obviously necessary). Sufficient 0.01*N* standard solution is transferred to the flask to maintain an excess of over 100% of bromine chloride* formed by the hydrochloric acid.

TABLE I.—DETERMINATION OF NICKEL ON 0.01*N* SCALE

Ni weighed, μg	Total 0.01 <i>N</i> BrCl ml	0.01 <i>N</i> $\text{Na}_2\text{S}_2\text{O}_3$ consumed, ml	0.01 <i>N</i> BrCl consumed, ml	Ni found, μg	Δ , μg	Δ , %
80.04	9.96	6.75	3.21	78.48	-1.56	-1.95
80.04	20.00	16.76	3.24	79.22	-0.82	-1.02
135.0	20.00	14.54	5.46	133.5	-1.5	-1.11
135.0	20.00	14.59	5.41	132.3	-2.7	-2.0
271.6	29.96	18.96	11.00	269.0	-2.6	-0.96
271.6	29.96	18.94	11.02	269.4	-2.2	-0.81

The flask is closed by the moistened attachment equipped with a tap. After standing for 15 min, the flask is cooled with tap water (a vacuum forms), and 10 ml of freshly prepared 5% solution of potassium iodide are introduced into the reaction mixture through the tap and the attachment. The liberated iodine is then immediately titrated with 0.01*N* sodium thiosulphate with starch as indicator.

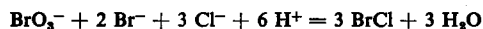
1 ml of 0.01*N* BrCl \equiv 24.45 μg of nickel (log 38828).

The error of the method ranges from -1 to -2% (Table I). This negative error on the 0.01*N* scale

TABLE II.—DETERMINATION OF NICKEL ON 0.1*N* SCALE

Ni weighed, mg	Total 0.1 <i>N</i> BrCl, ml	0.1 <i>N</i> $\text{Na}_2\text{S}_2\text{O}_3$ consumed, ml	0.1 <i>N</i> BrCl consumed, ml	Ni found, mg	Δ , mg	Δ , %
0.8004	9.96	6.69	3.27	0.7995	-0.0009	-0.11
0.8004	20.00	16.75	3.25	0.7946	-0.0058	-0.72
1.350	20.00	14.50	5.50	1.345	-0.005	-0.37
2.716	29.96	18.77	11.19	2.736	+0.020	+0.74
2.716	29.96	18.80	11.16	2.723	+0.007	+0.26

* Through the effect of hydrochloric acid, bromine chloride develops from the standard solution according to the equation:



(75 to 250 μg Ni) arises from the solubility of the precipitate proper, and is no longer invariably negative on the 0.1N scale (0.75 to 2.5 mg Ni):

For the determination on the 0.1N scale, the procedure is as follows:

Precipitation is carried out in a volume not exceeding 10 ml using 2 ml of dimethylglyoxime solution. In order to adjust to the required pH value, 2 ml of ammonium hydroxide solution are added to the neutral solution. A period of 5 min is necessary for the oxidation of hydroxylamine by bromine chloride. Otherwise the determination is conducted as previously described.

1 ml of 0.1N BrCl \equiv 0.2445 mg of nickel (log 38828).

The error of the method is in the range of $\pm 1\%$ (Table II).

Zusammenfassung—Ein neues selektives Verfahren wurde zur Bestimmung von sehr kleinen Mengen Nickel (75–250 μg) ausgearbeitet. Nickel wird als Nickeldimethylglyoxim gefällt. Der ausgewaschene Niederschlag wird in Salzsäure (20%) aufgelöst und hydrolytisch gespalten, wobei sich äquivalente Menge Hydroxylamin bildet. Der Hydroxylamingehalt der Lösung wird durch Oxydation (zu Salpetersäure) mittels Bromchloride bestimmt. Das Äquivalentgewicht des Nickels beträgt 1/24 des Atomgewichtes.

Résumé—L'auteur a développé une nouvelle méthode titrimétrique sélective de dosage de faibles quantités de nickel (75–250 μg). Le nickel est précipité à l'état de diméthylglyoxime de nickel. Le précipité lavé est dissous dans de l'acide chlorhydrique à 20 pour cent et est hydrolysé formant une quantité équivalente d'hydroxylamine. La teneur en hydroxylamine est mesurée dans l'hydrolysate par oxydation par du chlorure de brome (en donnant de l'acide nitrique). Le poids équivalent de nickel dans cette méthode correspond à 1/24 du poids atomique.

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SPOT TEST DETECTION AND COLORIMETRIC DETERMINATION OF ANILINE, NAPHTHYLAMINE AND ANTHRAMINE DERIVATIVES WITH 4-AZOBENZENEDIAZONIUM FLUOBORATE

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Summary—Some new sensitive procedures are introduced for the detection and determination of aniline, α - and β -naphthylamines, and α - and β -anthramines, as well as their *N*-alkyl and *N,N*-dialkyl derivatives. The chromogens are (*p*-phenylazophenylazo)-aniline, -naphthylamine and -anthramine dyes. For example with *N,N*-dimethylaniline, the blue di-cation of *N,N*-dimethyl-*p*-(*p*-phenylazophenylazo)aniline is formed. The absorptivity of *N,N*-dimethylaniline obtained in the colorimetric procedure is $0.823 \mu\text{g}^{-1} \text{ ml cm}^{-1}$. In the analysis for *N,N*-dimethylaniline, Beer's Law was obeyed from 0.1 to at least $3.6 \mu\text{g}$ per ml of final solution. Because of the widely differing rates of reaction, naphthylamine or anthramine derivatives can be determined in the presence of aniline derivatives. Also, with the help of a masking agent a dialkylaniline can be determined in the presence of primary and secondary amines. Spot tests for aniline, naphthylamine and anthramine derivatives are described, but their sensitivity does not compare with the sensitivities obtained in the colorimetric procedure.

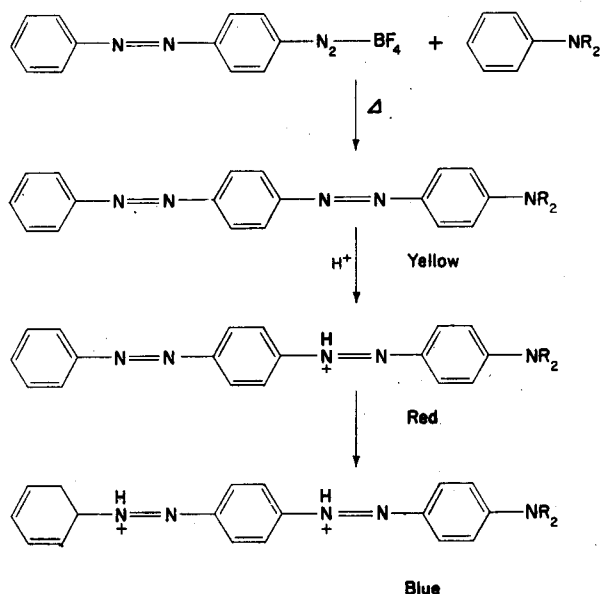
INTRODUCTION

As a result of our expanding industrialisation, various types of aniline derivatives have been introduced into the human environment. Many of these compounds have been shown to have toxic properties; threshold limits for aniline, *N,N*-dimethylaniline and *o*-toluidine have been placed¹ at 5 ppm. Consequently, it was desirable to develop methods of analysis for aniline derivatives. Colorimetric procedures for aniline²⁻⁴ and for polycyclic aromatic primary amines⁴ are available in the literature. Several methods for the determination of aniline and *N,N*-dimethylaniline in the air have been described.^{5,6} Although these methods are fairly sensitive, they have never been thoroughly evaluated, and are less sensitive and more complicated than the 4-azobenzenediazonium fluoborate procedure.

The use of diazotisation in the determination of aromatic amines has been known for a long time.⁷ The method involves the reaction of a diazotised aromatic amine with an aromatic amine coupling agent. In the determination of sulphanilamide through diazotisation and coupling with *H*-1-naphthylethylene-diamine, the final chromogen absorbs⁸ at $545 \text{ m}\mu$ with a molar absorptivity of 51,500. The chromogen obtained in the colorimetric determination of *N*-phenyl-1-naphthylamine with *p*-nitrobenzenediazonium chloride absorbs⁹ at $555 \text{ m}\mu$ with a molar absorptivity of 37,000.

In this paper a new and more sensitive diazotisation method for the determination of several types of aromatic amines is introduced. Some simple spot tests are also described.

The mechanism of the reaction as applied to *N,N*-dimethylaniline is as follows:



The compound is analysed at the blue stage because of the more intense colour of the di-cation as compared to the mono-cation.¹⁰

In a solvent containing 30 ml of 2-methoxyethanol diluted to 100 ml with concentrated hydrochloric acid, the pure dye absorbed at 632 $m\mu$, as did the solution obtained in the colorimetric determination of *N,N*-dimethylaniline. At this wavelength maximum, the latter solution had a molar absorptivity of 100,000 as compared to 100,000 obtained for the pure dye. These results indicate that a 100% yield of chromogen is obtained in the determination of *N,N*-dimethylaniline.

EXPERIMENTAL

Reagents and apparatus

4-Azobenzene diazonium fluoborate was prepared from 4-aminoazobenzene.⁴ A solution of 0.1% of 4-azobenzene diazonium fluoborate in 2-methoxyethanol was used as the reagent in the analytical work. All organic nitrogen compounds were obtained from commercial sources and were purified by crystallisation to a constant melting point or by distillation.

