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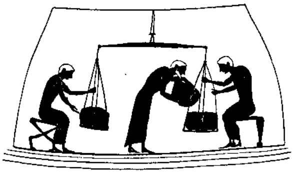

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GRAVIMETRIC DETERMINATION OF SCANDIUM USING MANDELIC ACID*

I. P. ALIMARIN and SHEN HAN-SI
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(*Received* 9 *May* 1961. *Accepted* 20 *June* 1961)

Summary—A new method for the gravimetric determination of scandium using mandelic acid and a method for separating scandium from rare earths and thorium have been developed. The composition of the precipitate corresponds to the formula $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. Thermogravimetric examination of this compound showed that it decomposes at 280°. Scandium mandelate dissolves in ammonia with the formation of $(NH_4)_3[Sc(C_8H_6O_3)_2]_3$.

THE analytical chemistry of scandium has been little studied up to the present.[1] For the determination and separation of this element from other elements inorganic precipitants have been recommended, *e.g.* hydrofluoric acid, fluosilicic acid, pyrophosphoric[2] and hypophosphorous[3] acids, *etc.* Considerably less study has been given to organic precipitants, among which we can mention oxalic acid, 8-hydroxyquinoline[4] and its halogen derivatives[5] and sodium alizarin sulphonate.[6] The most selective precipitant is phytic acid.[7] Scandium can also be precipitated by phenylarsonic acid. A number of colour reactions for scandium are known, among which azo-compounds containing an arsonium group[8] are the most interesting. Lately a method for separating scandium by extraction with organic solvents[9] has been used successfully, as well as a method using ion-exchange chromatography.[10]

On studying the analytical chemical reactions of the scandium ion one finds similar properties to those of the thorium ion and especially those of zirconium and hafnium. The ionic radii of these last two elements are very close to that of scandium. Besides this, the scandium ion, like that of zirconium, has a tendency to polymerisation.[11] This makes it possible to look for new reagents and reactions for scandium using the above similarity and also the difference in the pH of the solution with reactions using organic reagents. Thus, like thorium and zirconium, scandium can be precipitated by derivatives of selenic or telluric acids.[12]

Our investigations have shown that scandium is precipitated in a weakly acid medium by mandelic acid, which is known to be quite a selective reagent for zirconium.[13–18] In the present work the conditions for precipitation of scandium by mandelic acid and the composition of the precipitate have been studied. A method for separating it from rare earth elements and thorium is proposed.

EXPERIMENTAL

Reagents

Standard scandium solution: 0·5 g of spectrally pure scandium oxide were dissolved in 20 ml of concentrated hydrochloric acid with continuous careful heating until all cloudiness had disappeared. The solution obtained was carefully evaporated almost to dryness and the residue dissolved in 500 ml

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* Translated from the Russian, *Zhur. analit. Khim.*, 1960, **15**, 1.

of water. The titre of this solution was found by precipitation of the hydroxide with ammonia and weighing as Sc_2O_3.

Precipitation of scandium with mandelic acid

The following procedure was used:

To 35 ml of the standard solution of the scandium salt 15 ml of an 8% solution of mandelic acid were added. After heating in a water bath for 30 min and cooling to room temperature, the white flocculent precipitate which separated was washed with a 0·5% solution of mandelic acid, dried and heated at 800° to constant weight.

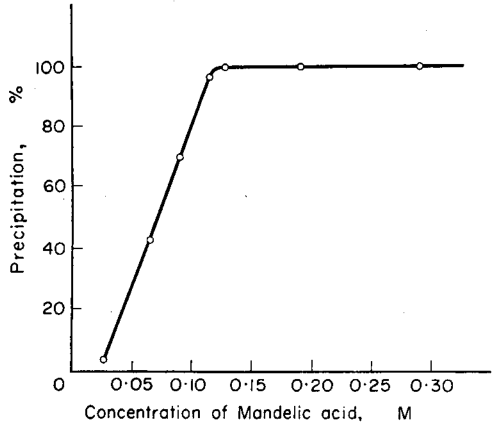


FIG. 1—Effect of concentration of mandelic acid on completeness of scandium precipitation.

To find the best conditions for the scandium precipitation the effect of reagent concentration and solution pH were studied. For this purpose, to a solution containing scandium (0·00495 mg of Sc_2O_3) various quantities of 8% mandelic acid solution were added and the precipitate treated as described above. The results of the experiments are shown in Fig. 1.

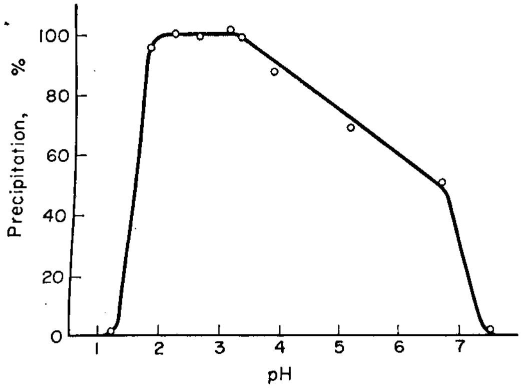


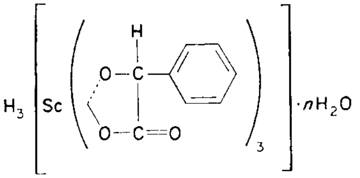
FIG. 2—Effect of pH on completeness of scandium precipitation.

To clarify the dependence of completeness of scandium separation on the pH of the solution, precipitation with mandelic acid at various pH was carried out. The pH was controlled using hydrochloric acid and ammonia. Measurement of the pH of the filtrates was carried out with a glass electrode. The results obtained are given in Fig. 2.

For complete precipitation of the scandium it is necessary to add an excess of reagent and keep the pH of the solution between 1·8–3·2. One should note that zirconium, unlike scandium, precipitates in a solution with 5–7*N* hydrochloric acid. The results from the determination of scandium in solutions of its salts are given in Table I.

Composition and properties of the precipitate

To study the composition of the compound of scandium with mandelic acid the precipitate obtained was filtered off through a glass crucible, washed with 0·5% mandelic acid solution and then, to get rid of the mandelic acid, washed again with ether, in which the precipitate does not dissolve. After this it was dried at 110° and weighed. Part of the precipitate was then heated to constant weight at 800° (about 20–50 mg) and the oxide, Sc_2O_3, weighed. The results (Table II) show that the precipitate separating from a weakly acid medium (pH 2·5) has the composition $H_3[Sc(C_8H_6O_3)]_3 \cdot nH_2O$. This compound, like zirconium mandelate[13,19,20] probably has the following structure:



In the precipitate there is always a trace of coprecipitated mandelic acid and this must be removed by ether washing before weighing. However, more reliable results are obtained by weighing the scandium oxide after calcining the precipitate.

TABLE I—PRECIPITATION OF SCANDIUM BY MANDELIC ACID

Sc_2O_3, *mg*		Error		Sc_2O_3, *mg*		Error	
Taken	Found	*mg*	%	Taken	Found	*mg*	%
9·90	9·92	+0·02	+0·2	4·95	4·90	−0·05	−1·0
9·90	9·90	±0·00	±0·0	4·95	4·98	+0·03	+0·6
4·95	4·95	±0·00	±0·0	0·99	1·02	+0·03	+2·0
4·95	4·94	−0·01	−0·2	0·99	0·98	−0·01	−1·0

TABLE II—ANALYSIS OF THE COMPOUND OF SCANDIUM WITH MANDELIC ACID

Weight of precipitate, *mg*	Found, *mg*		Molar ratio of Sc:$C_8H_7O_3$
	Sc	$C_8H_7O_3$	
24·5	2·2	22·3	1:3·0
34·1	3·0	31·1	1:3·1
55·7	4·9	50·8	1:3·1
55·1	4·9	50·2	1:3·0

The thermogravigram (Fig. 3) obtained from constant weighing shows that the compound is stable up to 280° and decomposes at higher temperatures. In the range 340–390° an intermediate compound is formed which is transformed to scandium oxide at 500°.

The scandium precipitate, like the analogous zirconium[21] and hafnium[22] compounds, dissolves easily in ammonia. The composition of this compound was studied by Hahn's method,[22] which was applied for the study of the analogous compound of hafnium.