A Cary Model 11 recording spectrophotometer with 1-cm cells was used in the colorimetric determination of aniline derivatives.

Microtube procedure

To 1 drop of the 2-methoxyethanol test solution were added 2 drops of 0.1% 4-azobenzene diazonium fluoborate. The tube was then heated in a boiling water bath for 6 min. Then 2 drops of concentrated hydrochloric acid were added. Because of the reagent's interfering yellow colour at low concentrations of test compound, a blank is advisable in doubtful cases. Colours and limits of identification are given in Table I.

Spot paper procedure

To 1 drop of the 2-methoxyethanol test solution spotted on paper were added 2 drops of 0.1% 4-azobenzene diazonium fluoborate. The spot was treated with a jet of steam for 30 sec and then with a jet of hydrogen chloride gas. Instead of the gas, a drop of concentrated hydrochloric may be placed

TABLE I.—COLORIMETRIC AND SPOT TEST RESULTS OBTAINED IN THE ANALYSIS FOR PHENYL-, NAPHTHYL- AND ANTHRYL-AMINES WITH 4-AZOBENZENE DIAZONIUM FLUOBORATE

Compounds	Colorimetric		Spot tests, ident. limit, μg			
	λ max., $m\mu$	$\epsilon \times 10^{-3}$	Colour ^a Microtube		Colour Paper	
Aniline	610	8	V	7	V	7
<i>o</i> -Methylthioaniline	610	9	B	9	B	9
<i>o</i> -Toluidine	618	23	V	15	V	4
<i>o</i> -Anisidine	626	48	V	9	V	2
<i>m</i> -Toluidine	612	63	R	4	B	2
<i>N</i> -Methylaniline	623	65	V	8	V	8
<i>N</i> -Ethylaniline	623	73	B	9	B	9
<i>N-n</i> -Propylaniline	623	85	RV	10	V	17
<i>N,N</i> -Dimethylaniline	632	100	B	1	B	17
<i>N</i> -Methyl- <i>N</i> -ethylaniline	633	80	B	5	B	17
<i>N,N</i> -Diethylaniline	635	72	B	5	B	11
<i>N</i> -Allyl- <i>N</i> -methylaniline	632	83	B	5	B	11
<i>N</i> -Benzyl- <i>N</i> -methylaniline	640	73	V	4	B	14
<i>N,N</i> -Di- <i>n</i> -propylaniline	637	82	B	6	B	13
<i>N,N</i> -Dimethyl- <i>m</i> -toluidine	630	120	B	5	B	0.6
α -Naphthylamine ^b	642	95	B	1	B	0.6
<i>N</i> -Methyl- α -naphthylamine ^b	645	99	B	18	B	0.7
<i>N</i> -Ethyl- α -naphthylamine ^b	645	99	B	3	B	0.8
<i>N</i> -1-Naphthylethylenediamine ^b	656	100	B	3	B	0.8
<i>N,N</i> -Dimethyl- α -naphthylamine ^b	642	22	B	2	B	2
β -Naphthylamine ^b	603	32	B	10	B	3
α -Anthramine ^b	675	42	G ^c	14	B	2
β -Anthramine ^b	625	56	G ^c	7	V	0.9

^a B = blue; G = green; V = violet; R = red. Colour of product in microtube changes to green if concentrations of amine falls below $\sim 10\text{--}40 \mu\text{g}$.

^b The standard colorimetric procedure was followed except that 10 min of standing at room temperature was substituted for the 6 min of heat on the water bath. In the standard colorimetric procedure involving heat the following wavelength maxima and molar absorptivities were obtained α -naphthylamine, 610 (41,000); β -naphthylamine, 605 (57,000); α -anthramine, 544 (28,000); and β -anthramine, 623 (44,000).

^c Colour obtained without heat or acid for α -anthramine is blue and identification limit is $7 \mu\text{g}$; for β -anthramine it is violet with identification limit of $7 \mu\text{g}$.

on the paper. However, the sensitivities are lower in the latter procedure because of diffusion. Colours and limits of identification are given in Table I.

Colorimetric procedure

To 5 ml of the 2-methoxyethanol test solution in a 50-ml volumetric flask were added 10 ml of 0.1% 4-azobenzene diazonium fluoborate. The mixture was heated for 6 min in a boiling water bath. It was cooled with an ice water bath, and then diluted to the mark with concentrated hydrochloric acid while cooling to room temperature. The absorption spectrum was then immediately determined. The wavelength maxima and molar absorptivities obtained for different aniline derivatives are given in Table I.

DISCUSSION

Qualitative tests

Two modifications of the spot test procedure are introduced in this paper. A blank must be run in conjunction with the test, especially in the microtube method, at concentrations near the identification limit. This is because the blank has a deep yellow colour and the presence of a small amount of blue chromogen would then give

the test solution a yellow-green colour. This interference could cause difficulty. α -Anthramine is characterised by the fact that it gives a blue colour in the microtube method without any hydrochloric acid. Neither the aniline nor naphthylamine derivatives do this.

Colorimetric procedure

The method introduced in this paper for the determination of *N,N*-dimethylaniline has a very high sensitivity potential for colorimetric analysis.

Other *N*-alkyl and *N,N*-dialkyl anilines give colours of differing intensity. This variation in intensity is mainly due to the varying yields of bisazo dyes obtained in the colorimetric procedure. A slower rate of reaction could have a drastic effect on the yield. In many cases the presence of an orange to red di-cationic tautomer (involving salt formation at an azo nitrogen and the amino nitrogen) also helps to decrease the intensity of the blue colour of the bisazo dye di-cation.¹⁰

Of the aromatic amines investigated, the ring-substituted aniline derivatives, *N,N*-dimethyl- α -naphthylamine and β -naphthylamine gave the lowest intensities. *m*-Toluidine and *N,N*-dimethyl-*m*-toluidine gave the highest relative intensities, mainly because of the electron donor effect of the *m*-methyl group of the toluidine in the final azo dye.

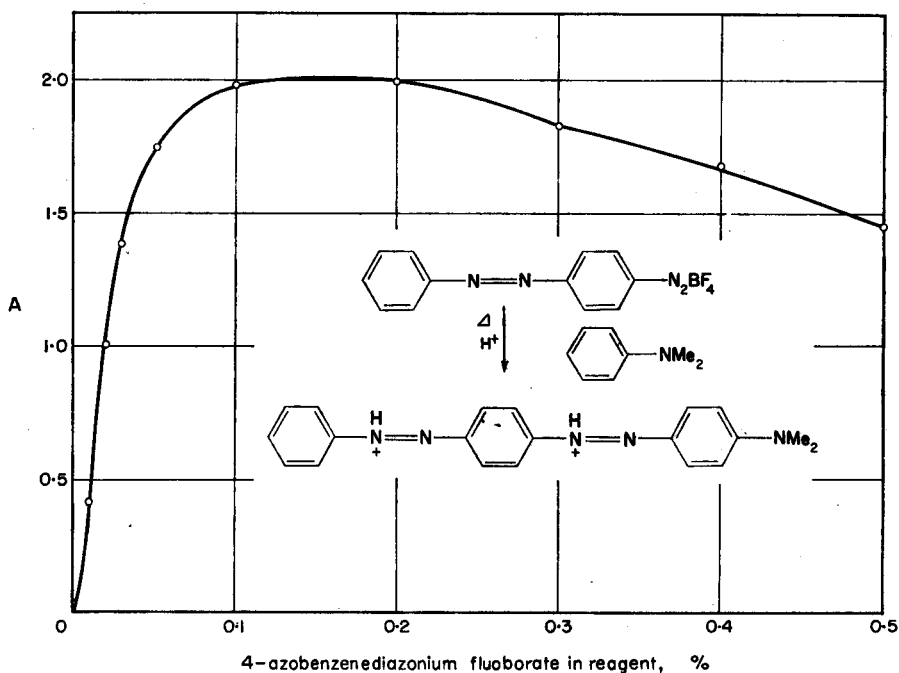


FIG. 1.—Effect of concentration of azobenzenediazonium fluoborate in the reagent solution on the absorbance obtained in the standard colorimetric procedure with *N,N*-dimethylaniline ($2 \times 10^{-5} M$) at λ_{\max} 632 m μ .

While aniline derivatives reacted readily with the reagent only at the boiling point of water, the naphthylamines and anthramines reacted at room temperature (Table I). After the reaction of anthramine and reagent at room temperature, dilution with

2-methoxyethanol to 50 ml gave a purple solution absorbing at $566\text{ m}\mu$ with a molar absorptivity of 20,000. These diverse reactions at room temperature and at the boiling point of water should be of value in characterising some of the amines.

The colorimetric procedure has been developed so as to give optimum results with *N,N*-dimethylaniline; in this case a 100% yield of the blue bisazo dye diocation was obtained. With proper modification of the standard colorimetric procedure, more intense colours could probably also be obtained for the other aromatic amines. This improvement with modification of conditions has been shown for the α -naphthylamines.