A measured amount of the precipitate, obtained as described above, was dissolved in an excess of standard 0·092*N* solution of ammonia, after which the excess ammonia was titrated with 0·1*N* hydrochloric acid using a glass electrode. The results of the determinations are given in Table III and Fig. 4 and indicate that the reaction for the solution of the precipitate in ammonia follows the equation:

$$H_3[Sc(C_8H_6O_3)_3] + 3NH_4OH \rightleftharpoons (NH_4)_3[Sc(C_8H_6O_3)_3] + 3H_2O.$$

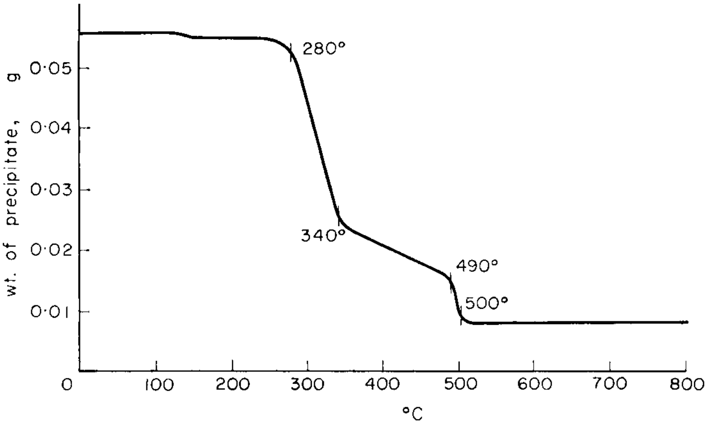


FIG. 3—Thermogravigram of precipitate of $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. Weight of precipitate in g.

TABLE III—DETERMINATION OF THE COMPOSITION OF THE PRECIPITATE AFTER DISSOLVING IN AMMONIA

Weight of precipitate, *mg*	Mean volume of NH_4OH, *ml*	Volume of HCl solution, *ml*	Excess NH_4OH, *ml*	NH_4OH to dissolve precipitate, *ml*	Ratio of $NH_4OH : H_3[Sc(C_8H_6O_3)_3]$
71·6	25·0	18·4	20·2	4·8	3·1:1
105·5	25·0	16·6	18·2	6·8	3·0:1
150·4	25·0	13·6	14·9	10·1	3·1:1
175·0	25·0	12·5	13·7	11·3	3·0:1
226·2	25·0	9·5	10·4	14·6	2·9:1

The precipitate is also soluble in organic solvents such as pyridine and ethylenediamine. The action of sodium hydroxide forms the hydroxide of scandium. From the titration curve (Fig. 4) it can clearly be seen that the precipitate is soluble in ammonia at a pH above 6.3.

Separation of scandium from the rare earth elements and thorium

The rare earth elements and thorium do not give a precipitate with mandelic acid at pH 2–3 and hence they can be separated from the scandium. For this purpose titrated solutions of the nitrates of the rare earths and thorium were used. The precipitation was carried out as described above. For quantitative separation of the rare earth elements the scandium had to be reprecipitated. For this the good solubility of the precipitate in concentrated ammonia was used. The ammonia was added in drops on to the filter. After washing the filter with distilled water the solution was neutralised with 4*N* hydrochloric acid to an acid reaction with methyl orange, and 15 ml of 8 % mandelic acid solution added. The solution was then heated on a water bath for 30 min and, after cooling, the precipitate was filtered off through the same filter.

The results of the determination of scandium in the presence of rare earth elements are given in Table IV.

The separation of scandium from thorium was carried out in the same way. One should note that large quantities of thorium interfere in the scandium determination.

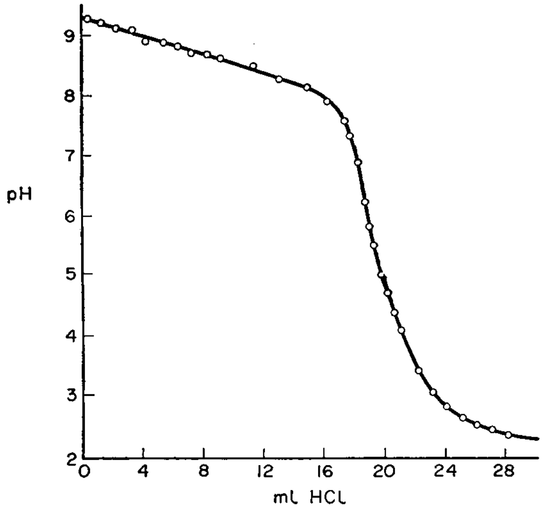


FIG. 4.—Potentiometric titration of ammoniacal solution of scandium mandelate with hydrochloric acid.

TABLE IV—DETERMINATION OF SCANDIUM IN THE PRESENCE OF RARE EARTH ELEMENTS

Ratio of Sc:R.E. elements	Sc_2O_3, *mg*		Error		No. of precipitations
	Taken	Found	*mg*	%	
1:1	2·97	3·12	+0·15	+5·0	1
	2·97	3·13	+0·16	+5·3	
	2·97	2·97	±0·00	±0·0	2
	2·97	3·01	+0·04	+1·3	
	2·97	2·95	−0·02	−0·7	
1:5	2·97	3·15	+0·18	+6·0	2
	2·97	3·10	+0·13	+4·3	
	2·97	3·04	+0·07	+2·3	3
	2·97	2·93	−0·04	−1·3	
1:10	2·97	2·96	−0·01	−0·3	3
	2·97	3·03	+0·06	+2·0	

If the pH is increased coprecipitation of thorium takes place. Complexing the thorium with organic acids such as trioxyglutaric or lactic acids was tried, but it appeared that the scandium is also masked by these acids and gives no precipitate. The results of the separation of scandium from thorium are given in Table V.

TABLE V—DETERMINATION OF SCANDIUM IN THE PRESENCE OF THORIUM
(ratio of Sc:Th = 1:1)

Sc_2O_3, *mg*		Error		Number of precipitations
Taken	Found	mg	%	
4·95	4·97	+0·02	+0·4	1
4·95	5·05	+0·10	+2·0	1
2·97	3·02	+0·05	+1·8	1
2·97	3·00	+0·03	+1·0	2

CONCLUSIONS

A new method has been developed for the determination of scandium using mandelic acid, as well as a method for the separation of scandium from the rare earth elements and thorium. The precipitate composition corresponds to the formula $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. This compound, as was shown by the thermogravigram, decomposes at 280°. Scandium mandelate dissolves in ammonia with the formation of $(NH_4)_3Sc(C_8H_6O_3)_3$.

Zusammenfassung—Neue Methoden zur gravimetrischen Bestimmung von Scandium mit Mandelsäure und zu dessen Abtrennung von den seltenen Erden werden beschrieben. Die Zusammensetzung des Niederschlages ist $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$ Thermogravimetrische Untersuchung der Verbindung zeigt Zersetzung bei 280°C. Scanidiummandelat löst sich in Ammoniak unter Bildung von $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

Résumé—Les auteurs ont mis au point une nouvelle méthode de dosage gravimétrique du scandium utilisant l'acide mandélique, et une méthode de séparation du scandium des terres rares et du thorium. La composition du précipité correspond à la formule $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. L'étude thermogravimétrique de ce composé montre qu'il se décompose à 280°. Le mandélate de scandium se dissout dans l'ammoniaque avec formation de $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

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DETERMINATION OF ZIRCONIUM USING *N*-BENZOYLPHENYLHYDROXYLAMINE*

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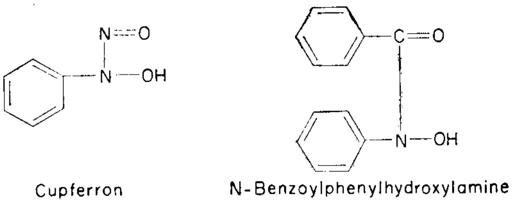
(*Received* 9 *May* 1961. *Accepted* 22 *June* 1961)

Summary—A new method has been developed for the quantitative precipitation of zirconium with *N*-benzoylphenylhydroxylamine. The influence of different mineral acids, tartaric acid and hydrogen peroxide on the completeness of the precipitation has been studied. Precipitation of zirconium in the presence of other elements has been investigated. It has been shown that zirconium can be separated from iron, aluminium, chromium, titanium, niobium and tantalum. The composition of zirconium benzoylphenylhydroxylaminate has been determined. The precipitate separated from a strong acid solution corresponds to the formula $Zr(BPHA)_4$.