Variables affecting the standard colorimetric procedure for *N,N*-dimethylaniline were investigated. Optimum results were obtained with 0.1% to approximately 0.2% of the reagent (Fig. 1). However, the blank was fairly dark, so 0.1% concentration was chosen as giving the best all-around results. When the reagent and the *N,N*-dimethylaniline test solution were heated in a boiling water bath, it took 6 minutes of heating to obtain the maximum intensity (Fig. 2). Shorter periods of heat had a

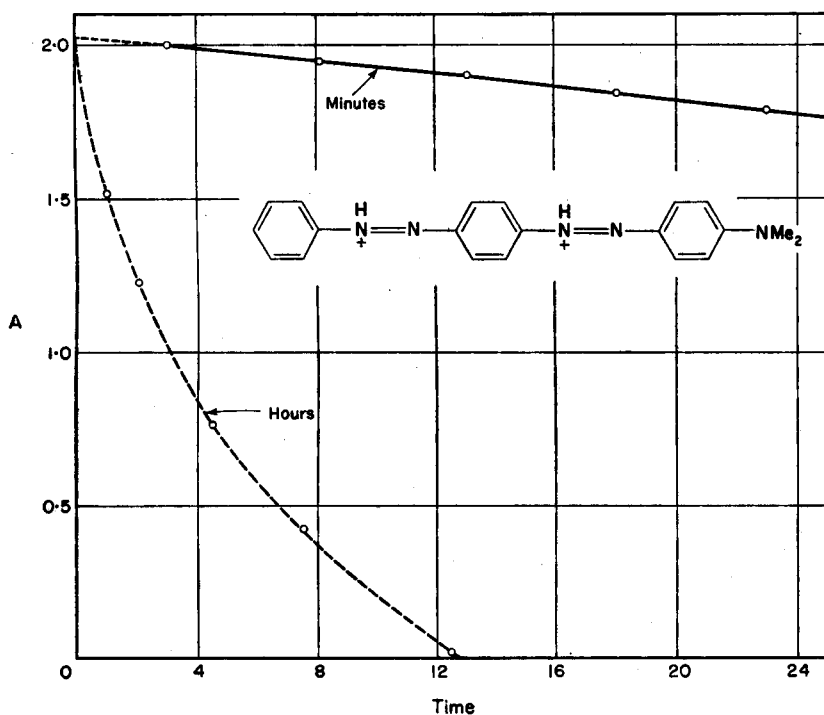


FIG. 2.—The effect on the absorbance at λ_{\max} $632\text{ m}\mu$ of the heating time at 100° of the reagent and *N,N*-dimethylaniline in the colorimetric procedure. Final concentration of *N,N*-dimethylaniline — $2 \times 10^{-5}\text{ M}$.

drastic effect on the intensity; longer periods had a slight effect. The stability of the colour was also investigated (Fig. 3). The absorbance decreased gradually at a steady rate. Readings were preferably taken on a fresh solution, or at least, within a few minutes after the acid was added. The colour obtained in the determination of *N,N*-dimethylaniline was found to obey Beer's Law from $5\text{ }\mu\text{g}$ to at least $180\text{ }\mu\text{g}$ per 50 ml of final solution.

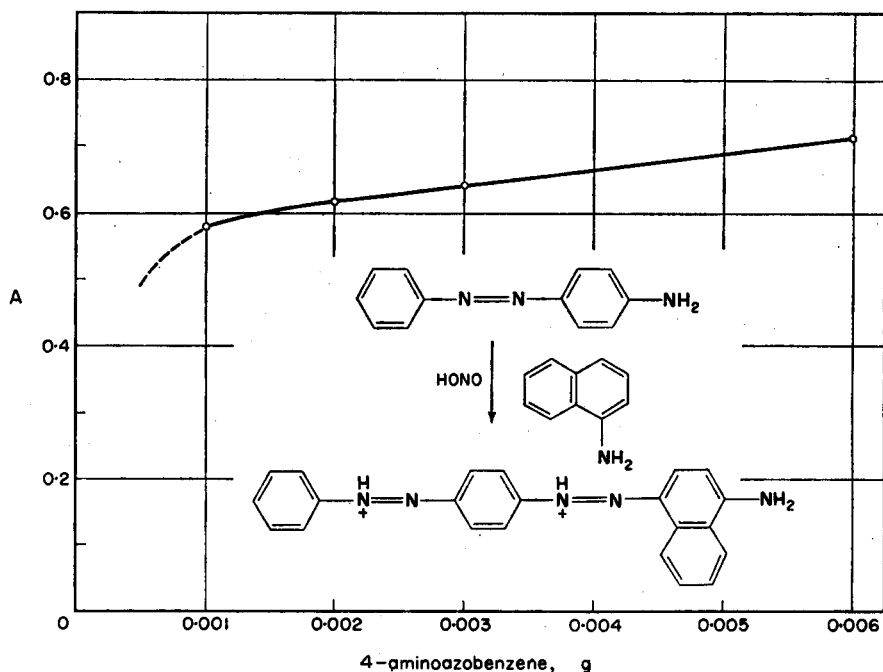


FIG. 3.—Change of absorbance with time at λ_{\max} 632 $m\mu$ of the final solution obtained with *N,N*-dimethylaniline (2×10^{-5} *M*) in the standard colorimetric procedure.

Decreased reactivity due to substituents

Some aniline derivatives gave a very weak to negligible colour in the standard colorimetric procedure. In compounds such as the nitroanilines, *o*-chloroaniline, *N,N*-dimethyl-*m*-aminobenzoic acid, *N,N*-dimethyl-*p*-bromaniline, *N,N*-dimethyl-*p*-aminobenzaldehyde, the *N,N*-dimethyl nitroanilines and *N,N*-dimethyl-*p*-toluidine, the presence of an electronegative group or a group *para* to the amino group had an adverse effect on the activity. In *N,N*-dimethyl-*o*-toluidine the low order of reactivity is due to the strong steric effect of the *o*-methyl group.¹¹ This effect forces the dimethylamino group out of the plane of the molecule and as a result causes a low yield of the bisazo dye di-cation.

Interferences

A few diphenylamines and heterocyclic imines were tested by the standard colorimetric procedure. *N*-Methyl-diphenylamine and diphenylamine gave bands at 640 $m\mu$ with molar absorptivities of approximately 13,000 and 17,000, respectively. Indole and carbazole gave bands at 560 and 605 $m\mu$ with molar absorptivities of 11,000 and 6,000, respectively. Because of their relatively weak basicity, diphenylamines, indoles and carbazoles can be readily separated from the more basic aromatic amines. In this way, aniline derivatives could be determined in the presence of these compounds.

Phenols could be expected to react with the reagent. In the standard colorimetric procedure, phenol itself gave an orange solution which had negligible absorption near

600 $m\mu$. α -Naphthol gave a band at 625 $m\mu$ with a molar absorptivity of 7,000. If necessary, phenols could be separated by alkaline extraction.

2,4-Pentadione treated by the standard colorimetric procedure gave a red solution with a band at 535 $m\mu$ and a molar absorptivity of 21,000.

Nitromethane, dibutylamine, isobutylamine, formaldehyde and acetone gave negative results.

Acetic anhydride tended to inhibit colour formation.

Determination of α -naphthylamine in a mixture.

A liquid mixture was prepared consisting of 71.5 μg of α -naphthylamine, 930 μg of aniline, 1070 μg of *N*-methylaniline, and 1210 μg of *N,N*-dimethylaniline. Reaction of this mixture in the standard colorimetric procedure (modified by substitution of 10 min of standing at room temperature for 6 min of heating on the water bath) gave an absorption spectrum with maxima at 500 and 642 $m\mu$. The band with a peak at 642 $m\mu$ had an absorbance of 0.96. The band with a peak at 500 $m\mu$ was mainly derived from aniline and *N*-methylaniline and apparently had little effect on the intensity of the long wavelength band, for 71.5 μg of α -naphthylamine reacted in the same procedure gave a band at 642 $m\mu$ with an absorbance of 0.95. The absorbance thus obtained in the mixture corresponds to 70.8 μg of α -naphthylamine which is in excellent agreement with the amount of α -naphthylamine calculated to be present.

*Determination of *N,N*-dimethylaniline in a mixture*

For the determination of *N,N*-dimethylaniline in the presence of primary and secondary amines, the use of acetic anhydrides as a masking agent was tried. A mixture of 12.1 μg of *N,N*-dimethylaniline and 2 μl of acetic anhydride were heated 10 min, cooled and treated by the standard colorimetric procedure. A molar absorptivity of 78,000 was obtained; without the acetic anhydride the molar absorptivity was 85,000. When a mixture of 12.1 μg of *N,N*-dimethylaniline and 14.3 μg of α -naphthylamine was similarly analysed, a molar absorptivity of 75,000 was obtained for *N,N*-dimethylaniline, essentially a 96% recovery. When a mixture of 12.1 μg *N,N*-dimethylaniline, 14.3 μg of α -naphthylamine, 10.7 μg of *N*-methyl-aniline, and 9.3 μg of aniline was analysed by the same procedure, a molar absorptivity of 85,000, or a 113% recovery of *N,N*-dimethylaniline, was obtained. These results show that the determination of a tertiary amine in the presence of primary and secondary amines with the help of an acylating masking agent is worthy of further investigation.

Zusammenfassung—Einige neue, sensitive Methoden zum Nachweis und zur Bestimmung von Anilin, alpha- und beta-Naphthylaminen, alpha- und beta-Anthraminen sowie deren *N*-Alkyl- und *N,N*-Dialkylderivaten werden beschrieben. Die Chromogene sind (p-Phenylazophenylazo)-anilin, -naphthylamin und -anthraminfarbstoffe. Z.B. mit *N,N*-dimethylanilin wird das blaue Dikation von *N,N*-dimethyl-p-(p-phenylazophenylazo)-anilin gebildet. Der Absorptionskoeffizient des in der kolorimetrischen Methode erhaltene beträgt 0.83 $\mu\text{g}^{-1} \text{ ml cm}^{-1}$. Für *N,N*-dimethylanilin ist Beers Gesetz erfüllt im Konzentrationsbereich 0.1 bis mindestens 3.6 μg per ml der fertigen Farblösung. Wegen des sehr grossen Unterschiedes in der Reaktionsgeschwindigkeit können Naphthylamin- und Anthraminderivate in Gegenwart von Anilinderivaten bestimmt werden. Ferner kann durch Einsatz eines Maskierungsmittels ein Dialkylamin in Gegenwart von sekundären und primären Aminen bestimmt werden. Tüpfelteste für Anilin-, Naphthylamin- und Anthraminderivate werden beschrieben. Die Empfindlichkeit dieser Nachweise ist jedoch nicht mit der der kolorimetrischen zu vergleichen.