Organic reagents, such as cupferron[1–6] and its analogue *N*-benzoylphenylhydroxylamine (BPHA), have recently been widely used for the determination of zirconium and its separation from other elements. BPHA was recommended as an analytical reagent for precipitation of metals by Bamberger.[7]



Shome[8–10] used BPHA for determining titanium, aluminium and copper gravimetrically and vanadium photometrically. He showed that BPHA differs from cupferron in its stability to the action of light and heat. Ryan and Lutwik[11] used BPHA for determining tin. Moshier and Schwarberg[12] and Majumdar and Mukherjee[13] used this reagent for determining titanium. Sinha[14] applied BFHA to the determination of molybdenum and Dyrssen[15] to the extraction of lanthanum, thorium and uranium.

The aim of the present work was to find more precisely the conditions needed for determining zirconium using *N*-benzoylphenylhydroxylamine, both in pure salts and in the presence of other elements, and also to attempt the separation of zirconium from tantalum and several other elements by this means.

EXPERIMENTAL

The *N*-benzoylphenylhydroxylamine was synthesised by Shome's method.[8] The product was recrystallised from ethyl alcohol (or hot water). This reagent consists of white needle-like crystals (m.p. 121°), sparingly soluble in cold water [at room temp. (25°) about 0·5 g/l.] and easily soluble in hot water, alkali solutions, ethyl alcohol, diethyl ether, chloroform and cyclohexanone. The reagent is quite stable in sulphuric or hydrochloric acid solution; only in strongly alkaline solutions can some decomposition be observed after a few days.

For these experiments a solution of zirconium oxychloride was used, the concentration of the solution being found gravimetrically.

* Translated from the Russian: *Zhur. analit. Khim.*, 1959, **14,** 5.

To determine the best conditions for the precipitation of zirconium by BPHA the relationship between the completeness of zirconium precipitation and the quantity of BPHA was studied. For this, various amounts of BPHA, dissolved in 40 ml of boiling water (mean volume 100 ml; hydrochloric acid concentration 0·15*N*), were added to 60 ml of a standard zirconium solution (0·0152 g of ZrO_2). The solution and precipitate were heated on a boiling water bath for 10–15 min with occasional stirring. In this way the zirconium benzoylphenylhydroxylaminate was separated as a white, well coagulated precipitate. On cooling, the precipitate was filtered off through a fine filter, washed with 0·1 % hydrochloric acid solution containing 0·05 % BPHA, dried and heated in a porcelain crucible at 1000–1100° to constant weight. The results obtained are shown in Fig. 1.

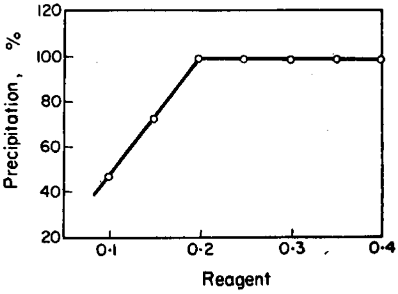


Fig. 1.—Dependence of completeness of precipitation of zirconium on the quantity of BPHA. (Weight in g)

One should note that, for practical purposes, it is as well to add an excess of reagent for complete precipitation, especially in a strongly acid medium.

To clarify the influence of acidity on the completeness of precipitation, zirconium precipitation by BPHA was carried out in various acid concentrations in the solution. The results are given in Fig. 2.

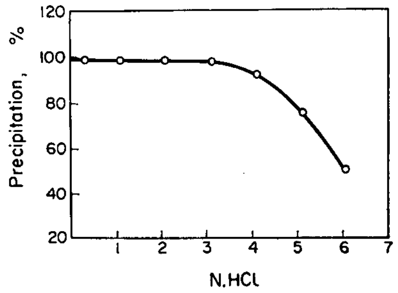


Fig. 2.—Effect of hydrochloric acid concentration on completeness of precipitation of zirconium by BPHA.

The effect of various mineral acids and tartaric acid on the zirconium precipitation was then studied. For this purpose, to a solution containing zirconium various amounts of hydrochloric, sulphuric or tartaric acids were added, the solution diluted to 150 ml, then 0·4–0·5 g of BPHA, dissolved in 100 ml of boiling water, added. The solution and precipitate were heated for 15–20 min on a boiling water bath with occasional stirring. The precipitate was immediately filtered off through a fine filter, because the BPHA-zirconium compound is practically insoluble in boiling water. The precipitate was washed with 1·0% hydrochloric acid solution containing 0·05% BPHA, dried and heated in a porcelain crucible at 1000–1100° to constant weight. The results obtained are shown in Table I.

To clarify the effect of the hydrogen peroxide, used for preventing titanium, niobium, tantalum and vanadium precipitation, on the completeness of zirconium precipitation, to 150 ml of solution containing zirconium about 1 ml of 30% hydrogen peroxide was added, then precipitation by BPHA carried out as described above. The precipitate was filtered off, calcined and weighed. The results of the experiments, given in Table I, show that hydrogen peroxide has no effect on the completeness of

TABLE I

ZrO_2, *g*		Error, *g*	Medium
Taken	Found		
0·0303	0·0303	±0·0000	2·4*N* HCl
0·0303	0·0304	+0·0001	
0·0152	0·0151	−0·0001	
0·0152	0·0153	+0·0001	
0·0062	0·0062	±0·0000	
0·0062	0·0062	±0·0000	
0·0062	0·0062	±0·0000	
0·0016	0·0016	±0·0000	
0·0016	0·0017	+0·0001	
0·0031	0·0031	±0·0000	2·4*N* HCl and 5% $C_4H_6O_6$
0·0031	0·0030	−0·0001	
0·0031	0·0031	+0·0000	2·4*N* HCl and 0·15% H_2O_2
0·0031	0·0033	+0·0002	
0·0152	0·0151	−0·0001	2·4*N* HCl (95°)
0·0152	0·0150	−0·0002	
0·0152	0·0153	+0·0001	3·6*N* H_2SO_4
0·0062	0·0064	+0·0002	
0·0152	0·0154	+0·0002	3·6*N* H_2SO_4 and 5% $C_4H_6O_6$
0·0062	0·0062	±0·0000	
0·0152	0·0152	±0·0000	3·6*N* H_2SO_4 and 0·15% H_2O_2
0·0062	0·0062	±0·0000	

zirconium precipitation. One should note that, in the presence of the hydrogen peroxide, the solution and precipitate are best heated on a weakly boiling water bath for not more than 15 min.

Zirconium precipitation in the presence of other elements was studied next. Standardised solutions of salts of iron, aluminium, chromium, titanium, niobium, tantalum and the rare earth elements were used. Precipitation and determination of zirconium were carried out as described above. The results of these experiments are given in Table II.

In the precipitates obtained only traces of iron were present; none of the other elements were found.

TABLE II*

Oxides of other metals added, *g*	ZrO_2 found, *g*	Error, *g*	Oxides of other metals added, *g*	ZrO_2 found, *g*	Error, *g*
Fe_2O_3 0·033	0·0032	+0·0001	Cr_2O_3 0·20	0·0031	±0·0000
Fe_2O_3 0·033	0·0031	±0·0000	Cr_2O_3 0·020	0·0031	±0·0000
Al_2O_3 0·150	0·0033	+0·0002	Cr_2O_3 0·010	0·0030	−0·0001
Al_2O_3 0·150	0·0030	−0·0001	Cr_2O_3 0·020	0·0029	−0·0002
TiO_2 0·018	0·0031	±0·0000	$(Nb, Ta)_2O_5$ 0·010	0·0030	−0·0001
TiO_2 0·018	0·0033	+0·0002	$(Nb, Ta)_2O_5$ 0·010	0·0030	−0·0001

* 0.0031 g of ZrO_2 taken.

The precipitate of zirconium benzoylphenylhydroxylaminate used for determining its composition was prepared as follows: To a solution containing zirconium various quantities of hydrochloric acid and 0·5–1·5 g of BPHA dissolved in 50–100 ml of boiling water (mean volume 100–150 ml) were added. The solution and precipitate were heated on a boiling water bath for 30 min and, without cooling, the precipitate was filtered off through a glass crucible and washed with hot 1% hydrochloric acid solution containing 0·05% BPHA and several times with boiling distilled water. The precipitate was then washed with 30 ml of ether (BPHA dissolves in ether while the zirconium compound does not) and dried at 105–110° to constant weight. Weighed portions of the precipitate were transferred to a porcelain crucible, heated at 1000–1100° to constant weight and weighed as ZrO_2. The results obtained are given in Table III and show that the composition of the precipitate separating from hydrochloric acid solution corresponds to the formula $Zr(BPHA)_4$.

TABLE III

Weight of ppt. of zirconium benzoylphenylhydroxylaminate, *g*	Found, *g*		Zr:BPHA	HCl Concn., *N*
	Zr	BPHA (by difference)		
0·1170	0·0119	0·1051	1:3·8	0·15
0·1168	0·0119	0·1049	1:3·8	0·15
0·1170	0·0119	0·1051	1:3·8	1·0
0·1150	0·0119	0·1031	1:3·7	1·0
0·1169	0·0119	0·1050	1:3·8	2·3
0·0554	0·0053	0·0501	1:4·0	3·1
0·0951	0·0091	0·0860	1:4·0	4·2
0·0940	0·0093	0·0847	1:4·0	5·3
0·0958	0·0094	0·0864	1:4·0	6·0

The $Zr(BPHA)_4$ compound can itself be used as a weighing form.

To find the stability of the compound to temperature a thermogravimetric analysis was carried out. From Fig. 3 it can be seen that the precipitate is stable up to 240°. To obtain ZrO_2 it is sufficient to heat the precipitate to 500°.

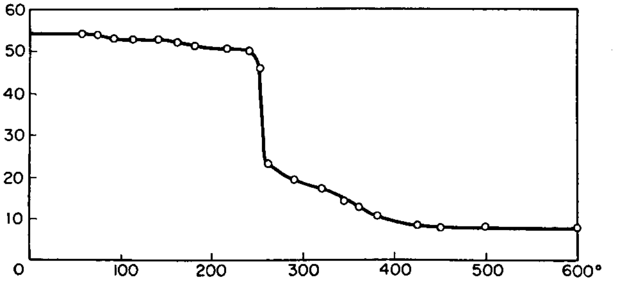


FIG. 3.—Thermoanalysis curve for zirconium benzoylphenylhydroxylaminate (Weight in mg).

CONCLUSIONS

A new method has been developed for the quantitative precipitation of zirconium with *N*-benzoylphenylhydroxylamine. The influence of different mineral acids, tartaric acid and hydrogen peroxide on the completeness of the zirconium precipitation with N-benzoylphenylhydroxylamine has been studied. Precipitation of zirconium in the presence of other elements has been investigated. It has been shown that zirconium can be separated from iron, aluminium, chromium, titanium, niobium

and tantalum. The composition of zirconium benzoylphenylhydroxylaminate has been determined; the precipitate separated from a strong acid solution corresponds to the formula $Zr(BPHA)_4$.

Zusammenfassung—Eine neue Methode zur quantitativen Fällung von Zirkonium mit N-benzoylphenylhydroxylamin wurde entwickelt. Der Einfluss verschiedener Mineralsäuren, sowie von Tartrat und Wasserstoffperoxyd auf die Vollständigkeit der Fällung wurde studiert. Die Fällung von Zirkonium in Gegenwart anderer Elemente wurde untersucht. Es wurde gezeigt, dass Zirkonium von Eisen, Aluminium, Chrom, Titan, Niob und Tantal getrennt werden kann. Die Zusammensatzung des Niederschlages wurde ernittelt: Zr: organischer Rest = 1:4, wenn aus stark saurem Medium gefällt wird.

Résumé—Les auteurs ont mis au point une nouvelle méthode de précipitation quantitative du zirconium par la N-benzylphénylhydroxylamine. L'influence de différents acides minéraux, de l'acide tartrique et de l'eau oxygénée sur la totalité de la précipitation a été étudiée. La précipitation du zirconium en présence d'autres éléments a été examinée. Les auteurs ont montré que le zirconium peut être séparé du fer, de l'aluminium, du chrome, du titane, du niobium et du tantale. La composition du benzylphénylhydroxylaminate de zirconium a été déterminée; le précipité séparé en solution fortement acide correspond à la formule $Zr(BPHA)_4$.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM AFTER OXIDATION WITH HYPOBROMITE

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Summary—In the presence of hypobromite at pH ~ 11, rhodium yields a violet colour, with a maximum at 530 mμ, suitable for the quantitative determination of 10–60 ppm of Rh in the presence of platinum. The solution turns blue on standing or on adding a reducing agent; a green colour is obtained at pH < 10 and a yellow one at low BrO^- concentration. Evidence is given for Rh^{VI} in the violet solutions and Rh^{V} in the blue solutions. The disproportioning: $3\ Rh^{V} \rightleftarrows 2\ Rh^{VI} + Rh^{III}$ proceeds in the forward direction in acidic medium.

VERY few references to the oxidation of rhodium solutions to a valency state higher than +3 are found in the literature. A mixture of oxidation states, the +6 being quite evident, was obtained by Grube *et al.*[1] by the electrolytic oxidation of sulphuric or perchloric acid solutions. Syrokomsky and Proshenkova[2] obtained violet Rh^{V} by treating a rhodium solution in sulphuric acid with sodium bismuthate. Ayres and Young[3] found that a blue colour is developed in the presence of an excess of hypochlorite in buffered solutions. This colour is suitable for the spectrophotometric determination of rhodium, and it can be attributed to the formation of Rh^{V}. A difference between buffered (blue) and acidic (purple) solutions seems to result from different forms,[4] anionic and cationic, respectively, of the same oxidation state.

The possibility of rhodium oxidation in strongly alkaline medium has not yet been fully investigated. In the present paper, which follows previous work on the chemistry of rhodium,[5–8] such a medium is taken into account; as a reagent, sodium hypobromite, whose reaction with rhodium has not previously been examined, is employed.

EXPERIMENTAL

Apparatus

The absorption curves were obtained with a Beckman DU spectrophotometer; a Metrohm E 148 c potentiometer was used for the measurement of pH.

Reagents

A standard 0·02*M* Rh solution was prepared from $Na_3RhCl_6.2H_2O$. Sodium hypobromite was prepared by dissolving 100 g of pure Br_2 in 200 ml of 6*N* NaOH, adding further NaOH to give a pH of 11·2 (potentiometrically controlled), and diluting the solution to 500 ml; the reagent was standardised iodometrically.

RESULTS

A violet colour is developed in a $rhodium^{III}$ solution with an excess of hypobromite at room temperature. The stability of this colour depends on the hypobromite concentration: the solution remains violet for several days with 1 *M* hypobromite, but turns blue within a few hours when the reagent is 0·1*M*; the variation in the absorption spectrum on standing is shown in Fig. 1. The violet species shows a maximum at 530 mμ, suitable for the spectrophotometric determination of rhodium. An extensive investigation of the factors which affect the spectrophotometric results was therefore carried out.

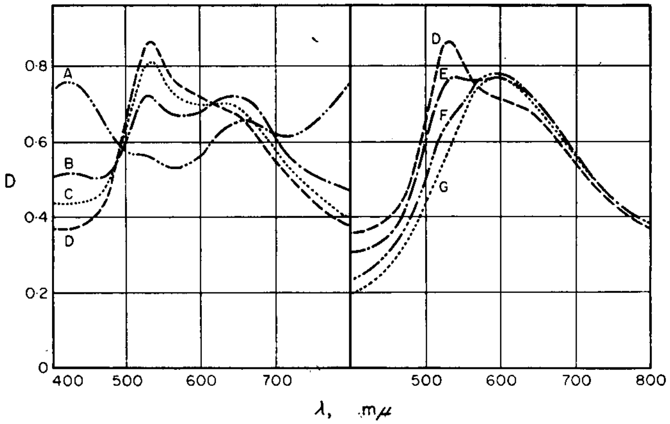

FIG. 1.—Ageing of 0·85mM Rh in 0·12M BrO$^-$.
Left side: formation of the violet colour; right side: formation of the blue colour.
Spectra are registered after (A) 5 min, (B) 15 min, (C) 25 min, (D) 40 min, (E) 1·5 hr, (F) 2·5 hr, (G) 5·5 hr.

Influence of pH

The alkalinity of the medium must be controlled with accuracy, if reproducible results are to be obtained. Although at pH > 10 a violet colour is always obtained, the strongest absorption is found at pH 11·2–11·3. The plot of optical density at 530 mμ *vs.* pH is shown in Fig. 2.