Résumé—Les auteurs ont mis au point de nouvelles techniques sensibles pour déceler et doser l'aniline, les α et β naphthylamines et les α et β anthramines, ainsi que leurs dérivés *N*-alkyle et *N,N*-dialkyle. Les chromogènes sont des colorants de la p-phénylazophénylazoaniline, de la p-phénylazophénylazonaphthylamine et de la p-phénylazophénylazoanthramine. Par exemple, avec la *N,N*-diméthylaniline, le di-cation bleu de la *N,N*-diméthyl-p-(p-phénylazophénylazo)-aniline est formé. L'absorption de la *N,N*-diméthylaniline obtenu dans le procédé colorimétrique est 0,83 $\text{g}^{-1} \text{ ml cm}^{-1}$. Dans l'analyse de la *N,N*-diméthylaniline, la loi de Beer est suivie de 0,1 à au moins 3,6 μg par ml de solution finale. A cause des vitesses de réaction largement différentes, les dérivés de la

naphtylamine et de l'anthramine peuvent être dosés en présence des dérivés de laniline. Ainsi, à l'aide d'un agent complexant, une dialkylaniline peut être dosée en présence d'amines primaires et secondaires. Des essais par touches sont décrits pour l'aniline, la naphtylamine et l'anthramine, mais leur sensibilité ne se compare pas à celles obtenues dans la méthode colorimétrique.

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THE PRECIPITATION OF NIOBIUM OXINATE OF DEFINITE COMPOSITION

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Summary—Since the composition of niobium oxinate, precipitated from aqueous solution, is apparently not definitely established, several new techniques have been used for the preparation of a compound of definite composition. Of these techniques, homogeneous precipitation of niobium oxinate by means of urea yielded the best results. The product is crystalline and agrees, within the limits of $\pm 0.5\%$, with the theoretical formula $\text{NbO}(\text{C}_9\text{H}_6\text{ON})_3$. Furthermore, the solubility in various organic solvents, the spectrum in the ultraviolet and infrared regions, and the electron diffraction have been determined; thermolysis has been carried out; and photomicrographs of the crystals have been taken.

NIOBIUM oxinate was first described by Süe¹ and the ratio $\text{Nb}_2\text{O}_5 : 5.5\text{C}_9\text{H}_7\text{ON} : 4\text{H}_2\text{O}$ was proposed for its composition. Methods for its preparation were recently investigated by Doan and Duval² who established, on the basis of thermolysis curves, that two moles of oxine were bound to one mole of niobium pentoxide, while the water content varied from experiment to experiment. Szymanski and Archibald³ found that after heating to 155° , niobium oxinate has the composition $\text{NbO}(\text{C}_9\text{H}_6\text{ON})_3$; however, they left open the question of its composition immediately after the precipitation from an aqueous solution.

Several methods by which it was hoped to improve the conditions for obtaining stoichiometric samples of niobium oxinate from aqueous solutions were tested and can be summarised as follows:

(i) The niobium fluoride complex was decomposed by adding boric acid to a solution containing excess oxine. Precipitation was carried out at pH 3.5, corresponding to that at which the maximum extraction of niobium oxinate in chloroform from an acidic medium⁴ was previously obtained by the present authors. This method yielded a voluminous, hardly filterable orange precipitate with 25% of the niobium left in solution.

(ii) In another group of experiments a solution of niobium hydrate was dissolved in dilute hydrofluoric acid and added to an ammoniacal solution of boric acid containing oxine. The concentration of reagents was chosen so as to give, after mixing, a pH of 9.4, equal to the pH at which the maximum extraction of niobium oxinate from an alkaline medium was obtained. The precipitate was greenish-yellow, less voluminous, settled more readily and after successive washings with water, alcohol and ether, gave a product containing a considerable excess of oxine. Two to 4% of the niobium was left unprecipitated.

(iii) A similar product was obtained when ammonium chloride was added to a solution of niobium hydrate in potassium hydroxide to give a pH of 9.2 after final dilution. By this method 85 to 90% of the niobium was recovered.

(iv) The only method which yielded a defined, crystalline product was based on

slow hydrolysis of urea in an acid solution, containing oxalic acid and an excess of the reagent. This method will, therefore, be described in greater detail.

EXPERIMENTAL

Precipitation of defined niobium oxinate

One g of niobium pentoxide was fused with an excess of potassium pyrosulphate, and the cool melt was dissolved in 100 ml of 1M oxalic acid⁵. After the addition of 10 ml of concentrated sulphuric acid, and oxine (50% excess), the solution was heated to boiling point. Urea was added in portions approximately five times greater than the theoretical amount, and the solution was diluted to 2000 ml and left in a water bath until it turned brown (pH 7-8). The precipitate obtained by this technique was coarse, crystalline and yellowish-green, and it settled rapidly and was easily washed.

The precipitation was almost quantitative (> 99%). The precipitate was filtered through a sintered-glass crucible, washed with warm water, then with alcohol and ether to speed up drying.

Analysis of the product

Niobium and oxine were determined in all products; precipitates obtained by methods (i) and (ii) were additionally analysed for boron and fluorine.

Niobium was determined by igniting the precipitate at 950° in a porcelain crucible and weighing as niobium pentoxide. The method of Berg⁶ was slightly modified for the determination of oxine. The precipitate was dissolved in hydrochloric acid, potassium bromide was added, and the solution was titrated with potassium bromate. The excess of the reagent was reduced by potassium iodide and re-titrated with sodium thiosulphate in the presence of carbon bisulphide. Fluorine was determined by the method of Ballczo and Kaufmann.⁷ The sample was dissolved in hydrofluoric acid and distilled, in the presence of perchloric acid, into a solution of sodium hydroxide. Subsequently, the solution was titrated with thorium nitrate using sodium alizarin sulphonate as indicator. Boron was determined spectrographically.

The products prepared by methods (i) and (ii) differ in their water content as well as in the quantity of the absorbed oxine. They were, therefore, dried at 150° before analysis, while the oxinate obtained by method (iv) was only washed with water, alcohol and ether and dried in air. Some samples have been warmed under vacuum at 10⁻⁴ mm of mercury and 90° in order to sublime the small amounts of oxine, which proved to be negligible.

RESULTS AND DISCUSSION

Table I gives the results of the analyses (a mean value of six precipitations) of oxinate by different methods.

TABLE I.

Method of precipitation	Nb, %*	C ₉ H ₇ ON, %*	F, %	B, %
Complexing at pH 3.5	20.9 ± 0.6	72.9 ± 0.2	0.98	0.04
Complexing at pH 9.4	17.1 ± 0.1	80.6 ± 0.5	0.02	0.04
Precipitation from niobate solution	16.5 ± 0.1	81.3 ± 0.2	—	—
Hydrolysis of urea	17.16 ± 0.2	79.74 ± 0.3	—	—

* The theoretical values for niobium and oxine are 17.16 % and 79.88 %, respectively.

The results in the first three horizontal rows were obtained for products dried at 155°, those in the last row for the product dried at room temperature. Only the samples precipitated from an acidic medium by complexing in fluoride solution yielded figures for both components which deviate considerably from theoretical

values. Furthermore, the adsorption of fluoride ions is appreciable, but boron is adsorbed to a much smaller extent.

Owing to the excellent characteristics of the precipitate obtained by the urea method (stoichiometric composition, crystalline nature, rapid settling and low percentage of niobium in the precipitate), this procedure was tested for its applicability to the gravimetric determination of niobium. In a solution labelled before precipitation with radioactive ^{95}Nb , only traces of niobium were detected by radiometric measurements (scintillation counting) in the final filtrate. The method of precipitation was essentially the same as that described above, the only differences being that smaller samples of niobium (50 mg of niobium pentoxide) were taken and the quantities of the reagents were proportionally reduced. Over 99% of niobium pentoxide was recovered in all experiments.

The solution of niobium must be fresh, because if the reagents are added to aged solutions niobic acid is precipitated. It is therefore advisable to decompose the samples immediately before the precipitation.

In order to obtain a thorough characterisation of the product obtained by the hydrolysis method, the following additional measurements were made:

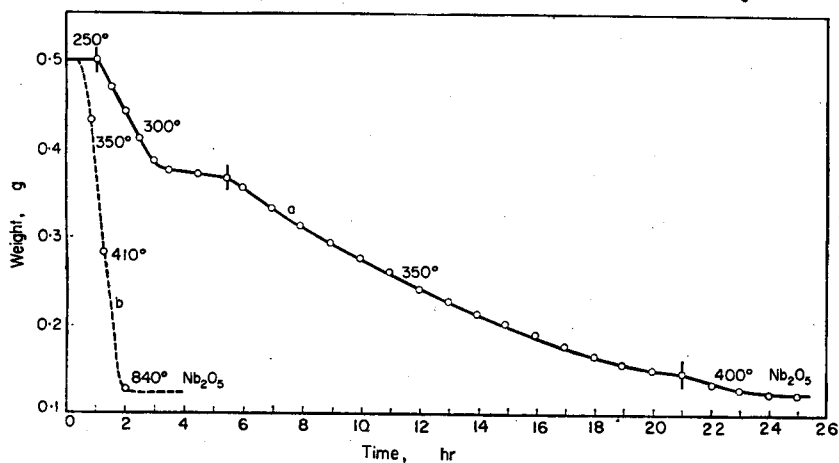


FIG. 1.—Thermolysis curves of niobium oxinate, taken with the Stanton thermobalance at two different rates of heating.