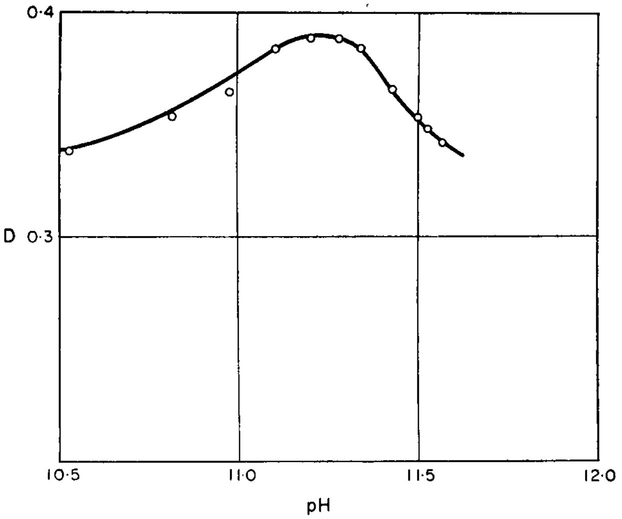

FIG. 2.—Variation of the absorbance at 530 mμ with pH.
0·3mM Rh in 0·6M BrO$^-$.

Rhodium concentration

With varying rhodium concentration, Beer's law is obeyed if measurements are carried out after stabilisation for 0·5–1 hour. The optimum analytical range is 10–60 ppm of rhodium. The molar extinction coefficient at 530 mμ is 1270 in 0·3M hypobromite.

Reagent concentration

Using varying amounts of hypobromite, variation in the absorbance measurements may be expected in accordance with the plot in Fig. 3A. However, if the concentration of hypobromite is greater than 0·2*M*, no rigorous control is necessary, the variation of the spectrum with the concentration of hypobromite being very small.

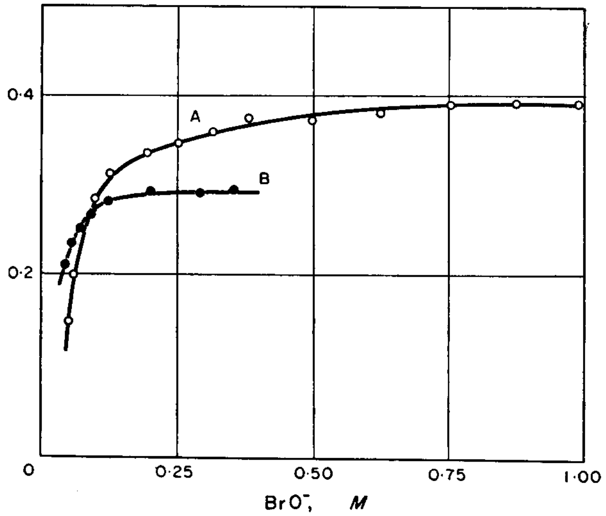

FIG. 3.—Variation in the absorbance of 0·3*mM* Rh with [BrO^-].
A: violet solutions, $\lambda = 530$ mμ.
B: blue solutions, $\lambda = 590$ mμ.

Interference of anions

According to the results in Table I, the presence of the anions which are commonly encountered affects the rhodium-hypobromite reaction very little. A solution containing a relatively high amount of sulphate or phosphate ions can be used; no interference is found in practice in the presence of chloride or nitrate, and therefore the spectrophotometric determination can be performed on solutions obtained by treatment of the sample with *aqua regia*.

TABLE I.—PERMISSIBLE SALT CONCENTRATION IN SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM

Salt	Limiting concentration, *moles/litre*	
	Violet solutions $\lambda = 530$ mμ	Blue solutions $\lambda = 590$ mμ
KCl	1	1·5
$NaNO_3$	0·8	1
K_2HPO_4	0·2	0·15
K_2SO_4	0·2	0·4
KBr	1	*

* The formation of the blue colour is progressively delayed with increase in bromide concentration.

Presence of noble metals

The main interference in the determination of rhodium might be expected to be caused by the presence of platinum metals. A marked alteration is in fact found in the spectrum when iridium or ruthenium are present, while a lesser interference is produced by palladium, osmium or platinum. In Table II the amount of interfering ion which produces a variation of less than 0·01 in optical density is indicated.

TABLE II.—PERMISSIBLE AMOUNTS OF PLATINUM METALS IN SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM

Element	Limiting concentration, *ppm*	
	Violet solutions $\lambda = 530$ mμ	Blue solutions $\lambda = 590$ mμ
Iridium	2	1
Osmium	50	80
Palladium	13	7
Platinum	260	400
Ruthenium	1	2

Because of the slight interference from platinum, it is possible to determine rhodium in the presence of appreciable amounts of platinum, of the order found in the platinum-rhodium alloys used for thermocouples. The absorption of Pt^{IV} at 530 mμ is not, however, negligible for a Pt : Rh ratio greater than 10 : 1. In such a case it is convenient to perform all measurements, including the calibration curve, at 540 mμ; at this wavelength the absorption of rhodium is only a little lower than at 530 mμ, while that of platinum is practically negligible. In this way it was found possible to determine rhodium with a Pt : Rh ratio higher than 20 : 1, as shown by the results in Table III.

TABLE III.—DETERMINATION OF RHODIUM IN THE PRESENCE OF PLATINUM.
(Measurements on 10 ml, 0·3*M* in BrO^-, violet colour, after 1 hr.)

Taken, *mg*		D 540 mμ	Rh found, *mg*
Rh	Pt		
0·165	1·05	0·182	0·167
0·165	2·38	0·186	0·171
0·165	3·43	0·184	0·169
0·288	1·32	0·310	0·287
0·288	2·64	0·314	0·290
0·288	4·22	0·306	0·284
0·329	3·70	0·363	0·335
0·329	4·75	0·357	0·329
0·329	5·28	0·365	0·337

Analytical procedure

The spectrophotometric determination can be performed in the following way. From the sample solution, which generally is an acidic one, take a volume corresponding to 0·1–1 mg of Rh. Add NaOH solution dropwise to neutralisation point. Add 10 ml of hypobromite reagent, and dilute to 25 ml in a volumetric flask. After a 1-hour interval to stabilise the violet colour, measure the absorbance at 530 mμ and compare with a calibration curve obtained under the same conditions.

Blue solutions

As indicated in Fig. 1, the violet solutions on standing turn blue at any pH higher than 10. This change occurs more slowly with higher hypobromite concentration and lower rhodium concentration. The stability of the violet solutions is also affected by bromide concentration: with 3*M* bromide the violet colour can still be observed after four days. An absorption maximum is found at 590 mμ in the blue solutions, quite different from the one at 665 mμ observed in the blue solutions reported by Ayres and Young;[3] taking into account the difference in pH, it is reasonable to attribute the two such colours, similar in appearance although they may be, to two different ionic forms.

With low rhodium concentrations, the absorbance at 590 mμ follows Beer's law, the molecular extinction coefficient being 920; for higher values a blue-black precipitate is obtained on ageing. This phenomenon prevents the use of the blue colour for analytical purposes. The influence of the variation in hypobromite concentration is shown in Fig. 3B; in Tables I and II the effect of the presence of both foreign anions and foreign cations is shown. The values are practically the same as for the violet solutions.

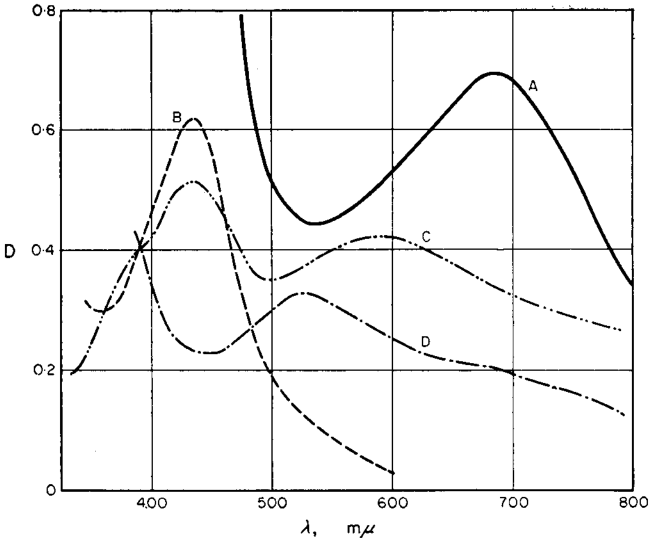

FIG. 4.—A: 0·4*mM* Rh in 0·2*M* BrO^- + CH_3COOH up to pH 8·3 (green).
B: 1*mM* Rh + 6*mM* BrO^- (yellow).
C: 0.7*mM* Rh + 12*mM* BrO^- (green).
D: 0·65*mM* Rh in 0·12*M* BrO^- (violet colour, by adding CH_3COOH up to pH 5·3 to a blue solution).

Green solutions

When the reaction with hypobromite takes place at $pH < 10$, a green colour is obtained instead of a violet one. A maximum occurs at 690 mμ in the spectrum (Fig. 4A); it does not seem that this colour can be a sum of blue and yellow. Because of the very low stability of the colour, it is of no value for colorimetric determination.

Yellow solutions

With a concentration of hypobromite in the same range as that of rhodium, a yellow colour appears at the same pH as for the violet solutions, with an absorption maximum at 435 mμ (Fig. 4B). With a slight increase in the reagent concentration a green solution is obtained; this colour, however, is quite different from that produced at $pH < 10$; two maxima are now evident (Fig. 4C), and this colour can be attributed to a sum of the yellow and blue products. It is not easy to determine the reagent ratio in the rhodium-hypobromite reaction; an attempt was made to do this in the yellow solutions by employing Job's method: from Fig. 5 a ratio between 1 : 3 and 1 : 4 is indicated. Such a value leads to the conclusion that an excess of the reagent is necessary to obtain the yellow colour.

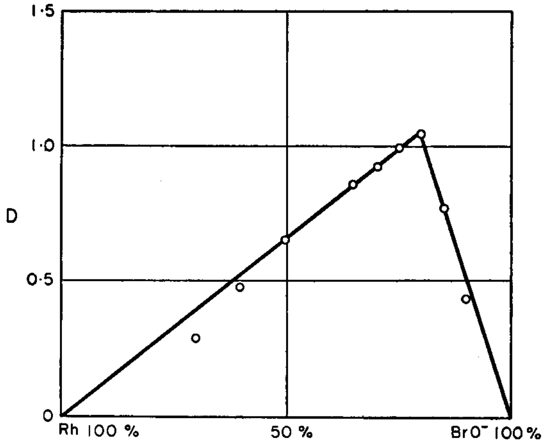

FIG. 5.—Absorbance at 435 mμ versus the rhodium:hypobromite ratio ($Rh + BrO^- = 2mM$).

CONCLUSIONS

Nature of the species in solution

On adding H^+ to the blue solutions to produce a pH of 5–6, a violet colour is again observed (spectrum in Fig. 4D), practically identical to the colour from which the blue solutions were originally derived. For absorbance, however, particularly at the maximum at 530 mμ, values exactly two-thirds of those observed on the first violet colour, with the same amount of rhodium, were obtained. At this pH value it was feasible to absorb the violet solutions by a cation-exchange resin. After washing the resin, it is possible to elute with 2*N* HCl, and the eluted solution shows the same violet colour. On adding OH^- to give a pH of 10–11, the blue colour is restored: the colour change is completely reversible with variation in pH. Iodometric titrations were carried out on the eluted violet solutions: the redox equivalents found for 4·1, 8·2, 10·3, 12·4 and 14·5 mg of Rh, were respectively 2·24, 2·12, 2·07, 2·15 and 2·04.

It would appear possible that the rhodium may be present in the +5 oxidation state, but other phenomena have to be taken into account.

The blue colour, with its absorption maximum at 590 mμ, can be obtained from the violet alkaline solutions not only by ageing, but also by adding a reducing agent. Moderate amounts of hypophosphite, sulphite, thiosulphate, formate or thiourea were used successfully: the blue colour was obtained in each case, with a sufficiently reproducible absorbance. In addition, the violet colour in alkaline medium can be restored, with a quantitatively identical absorbance, by adding a moderate excess of hypobromite to the blue solutions: on the whole, some oxidation-reduction phenomena must clearly be involved in the colour change.

On the basis of the above mentioned iodometric titrations, the +5 oxidation state can be ascribed to rhodium in the blue solutions*; consequently the violet colour in alkaline medium should correspond to a valency state +6. The appearance of the violet colour on acidification of the blue solutions could be explained by assuming that rhodium^{V} is not stable in acid medium and undergoes a disproportioning according to the schematic reaction:

$$3\,\mathrm{Rh}^{V} \underset{\mathrm{OH}^-}{\overset{\mathrm{H}^+}{\rightleftarrows}} 2\,\mathrm{Rh}^{VI} + \mathrm{Rh}^{III}.$$

This would agree with the experimental observation that the spectrum of the violet solution obtained on acidification of the blue solution shows only two-thirds of the absorbance appropriate to the actual total rhodium concentration.

Zusammenfassung—In Gegenwart von Hypobromit bei pH 11 gibt Rodium eine violette Färbung, (Maximum bei 530 mμ), die geeinget ist, dieses Element im Bereich von 10 bis 60 ppm zu bestimmen Die Bestimmung kann auch in Gegenwart von Platin erfolgen. Die Lösung wird blau, wenn stehen gelassen oder auf Zusatz eines Reduktionsmittels. Ein grüne Farbe wird erhalten bei pH unterhalb 10 und eine gelbe Farbe bei geringer Hypobromitkonzentration. Evidenz besteht dass Rh(VI) in der violetten und Rh(V) in der blauen Lösung anwesend sind. Die Disproportionierung 3 Rh(V) $\rightleftarrows$ 2 Rh(VI) + Rh(III) findet in saurem Medium statt.

Résumé—En présence d'hypobromite à pH 11, le rhodium donne une coloration violette, avec un maximum d'absorption à 530 mμ; cette coloration convient pour un dosage de 10–60 ppm de Rh, même en présence de platine. La solution vire au bleu per abandon ou par addition d'un agent réducteur, une couleur verte est obtenue à pH < 10 et une couleur jaune pour de faibles concentrations de BrO^-. L'auteur montre que Rh(VI) est présent dans les solutions violettes et Rh(V) dans les solutions bleues. La dismutation: 3 Rh(V) $\rightleftarrows$ 2 Rh(VI) + Rh(III) a lieu en milieu acide.

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* In fact the *average* oxidation state should remain unchanged with the variation of pH.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—IX*

THE DETERMINATION AND MASKING OF ALUMINIUM

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Summary—It has been found that aluminium forms complexes with 1,2-diaminocyclohexane tetraacetic acid(CDTA)almost instantaneously, even at room temperature and in the presence of large excess of neutral salts. Contrary to general opinion, it is also possible to mask aluminium with ammonium fluoride at room temperature. If further determinations are being made with EDTA, a concentration of fluoride equivalent to the molar ratio 1:5 to 1:6 is sufficient for screening of aluminium. If the determinations are with CDTA it is necessary to add 30–50% excess of fluoride, corresponding to the molar ratio Al:F = 1:6. These findings has been utilised to develop a very simple and accurate method for the determination of aluminium and iron in their mixtures. Both determinations are based on the back-titration of an excess of EDTA with lead nitrate using Xylenol Orange as indicator. The further possibility of the determination of tervalent chromium, titanium and manganese in the presence of aluminium and iron has been discussed.

MANY papers have reported that the complexing of aluminium with EDTA is very slow, when carried out at ordinary temperature and in weakly acid medium. This is explained as resulting from the existence of strongly hydrated Al^{III} ions which, however, react quantitatively with EDTA at 100°. In the pH range 1–8 the predominant product of the reaction is the aquo-complex $[Al(H_2O)_2Y]^-$.

For this reason the complexometric determination of aluminium is mostly carried out indirectly; the solution of the aluminium salt is boiled with an excess of EDTA, and after cooling, the excess of EDTA is titrated with a metal salt using a suitable indicator. Direct titrations of aluminium so far described, using Chromazurol S[1] or PAN and the Cu-EDTA-complex[2] as indicators, are carried out almost at the boiling point. Various methods for determination of aluminium are described in a recent survey[3] and will not, therefore, be dealt with here.

Contrary to statements in the literature, however, we have found the reaction of aluminium with excess of EDTA to be virtually instantaneous even at ordinary temperatures, provided that no other neutral salts are present.[4] With increased ionic strength, however, the formation of the Al-EDTA complex is strongly retarded (see Table I). This finding is, of course, only of theoretical interest when determining aluminium in, for example, ores, which must first be decomposed by fusing with sodium hydroxide, potassium-sodium carbonates, sodium peroxide or similar materials. However, it is of much more interest that 1,2-diaminocyclohexanetetraacetic acid (CDTA) reacts with aluminium quantitatively, even in the presence of high concentrations of sodium or potassium salts (see Table I). It is therefore possible to determine aluminium very simply, by adding CDTA to a weakly acid

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* Part VIII: *Talanta*, 1961, **8**, 880.

solution of aluminium salt, adjusting the pH to 5–6 with hexamethylenetetramine, and back-titrating with lead nitrate using Xylenol Orange as indicator. The same conditions can be used for the determination of iron.