1. The thermolysis curve (Fig. 1) proved the stability of the compound up to 250° . After constant heating, to 400° , decomposition was complete in 24 hr. On increasing the rate of heating, the last traces of oxine sublimed at approximately 600° . The thermolysis curves were taken with a Stanton thermobalance.

2. The absorption spectrum of the emulsion of niobium oxinate in liquid paraffin measured with a Perkin-Elmer, Model 21 infrared spectrophotometer, using a sodium chloride prism, shows a maximum at $10.9\ \mu$ which is characteristic of the NbO group^{8,9}, and which seems to confirm the formula $\text{NbO}(\text{C}_9\text{H}_6\text{ON})_3$. Infrared spectra of niobium oxide and oxine are presented for comparison (Fig. 2).

3. In Fig. 3 the absorption spectrum of niobium oxinate in the ultraviolet-visible region, taken with a grating spectrophotometer (Optica Milano, Model CF₄), is compared with that of oxine. The samples were dissolved in chloroform at a molar concentration of 1×10^4 and the absorption was measured against the solvent.

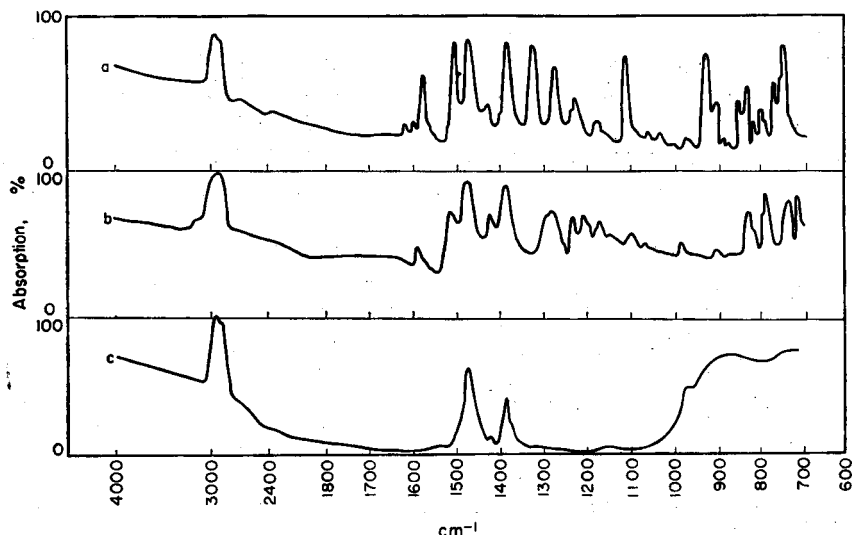


FIG. 2.—Infrared absorption spectra of (a) niobium oxinate, (b) oxine and (c) niobium oxide, measured with the Perkin-Elmer, Model 21, spectrophotometer

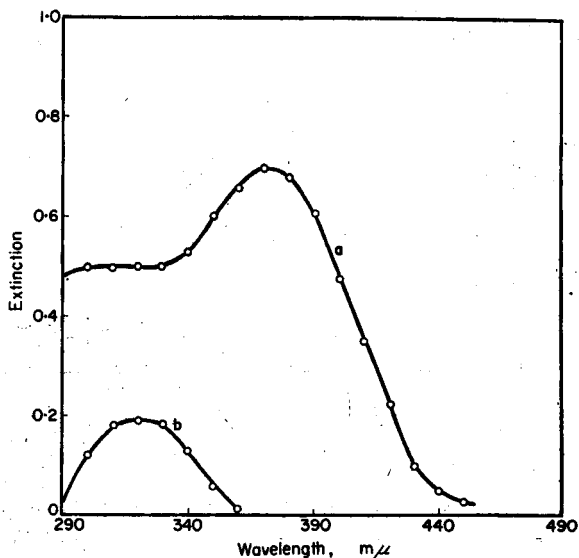


FIG. 3.—Ultraviolet and visible absorption spectra of (a) niobium oxinate and (b) oxine, taken with the grating spectrophotometer CF4, Optica, Milano

4. Figs. 4 and 5 represent the photomicrographic (Reichert MeF optical microscope) and electron microscopic pictures (AEG-Zeiss, EM 8) of the precipitate and these disclose, together with the electron diffraction picture (Fig. 6), the crystalline nature of niobium oxinate when prepared by the procedure described.

5. Since data on the solubility of niobium oxinate are lacking, some determinations were made by the radiometric and the classical method in the solvents listed in Table II. The measurements were made by shaking samples in a thermostatted room (24°) for 24 hr with the selected solvent. The results in Table II represent the mean value of

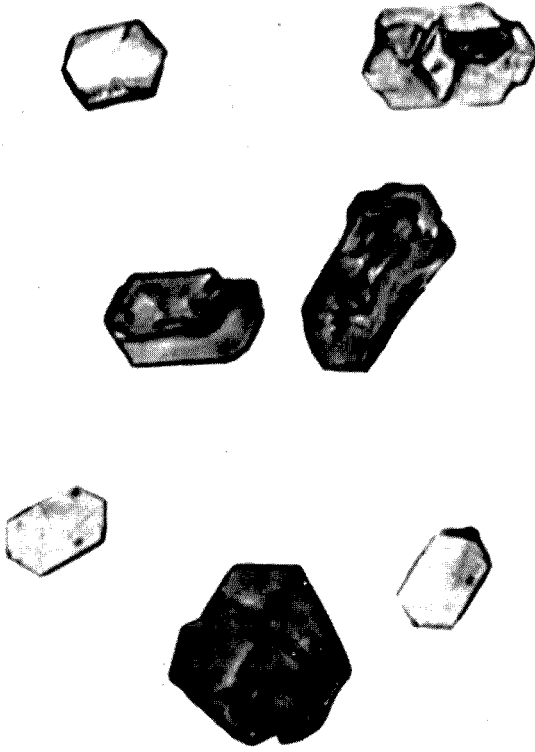


FIG. 4.—Photomicrographs of the crystals of niobium oxinate

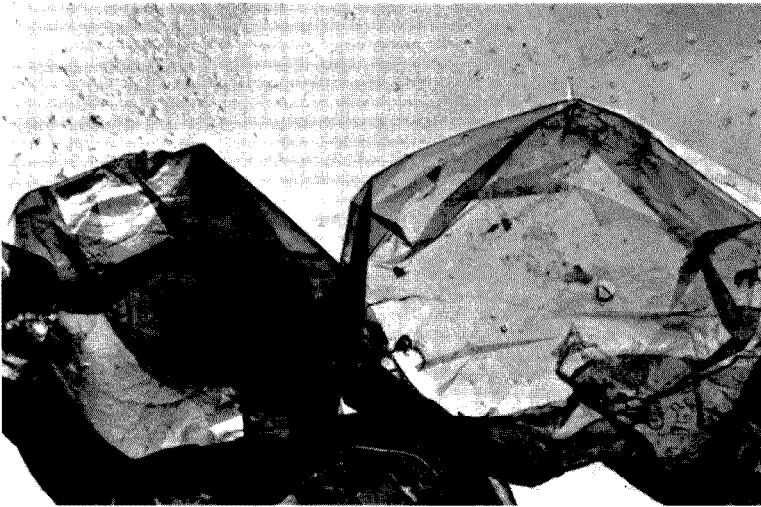


FIG. 5.—Electron-microscopic picture of crystallised niobium oxinate
(Electron microscope AEG-Zeiss, EM8)

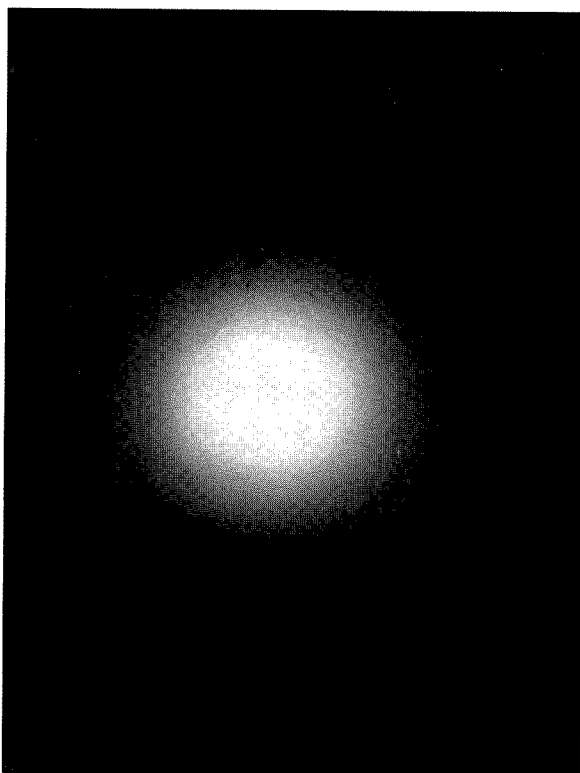


FIG. 6.—Electron-diffraction picture of niobium oxinate.