TABLE I.—DETERMINATION OF ALUMINIUM WITH FDTA AND CDTA
(Volume 150 ml.)

			Al found, *mg*	
Neutral salt, *g*		Al taken, *mg*	With EDTA	With DCTA
$NaNO_3$	0	6·55	6·57	6·55
	1		6·15	6·55
	3		6·04	6·57
	5		5·79	6·55
	10		5·07	6·53
	10[a]		6·02	6·52
	0	13·42	13·41 13·42	13·42 13·42
	1		13·37 13·38	13·42 13·39
	3		13·30 13·23	13·41 13·42
	5		13·17 12·93	13·36 13·49
	10		12·30 12·67	13·36 13·41
	10[b]		13·49 13·52	13·49 13·47
NaCl	1	6·55	6·53	6·54
	3		6·49	6·60
	5		6·49	6·55
	10		6·26	6·55
	10[a]		5·99	6·58

[a] Titrated after 1 hr [b] Titrated after boiling

Because of the simplicity of the procedure, it is of interest to investigate the conditions under which it would be possible to determine iron and aluminium in their mixtures. We therefore decided to re-examine the conditions necessary for the screening of aluminium with ammonium fluoride. For the masking of aluminium it is generally recommended that the solutions should be boiled with an excess of ammonium fluoride. This treatment gives rise to sparingly soluble cryolite. We have, however, found that aluminium can be reliably masked against EDTA, even in the cold, if the molar concentration ratio Al:F is as low as 1:5–1:6. When masking aluminium against CDTA, only a 30–50% excess is necessary, corresponding to the ratio Al:F = 1:6. The results of experiments with EDTA and CDTA given in Table II were obtained with "pure solutions" of aluminium salt, that is in the absence of excessive sodium or potassium salts.

Determination of Iron and Aluminium

Procedure

To the acid sample containing aluminium and iron add 0·05*M* CDTA in excess. Bring pH to 5–5·5 with hexamethylenetetramine, add several drops of 0·5% Xylenol Orange, and titrate with 0·05*M* lead nitrate. The consumption of CDTA gives the sum of Fe and Al.

To an aliquot of the solution add 1*M* ammonium fluoride (0·5–0·8 ml for 1 mg of Al). After 5 min add a measured volume of CDTA, adjust the pH again to 5–5·5 and titrate with 0·05*M* lead nitrate. The consumption of CDTA gives the content of Fe. Some results are given in Table III.

TABLE II.—MASKING OF ALUMINIUM WITH NH_4F AND DETERMINATION OF IRON

Taken, *mg*			Taken, *g*		Fe found, *mg*	Fe difference, *mg*
Al	Fe	F^-	$NaNO_3$	NaCl		
1·31	28·13	19	—	—	28·20	0·07
26·18	14·06	190	—	—	13·97	0·09
13·09	28·13	190	—	—	28·15	0·02
6·54	56·25	380	—	—	56·20	0·05
1·31	28·13	19	1	5	28·20	0·07
39·05	56·41	190	—	—	56·46	0·05
39·05	2·82	190	—	—	2·90	0·08
13·09	28·13	190	5	5	28·01	0·12[a]
6·54	56·25	380	5	1	56·31	0·06[a]
26·18	2·81	760	10	—	2·82	0·01[a]
39·05	56·41	190	2	5	56·60	0·19[a]
26·18	2·81	95	—	—	2·88	0·07[b]
26·18	2·81	9·5	10	—	6·01	3·20[c]

[a] Because of the high content of salts in the titrated solution (150–200 ml) it is advisable to speed up the screening of aluminium with fluoride by heating up to 50°. It is necessary only for the screening of aluminium, The salts do not interfere in the Al determination using CDTA.

[b] Ratio Al:F = 1:5.

[c] Insufficient fluoride was used.

TABLE III.—DETERMINATION OF ALUMINIUM AND IRON

Taken, *mg*		Found, *mg*		Difference, *mg*	
Al	Fe	Al	Fe	Al	Fe
7·07	18·10	7·12	18·27	0·05	0·17
1·41	18·10	1·43	18·15	0·02	0·05
28·25	9·05	28·40	9·18	0·15	0·13
14·12	1·81	14·15	1·92	0·03	0·11
14·12	18·10	14·13	18·08	0·01	0·02
7·07	54·26	6·99	54·29	0·08	0·03

Remarks: The colour changes in these titrations from yellow to red-violet or red (depending on the content of Fe), are very sharp. By means of this procedure even high concentrations of iron can be determined if the solution is sufficiently diluted. The limit of the amount of aluminium is 40 mg in 150–200 ml. Above this concentration the masking of aluminium by fluoride is not reliable, the colour changes are less sharp because of the blocking of indicator, and the results for iron are higher.

CONCLUSIONS

The determination of iron and aluminium with CDTA instead of with EDTA has the following advantages:

(*a*) The determination of the sum of aluminium and iron by indirect titration is carried out at normal temperature, this being so even in the presence of high concentration of sodium or potassium salts.

(*b*) The masking of aluminium by means of ammonium fluoride and the subsequent determination of iron is also carried out in the cold.

(*c*) Since the procedure is carried out at normal temperature, the two determinations are not affected by the presence of chromium^{III}.

(*d*) The determination of iron and aluminium is essentially simpler than the Sajó method,[4] which requires both a potentiometric apparatus and another indicating oxidation-reduction system.

Further experiments suggest that a simple procedure will be applicable in determination of titanium, chromium^{III} and manganese in one and the same solution. This will be described in the near future.

Zusammenfassung—Es wurde gefunden dass die Komplexbildung zwischen Aluminium und Diaminocyclohexantetraessigsäure (CDTE) auch bei Raumtemperatur und in Gegenwart grosser Mengen von Neutralsalzen praktisch momentan verläuft. Trotz allgemeiner Anschauung kann Aluminium mit Ammoniumfluorid auch bei Raumtemperatur maskiert werden. Bei einer Aluminiumbestimmung mit ÄDTE ist das Molverhältniss Al:F = 1:5 oder 1:6 zur Maskierung von Aluminium ausreichend. Bei der Bestimmung mit CDTE ist mindestens ein 30% iger Überschuss über das Verhaltnis 1:6 nötig. Diese Befunde wurden zur Ausarbeitung einer einfachen Methode für die Bestimmung von Eisen und Aluminium in Gemischen herangezogen. Beide Bestimmungen beruhen auf der Rücktitration von CDTE mit Bleinitrat unter Verwendung von Xylenolorange als Indicator. Die Möglichkeiten der Bestimmung von dreiwertigem Chrom, Titan und Mangan in Gegenwart von Eisen und Aluminium werden diskutiert.

Résumé—Les auteurs ont montré que l'aluminium forme pratiquement instantanément des complexes avec l'acide 1,2-diaminocyclohexane-tétracétique (CDTA) même à la température ordinaire et en présence d'un grand excès de sels neutres. Contrairement à l'opinion générale, il est possible de complexer l'aluminium par du fluorure d'ammonium à la température ordinaire. D'après un dosage ultérieur par l'EDTA, une concentration de fluorure égale au rapport molaire 1/5 à 1/6 est suffisante pour complexer l'aluminium. Pour le dosage par le CDTA, il est nécessaire d'ajouter 30–50% d'excès de fluorure qui correspond au rapport molaire Al/F = 1/6. Ces conclusions ont été utilisées pour mettre au point une méthode très simple et précise de dosage de l'aluminium et du fer dans leurs mélanges. Les deux dosages sont basés sur le titrage en retour de l'excès de CDTA par du nitrate de plomb, en utilisant le xylénol orange comme indicateur. Des possibilités nouvelles de dosages du chrome trivalent, du titane et du manganèse en présence d'aluminium et de fer ont été discutées.