TABLE II.

Solvent	Solubility, mg/ml
Chloroform	11.2
Acetone	0.65
Ethyl alcohol	0.62
Diethyl ether	0.01
Tetrahydrofuran	1.4
Isopropyl alcohol	0.22
Methyl isobutyl ketone	0.15

6-8 determinations, but there is considerable inconsistency between individual measurements.

Tentative measurements were also made with amyl acetate, nitromethane, mesityl oxide, nitrobenzene, carbon tetrachloride, methyl isopropyl ketone, cyclohexanone, carbon bisulphide and toluene. Of these only nitrobenzene and nitromethane readily dissolved niobium oxinate (6.6 and 1.3 mg/ml, respectively), and other solvents dissolved less than 0.5 mg/ml of the compound.

Like other oxinates, niobium oxinate fluoresces intensely in ultraviolet light.

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Zusammenfassung—Da es den Anschein hat, dass die Zusammensetzung des Nioboxinates, wenn aus wässriger Lösung gefällt, nicht wohldefiniert ist, wurden verschiedene Methoden angewandt um einen stöchiometrisch zusammengesetzten Niederschlag zu erhalten. Von allen studierten Methoden liefert die Fällung von Nioboxinat aus homogener Lösung durch Hydrolyse von Harnstoff die besten Resultate. Die Kristalle sind gut entwickelt und die Zusammensetzung des Niederschlages entspricht innerhalb eines halben Prozentes der Formel $\text{NbO}(\text{Oxin})_3$. Die Löslichkeit des Niederschlages in verschiedenen organischen Solventien, die UV- und IR-Spektren sowie Elektronenbeugung wurden untersucht; Thermolysiskurven und Mikrographien wurden gemacht.

Résumé—Comme la composition de l'oxinate de niobium, précipité en solution aqueuse, ne semble pas être définitivement établie, de nombreuses techniques nouvelles sont utilisées pour la préparation d'un composé bien défini. Parmi les méthodes étudiées, la précipitation en milieu homogène d'oxinate de niobium par l'urée conduisait aux meilleurs résultats. Le produit est cristallin et correspond à la composition $\text{NbO}(\text{C}_6\text{H}_5\text{ON})_3$, à $\pm 0,5$ pour cent près. Les solubilités dans différents solvants organiques ont été étudiées, ainsi que les spectres ultraviolet et infrarouge et la diffraction électronique la thermolyse a été effectuée, et des micrographies des cristaux ont été prises.

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PRELIMINARY COMMUNICATIONS

Contributions to the basic problems of complexometry—V Mutual masking of iron and manganese

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THE masking of iron with triethanolamine¹ in the complexometric determination of calcium, magnesium or manganese is widely used in the analysis of lime, dolomite and other calcareous materials such as cements, glasses, *etc.* Using a modified procedure² it is possible to mask relatively large concentrations of iron as the colourless complex with triethanolamine. The determination of manganese in the presence of iron in an alkaline reducing medium (hydroxylamine) can be carried out without difficulty, and this fact has been utilised with success in the analysis of ferromanganese.³ This method has recently been re-examined and modified slightly.^{4,5}

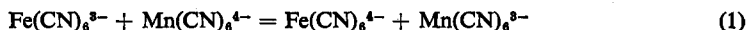
More difficulties occur in the screening of manganese. Only small amounts of this element can be masked by triethanolamine because of the formation of an intensely green $\text{Mn}^{\text{III}}\text{-TEA}$ complex.⁶ Only recently, a relatively simple method has been developed that enables the masking of manganese in amounts up to 80 mg.⁷ The method is based on the fact that in a strongly alkaline medium containing triethanolamine, the manganese is oxidised by atmospheric oxygen to a deep green $\text{Mn}^{\text{III}}\text{-TEA}$ complex. On adding potassium cyanide and raising the pH to 10 with acetic acid, a colourless or slightly yellow $\text{Mn}(\text{CN})_6^{3-}$ complex is formed. This method can be used for determination of calcium, or of the sum of calcium and manganese, provided that iron and aluminium have first been separated by precipitation with pyridine.

As triethanolamine itself is a very good masking agent for iron as well as for aluminium, it was thought that it might be possible to find a procedure that would work without first precipitating iron and aluminium. This would be especially useful for various materials rich in manganese, such as manganese slags, welding fluxes, *etc.*

Preliminary experiments were aimed at a transformation of both the iron and the manganese into the Fe-TEA and $\text{Mn}(\text{CN})_6^{3-}$ complexes, because only these complexes ensure the complete screening of both elements in complexometric titrations. To the solutions of manganese and iron were added triethanolamine, potassium cyanide, and ammonia or sodium hydroxide, under various conditions, and over various ranges. In view of the alkaline reaction of all the reagents added, the possibility of preventing the precipitation of ferric or manganic hydroxides was carefully studied; such precipitation would make subsequent complexometric titrations impossible. The following procedure proved to be satisfactory.

Procedure

To an acid solution of iron and manganese add excess of 20% triethanolamine in such a way as to avoid the precipitation of hydroxides. Then add at once 20–30 ml of concentrated ammonia containing 1–2 g potassium cyanide. The solution becomes orange and on heating changes to colourless or slightly yellow. Ferric ions form ferricyanide, which immediately oxidises manganese according to the equation:



The resulting solution contains both complex cyanides of iron^{II} and manganese^{III}, which are complexometrically inactive. The reaction proceeds quantitatively, if the solution contains more iron than is equivalent to the manganese according to equation (1). If the solution contains more manganese than iron, part of the manganese remains unoxidised as $\text{Mn}(\text{CN})_6^{4-}$ and can be titrated with EDTA (see Table 1, experiments 6–9). With iron deficiency there is no quantitative relation between iron and manganese concentrations, because manganese is partly oxidised by atmospheric oxygen. Excess of iron does not interfere in the titration because ferrocyanide is first formed according to equation

(1) and the excess is then bound as the stable Fe-TEA complex. The presence of large amounts of free ferricyanide is improbable, the solutions being almost colourless.

A series of experiments was carried out in manner described. In some of them the consumption of EDTA was determined (blank experiments—see Table I, experiments 10–12), in others the taken EDTA used was determined by back-titration with calcium chloride, after proper masking. With iron and manganese properly screened, the losses of EDTA were within experimental error, that is 0.02 ml.

TABLE 1.—MUTUAL MASKING WITH VARYING Fe:Mn RATIO. AFTER Fe AND Mn WERE MASKED EDTA WAS ADDED AND TITRATED WITH CaCl₂.

No.	ml			ml		0.05M EDTA ml
	Fe	Al	Mn	Taken	Found	
1	4.94	—	0.51	2.01	2.00	−0.01
2	5.14	—	5.10	2.01	1.99	−0.02
3	4.94	1.05	3.06	2.01	2.00	−0.01
4	11.65	25.96	2.98	19.86	19.79	−0.07
5	23.30	20.76	9.95	9.93	9.90	−0.03
6	2.96	—	5.10	2.01	1.29	−0.72
7	4.45	—	5.10	2.01	1.14	−0.87
8	4.94	—	5.10	2.01	0.80	−1.21
9	2.96	10.47	5.10	5.03	2.81	−2.22
10	10.79	—	9.46	0.07*		
11	21.58	—	18.91	0.09*		
12	21.58	—	18.91	0.11*		

* Consumption of EDTA by direct titration.

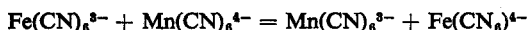
During further experiments some unexpected difficulties occurred in the complexometric determination of alkaline earths because of the formation of a white crystalline precipitate in the solutions of complex Fe- and Mn-cyanides. The cause of it is formation of calcium salts of manganese^{III} cyanide, which dissolves with difficulty in EDTA even in hot solution.

CONCLUSIONS

It can be presumed that by this simple procedure the selectivity of the complexometric determination of calcium or magnesium may be improved for the following reasons:

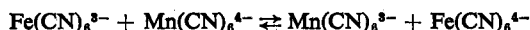
- (1) The determination is not affected by iron, aluminium or manganese.
- (2) The addition of potassium cyanide also masks other elements (Ag, Hg, Zn, Cd, Ni, Co, Cu).
- (3) Other heavy elements, such as lead or bismuth, if present, can be masked by other complex-forming reagents such as BAL⁸ or thioglycolic acid.⁹

Summary—The screening of iron and manganese in some further complexometric titrations has been studied. It was found that by masking with triethanolamine and potassium cyanide, ferricyanide is formed, which immediately oxidises manganese according to the equation:



The resulting solutions contain both the complex cyanides of iron(II) and manganese(III), which are "complexometrically" inactive. The difficulties in further determinations after proper masking of iron and manganese are mentioned.

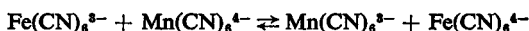
Zusammenfassung—Die Maskierung von Eisen und Mangan in einigen weiteren chelometrischen Titrationen wurde studiert. Beim Maskieren mit Triäthanolamin und Kaliumcyanid wird das Eisen in Ferricyanid übergeführt, welches das Mangan sofort nach folgender Gleichung oxydiert



Die resultierende Lösung enthält die komplexen Cyanide von Eisen(II) und Mangan(III), welche

"komplexometrisch" inaktiv sind. Schwierigkeiten werden diskutiert, die bestehen, wenn in der Lösung andere Metalle bestimmt werden sollen.

Résumé—Les auteurs ont étudié le comportement du fer et du manganèse dans quelques titrages complexométriques. En complexant avec de la tritéhanolamine et du cyanure de potassium, il se forme du ferricyanure qui oxyde immédiatement le manganèse suivant la réaction:



Les solutions résultantes contiennent les complexes cyanure du fer(II) et du manganèse(III), qui sont inactifs "au point de vue complexométrie". Les difficultés rencontrées dans les déterminations ultérieures, après que le fer et le manganèse aient été complexés, sont mentionnées.

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Extraction of As^V from H₂SO₄-KBr solutions and its analytical use

(Received 16 January 1961)

It has long been known that some halides of As^{III} and As^V may be extracted into organic solvents. Thus, the extraction of As^{III} from HCl medium into tetrachloromethane,^{1,2} ether,³ dichlorodiethyl-ether,⁴ and other solvents,⁵ has been described; so also has the extraction of As^V from the same medium into ether,⁶ tetrachloromethane,⁶ and isobutylmethylketone.⁷

The extraction of other halides of arsenic has not been studied so closely. Bock and co-workers⁸ describe the extraction of AsBr₃ into ether and Brinck and co-workers⁹ describe the extraction of As^{III} from HI solution. None of the methods mentioned is quantitative.

It is known that some relation exists between extraction and distillation of certain covalent compounds. In the literature the distillation of As^V from H₂SO₄-KBr medium⁹ has been described and has been successfully applied. For this reason the extraction of As^V from this medium into organic solvents was investigated.

This extraction is found to be easily reproducible. An optimum concentration of sulphuric acid is 14–17*N*; at lower concentration the extraction is not quantitative, and in 10*N* acid does not take place at all. At higher concentration, HBr and Br₂ are freely liberated, and the phases are difficult to separate.

The necessary amount of KBr is about 200 mg for the extraction of 100 μg of arsenic from 25 ml; with smaller amounts of KBr the extraction does not take place quantitatively, but larger amounts of KBr do not interfere.

Many organic solvents were studied. Preliminary investigations showed tetrachloromethane to be the best. Alcohols, ketones and ethers are unsuitable because of their high solubility in the aqueous medium.

When 100 μg of arsenic were extracted from the H₂SO₄-KBr medium described into 25 ml of

tetrachloromethane, and the arsenic was then re-extracted with 25 ml of water and neutralised with sodium hydroxide, photometric determination through molybdenum blue showed that the extraction and re-extraction of arsenic are very rapid and quantitative. From the character of the reaction a high selectivity is to be expected, and this selectivity has been proved experimentally.

The extraction of arsenic by this procedure will be more fully described in a further communication.

Acknowledgement—It is my pleasant duty to thank Dr. R. Přibil for his interest in this work.

Summary—By the use of tetrachloromethane, arsenic^V can be completely extracted from a 14-17*N* aqueous sulphuric acid solution containing 200 mg of potassium bromide per 25 ml of solution.

Zusammenfassung—Tetrachlorkohlenstoff ist geeignet fünfwertiges Arsen aus Lösungen zu extrahieren, die 14-17 normal in Schwefelsäure sind und etwa 200 mg Kaliumbromid per 25 ml Lösung enthalten.

Résumé—En utilisant le tétrachlorométhane, l'arsenic (V) peut être extrait à partir d'une solution aqueuse d'acide sulfurique 14-17 *N* contenant environ 200 mg de bromure de potassium pour 25 ml de solution.

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Applications de la chelatometrie—VII. Dosage volumetrique des *ortho*-acyl-phénols

(Received 15 December 1960)

INTRODUCTION

Les *ortho*-acyl-phénols trouvent actuellement un débouché industriel croissant, notamment pour la fabrication des γ -benzopyrones (chromones, flavones et isoflavones) et des coumarines substituées.

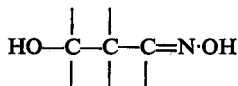
Ils sont généralement préparés par réaction de Fries¹ à partir des esters phénoliques correspondants et on sait que cette réaction conduit toujours, bien que dans des proportions variables, aux deux isomères *ortho* et *para* en même temps qu'une décomposition partielle régénère le phénol de départ.

Le dosage de l'isomère *ortho* en présence de l'isomère *para* et de phénols non acylés n'a guère été étudié à notre connaissance: Fritz et Keen ont montré la possibilité de doser les phénols substitués de cette famille par anhydrotitrimétrie dans la diméthyl-formamide comme solvant et en présence d'azoviolet comme indicateur²; toutefois cette méthode ne permet pas de distinguer les constituants du mélange signalé ci-dessus qui sont dosés tous ensemble; de Lorenzi et Credali ont appliqué une méthode identique dans le cas particulier de la *para*-hydroxypropiophénone⁴ tandis que Baudet et Pacheco opéraient en milieu alcoolique^{3a} avec l'aide du bleu C-4-B et que Mouton et Masson

décrivaient un procédé spectrophotométrique dans l'U.-V. pour le même produit³; nous n'avons pas expérimenté cette dernière technique sur les mélanges précités, désireux que nous étions de trouver une méthode générale pour tous les acyl-phénols en position ortho. Ramanujam a récemment publié un mode de dosage par bromométrie des corps de la série des hydroxyacétophénonnes,⁴ mais cette technique ne résoud pas non plus le problème que nous préoccupé.

PRINCIPE

Le procédé dont nous avons eu l'idée repose sur une observation d'Ephraïm⁵ qui dès 1931 remarqua que le groupe



était spécifique du cuivre avec les ions duquel il donnait des précipités quantitatifs à la manière de l'aldéhyde salicylique dont l'emploi pour le dosage gravimétrique du cuivre et du nickel est bien connu. D'autres auteurs ont appliqué ensuite les oximes de différents corps de cette série également pour le dosage du nickel⁶⁻⁸ du palladium⁷, du vanadium^{7,10}, du zinc⁹, du cobalt⁸ et du titane⁷. Il semble bien toutefois, d'après nos essais, que le cuivre est le métal le plus généralement précipité par les oximes de ce groupe et nous avons finalement retenu celui-ci pour la mise en oeuvre de notre procédé: après oximation de l'échantillon par un moyen classique tel que l'emploi du chlorhydrate d'hydroxylamine en milieu alcalin, la solution résultante est traitée par une liqueur contenant un sel de cuivre en quantité connue et ayant un effet tampon convenable sur le pH du milieu réactionnel. Après filtration on titre le cuivre restant dans le filtrat et détermine la quantité d'ortho-acyl-phénol par différence.

Après divers essais, nous avons retenu une méthode chélatométrique avec indicateur métallochrome comme étant la plus intéressante pour évaluer volumétriquement le cuivre dans le filtrat. Nous avons parallèlement contrôlé la possibilité de doser le cuivre présent dans le précipité.

Nous poursuivons actuellement nos travaux sur un certain nombre d'acyl-phénols variés.

Les résultats de ces travaux seront publiés ultérieurement dans cette revue avec le détail du mode opératoire.

Augers-en-Brie,
(S et M.), France

CLAUDE HENNART[®]
avec la collaboration de
(Mme.) YVETTE LEFEVRE
pour la partie expérimentale

Résumé—Les ortho-Acyl-Phénols, tels que l'ortho-hydroxyacétophénone et ses homologues, peuvent être dosés volumétriquement après oximation. On précipite le complexe cuivrique et un dosage chélatométrique est effectué.

Summary—The ortho-acyl-phénols, such as ortho-hydroxyacetophenone and its homologues, can be determined titrimetrically after oximation. The precipitation of cupric complex is carried out and subsequent titration is made by chelatometry.

Zusammenfassung—Die ortho-Acyl-Phenollen, ist wie die ortho-oxyacetophenon und ihre Homologe, können volumetrisch bestimmt werden nach Oximation. Die Kupferzusammensetzung wird gefällt und chelatometrisch bestimmt.

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LETTER TO THE EDITOR

Explosion in analytical laboratory of Jas. Anderson & Co. (Colours) Ltd. on Friday 13th January, 1961

SIR:

WHILE carrying out a wet oxidation of a red azo pigment, C.I. Pigment Red 38, using the method of G. Frederick Smith and Harvey Diehl from *Talanta*, 1960, 4, 185, a violent explosion occurred. The authors described the reaction as "hazard free" but this is clearly not the case.

The wet oxidation technique was being considered for use in the trace metals analysis of pigments and a sample was being examined as follows using a slight modification of the Bethge apparatus.

Five g of sample were added to the 250-ml round bottomed flask with 15.0 ml of 60% perchloric acid, 3.0 g of 50/50 W/W paraperiodic acid and 1 mg of sodium metavanadate. No reaction took place immediately and slight heat was applied to agitate the mixture and promote the reaction. After 2-3 min heat was removed and the reaction proceeded as suggested, with iodine being liberated and subliming into the reflux apparatus and eventually into the condenser. The reaction slowed down considerably but by this time the pigment had been wetted out, although the bulk of it was still unaffected. Slight heat was again applied, and reaction slowly advanced until a boiling action commenced, but at this time only 2-3 ml of liquid had refluxed, and was now lying in the trap of the return apparatus. (This was possibly water owing to the low temperature.)

Suddenly the mixture in the flask began to darken considerably until it was black and one or two small flames appeared for an instant. Heat was removed, the safety shield put in place, the fume cupboard window closed and a safe position adopted. The flashes had by this time increased in number and proportions, and every 5 sec or so a more violent flash would bump the entire apparatus and leap up the tube to the exit of the condenser. After about a minute from the time of darkening, the flask completely shattered with an explosion which splashed the acid and glass fragments around the inside of the fume cupboard but left the reflux system and condenser intact.

Owing to the warning signs and time lag of the explosion no injuries were sustained by the operator.

Hawkhead Road
Paisley, Scotland
16 January 1961

J. THOMSON

NOTICES

The following meetings have been arranged in the Bourquelot lecture theatre, Faculty of Pharmacy, Paris, at 5.45 p.m., under the direction of Professors J. A. GAUTIER and P. MALANGEAU:

Tuesday 11 April 1961: Lithium Aluminium Hydride as a Reagent in Analytical Chemistry:
M. E. A. M. DAHMEN.

Tuesday 25 April 1961: Ionisation Constants and Structures of Organic Compounds: Professor P. RUMPF.

Tuesday 9 May 1961: Determination of Gases and Toxic Vapours by Galvanic Piles (Osmopiles):
M. A. BERTON.

Tuesday 30 May 1961: Humidity and Dry Extract of Foodstuff Materials and Drugs: Pharmacien Lieutenant-Colonel J. KIGER.

The following meetings have been arranged:

Wednesday 3 May 1961: Society for Analytical Chemistry: Meeting for reading of Original Papers. Burlington House, London, W.I. 7.00 p.m.

Friday 12 May 1961: Society for Analytical Chemistry, Midlands Section and Microchemistry Group: Joint Meeting: Automation in the Analytical Laboratory. Technical College, Nottingham. 7.15 p.m.

Friday-Saturday 26-27 May 1961: Society for Analytical Chemistry, Midlands Section and Western Section: Joint Meeting. Hereford. *Friday:* Afternoon visit to Bulmers (Cider) Ltd.

Evening lecture on *Use of Ion-Exchange and Column Chromatography in Metallurgical Analysis.* Town Hall, Hereford.

Saturday: Morning coach tour of countryside around Hereford. Evening dinner at *Green Dragon Hotel*, Hereford.

Sunday-Friday 16-21 July 1961: Symposium on The Teaching of Analytical Chemistry. University of Aberdeen, Scotland.

The symposium will take the form of a series of discussions on the teaching of analytical chemistry, considered first in its own right, then in conjunction with the other branches of chemistry. A social programme and a ladies' programme have been arranged.

Monday 17 July

9.30 a.m. Opening of Symposium: Professor G. M. BURNETT.

The Teaching of Analytical Chemistry:

(a) *Theory:* Dr. R. A. CHALMERS.

2.30 p.m. (b) *Practical Work:* Mr. L. S. BARK and Mr. L. DAVIES.

Tuesday 18 July

9.30 a.m. *Analytical and Organic Chemistry:* Professor S. VOEIBEL.

Wednesday 19 July

9.30 a.m. *Analytical and Inorganic Chemistry:* Dr. G. W. A. FOWLES.

2.30 p.m. *Analytical and Physical Chemistry:* Professor F. ČŮTA.

Friday 21 July

9.30 a.m. *The Teaching of Chemistry in Czechoslovakia:* Dr. J. ZÝKA.

Further details may be obtained from Miss D. A. THOMSON, Chemistry Department, The University, Old Aberdeen, Scotland.

Sunday-Friday 13-18 August 1961: Metropolitan Microchemical Society under the sponsorship of the **International Union of Pure and Applied Chemistry: International Symposium on Microchemical Techniques**. Pennsylvania State University, U.S.A.

The technical programme will consist of a number of main introductory lectures and a full schedule of invited papers directed toward new methods and techniques or unique applications of microchemical or microanalytical interest.

A series of social activities will be held to facilitate the informal meeting of the participants. In addition, a ladies' programme is planned.

A commercial exhibit of laboratory equipment, chemicals and specialities will be held in conjunction with the meeting programme. It is also hoped to schedule one session at which participants can demonstrate novel, non-commercialised techniques and apparatus which they have personally developed.

Further details may be obtained from Mr. HOWARD J. FRANCIS, Jr., c/o Pennsalt Chemicals Corporation, Post Office Box 4388, Philadelphia, Pennsylvania, U.S.A.

Monday-Wednesday 18-20 September 1961: Canadian Association for Applied Spectroscopy: Eighth Ottawa Symposium on Applied Spectroscopy. Ottawa.

Papers are invited for presentation on the subjects of applied spectroscopy, including emission, ultraviolet, infrared, X-ray and nuclear magnetic resonance work in the field of instrumental analysis.

Titles and brief abstracts of papers should be submitted before 6 June, 1961, to ROLAND LAUZON, Programme Chairman, Eighth Ottawa Symposium on Applied Spectroscopy, c/o Division of Pure Chemistry, National Research Council, Ottawa, Ontario, Canada.

B.S.I. News announces the following addendum to a British Standard:

Addendum 1: 1960 to B.S. 2690: Methods of testing water used in industry. It provides methods for determining solids content, carbon dioxide, dissolved silica, total iron and dissolved oxygen in high purity water. (Price 6s.)

The following revised British Standard is also announced:

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 10: 1960: Arsenic in coal and coke. A colorimetric method, using either wet or dry oxidation, and a paper stain (modified Gutzeit) method for arsenic are described. (Price 6s.)

PAPERS RECEIVED

- The distribution of vanadium between alcoholic hydrochloric acid solutions and the strongly basic anion-exchanger Dowex-1: Separation of vanadium and nickel from iron and copper. G. E. JANAUER and J. KORKISCH. (28 January 1961).
- Über die Anwendung von Cystein als Maskierungsreagens bei komplexometrischen Titrationsen. WOLFGANG BERNDT und JOSEF ŠÁRA. (28 January 1961).
- Contributions to the basic problems of complexometry—VI: The masking of trivalent chromium. RUDOLF PŘIBIL and VLADIMIR VESELÝ. (30 January 1961).
- Diammonium-5,5'-indigeo disulphonate as an analytical reagent—I: Gravimetric determination of thorium and cerium^{III} and their separation from uranium^{VI}. B. D. JAIN and J. J. SINGH. (6 February 1961).
- Applications of infrared spectroscopy—V: The retention of water and organic solvents by carbohydrate materials. D. M. W. ANDERSON and N. J. KING. (6 February 1961).
- Sur un principe de colorimétrie en milieu non-aqueux—II: Emploi du bromure de p-nitrophénacyle pour l'identification et le dosage des acides carboxyliques. JAROSLAV BARTOS. (6 February 1961).
- Iodometric determination of copper and iron in one solution. J. AGTERDENBOS and E. J. V. TELLINGEN. (8 February 1961).
- Gravimetric determination of tungsten by homogeneous precipitation. R. DAMS and J. HOSTE. (9 February 1961).
- Eine neue Methode zur spektrophotometrischen Bestimmung von Mikrogrammengen Titan. J. KORKISCH. (14 February 1961).
- Determination of ferrocyanides. G. V. L. N. MURTHY and T. S. VISWANATHAN. (18 February 1961).
- Die Bestimmung kleiner Fluormengen—I: Eine kritische Übersicht. ROMAN VALACH. (20 February 1961).
- EDTA as a complexing reagent in strip paper chromatographic separation of some metal ions. ERIC JOHN SINGH and ARUN K. DEY. (21 February 1961).
- The determination of traces of palladium in samples of platinum by neutron-activation analysis. R. A. KILLICK and D. F. C. MORRIS. (22 February 1961).

PUBLICATIONS RECEIVED

- Aplicaciones analíticas del AEDT y analogos:** F. BERMEJO and A. PRIETO. Imprenta del Seminario Conciliar, Santiago de Compostela, 1960. Pp. xii + 625. \$10.00.
- Spot Tests in Organic Analysis,** 6th Edition: FRITZ FEIGL. Elsevier Publishing Company, Amsterdam: D. Van Nostrand Company, Ltd., London, 1960. Pp. xx + 675. 65s.
- Oxide Ceramics: Physical Chemistry and Technology:** EUGENE RYSHKEWITCH. Academic Press, New York and London, 1960. Pp. viii + 472. \$16.00.
- Analyse qualitative rapide des cations et des anions,** 3rd Edition: G. CHARLOT. Dunod, Paris, 1961. Pp. 96. 9.50 NF.
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- Proceedings of the Symposium on the Chemistry of Co-ordination Compounds,** Agra, February 7 and 8, 1959: In three parts. National Academy of Sciences, India, Lajpatrai Road, Allahabad, India, 1960. Part I, pp. iii + 148. Rs. 15.00. Part II, pp. ii + 203. Rs. 25.00. Part III, pp. x + 302. Rs. 35.00. Three parts, Rs. 75.00.
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- The Radiochemistry of Zinc:** HARRY G. HICKS. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., June 1960. NAS-NS 3015. Pp. vi + 58. \$0.75.
- The Radiochemistry of Protactinium:** H. W. KIRBY. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., December 1959. NAS-NS 3016. Pp. vi + 80. \$1.00.
- The Radiochemistry of Iron:** J. M. NIELSEN. National Academy of Sciences, National Research Council, Washington, D.C., U.S.A., August 1960. NAS-NS 3017. Pp. v + 42. \$0.50.

NOTES FOR CONTRIBUTORS

1. General

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

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

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a high standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

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

3. Because the bulk of material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for re-typing, resulting in a serious delay in publication.

4. The essential contents of each paper should be briefly recapitulated in a summary placed at the beginning of a paper, or at the end of a preliminary or short communication. This should be in the language

of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

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

▲ △ □ ◻ ● ○ △ ○ ⊕ ⊖ ⊙ ⊗

6. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

7. The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

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

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

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

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

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

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