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A pH-METRIC STUDY OF SOME BIVALENT METAL-5-SULPHOSALICYLIC ACID COMPLEXES

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Summary—The stabilities of 5-sulphosalicylate complexes of manganese, cobalt, nickel and copper have been studied at 25°, at constant ionic strength ($I = 0{\cdot}1$) using a cell without liquid junction. The values of log K obtained by the Bjerrum method are Mn: $pK_1 = 5{\cdot}25, pK_2 = 3{\cdot}4$; Co: $pK_1 = 6{\cdot}47$, $pK_2 = 4{\cdot}3$; Ni: $pK_1 = 6{\cdot}61, pK_2 = 4{\cdot}2$; and Cu: $pK_1 = 9{\cdot}35, pK_2 = 6{\cdot}92$.

SULPHOSALICYLIC acid is known to form stable soluble complexes with many metals. Turner and Anderson[1] reported the stability of the copper complex obtained by a spectrophotometric study. Perrin[2] obtained values for the relative stabilities of a number of metal complexes of substituted salicylic acids which are of physiological importance. Recently Banks and Singh[3] investigated the systems of 5-sulphosalicylic acid with copper, beryllium, cobalt and nickel. A titration technique was used by the last two groups of workers employing a glass electrode-calomel electrode system and no attempt was made to keep the ionic strength constant. It was thought desirable to study some of these complexes in a cell without liquid junction at a low constant ionic strength.

EXPERIMENTAL

Reagents

5-Sulphosalicylic acid (Hopkin and Williams) of m.p. 117°–119° was used. The solutions were standardised by pH titration with standard carbonate-free sodium hydroxide.

The metals were added in the form of their chlorides. Stock solutions of the AnalaR salts prepared in conductivity water were analysed for chloride gravimetrically as silver chloride. Duplicates agreed to $\pm 0{\cdot}02\%$. AnalaR potassium chloride was used to keep the ionic strength of all solutions constant at $0{\cdot}1M$.

Carbonate-free sodium hydroxide was prepared by dilution of saturated sodium hydroxide solutions (from pellets) in conductivity water freed from dissolved air by passing nitrogen and was preserved free from carbon dioxide with soda-lime guard tubes.

Grade A glassware was used in all the experiments.

Electrodes

The electrode system consisted of a wide-range glass electrode (Cambridge Instrument Co., "Yellow top") fitted with a B14 cone and a silver-silver chloride electrode. The latter was of the thermal-electrolytic type prepared by decomposing a paste of spectroscopically pure silver oxide (Johnson Mathey and Co.,) at 450° on a platinum helix fused into a glass tube fitted with a B14 cone. The platinum-glass seal was made by casting a little "Araldite" resin at the bottom of the electrode tubes. The silver was then chloridised in the absence of light by electrolysis in $1N$ hydrochloric acid solution prepared from constant-boiling acid, at a current density of 2 mA/cm^2 for approximately 2 hr. About 15 to 20% of chloridisation of the silver was thus ensured.[4] The electrode was then warmed in water at 50° for 2 hr.[5] and preserved in amber-coloured bottles in water containing a pinch of potassium chloride.

The electrode system was standardised in a buffer solution of $0{\cdot}1M$ ionic strength (and $0{\cdot}1M$ chloride concentration). A mixture of $0{\cdot}01M$ hydrochloric acid (prepared from constant-boiling acid) and $0{\cdot}09M$ potassium chloride has a pH of 2·10 at 25°.[6]

Cell (*Fig.* 1)

A B55 socket tube closed at one end has a bent jet inlet tube for bubbling pre-saturated oxygen-free nitrogen through the cell solution enabling the contents of the cell to be stirred well during the titration. The capacity of the cell is about 70 ml and an alternate inlet for nitrogen is provided for the cell above this level. A pre-saturator containing the cell solution and made integral to the cell is used for admitting nitrogen previously saturated with water vapour by passing through a gas-washing bottle. The nitrogen stream can be used to flush out the air in the cell and thus provide a carbon dioxide-free atmosphere. A B55 cone carrying three B14 sockets and a capillary exit tube forms the top of the cell. The glass electrode and the silver-silver chloride electrode are mounted on two of the B14 sockets. The alkali for titrations is in a semi-automatic grade A burette (capable of reading to 0·01 ml) fitted to a reservoir of standard sodium hydroxide. A B14 cone adaptor with a fine-drawn capillary tube enables the end of the burette to be fitted into the third B14 socket in the lid of the cell.

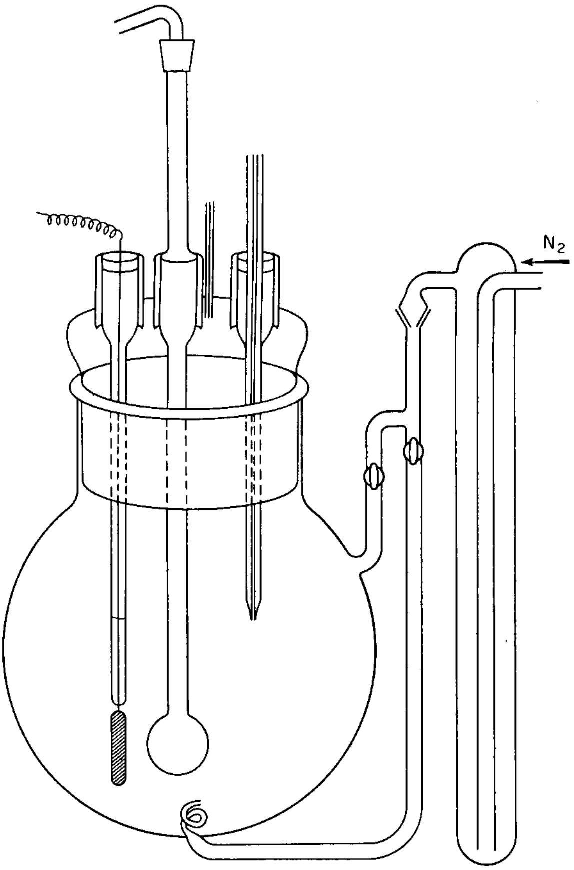


FIG. 1.—The cell

Solutions

Solutions were made up by volume in graduated flasks such that they were 0·1M in potassium chloride and 0·01M in sulphosalicylic acid and sodium hydroxide. These were the reference solutions, and the experimental solutions contained 0·002M bivalent metal chloride in addition to the above. Another set of experiments was carried out in 0·1M potassium chloride using 0·009M sulphosalicylic acid and sodium hydroxide, and 0·0015M metal chloride.

Procedure

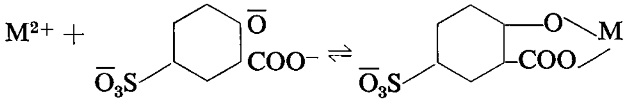
The cell used was:

Ag.AgCl|HCl|glass|Exptl. soln.(0·1M KCl, 0·01M H_3SSA, 0·01M NaOH. 0·002M MCl_2)|AgCl,Ag.

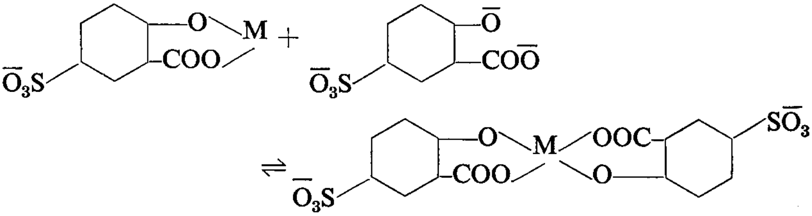
The electrode system was standardised with the HCl–KCl buffer solution (pH = 2·10 at 25°) in a thermostat. For the blank experiment 50 ml of the reference solution were taken in the cell, previously cleaned and dried, which was then introduced in a thermostat kept at 25 ± 0·05°. The calibrated electrodes were fitted on to the cell through the B14 sockets, and the alkali inlet was also introduced in a similar way so that the capillary nozzle was above the level of the liquid in the cell. Nitrogen ("white spot") saturated with water vapour was passed through the pre-saturator containing the solution at the same temperature as the cell, and allowed to bubble through the cell solution for about 15 min. The surface of the solution was flushed with nitrogen through the alternate inlet. The pH was measured. Small volumes of the standard alkali were added, the solution was stirred with nitrogen after each addition and the pH was measured after attainment of equilibrium. After the blank titration, the cell was washed and dried and the experiment was repeated using 50 ml of the experimental solution containing the bivalent metal. The standardisation of the electrode system was checked after every titration.

RESULTS AND DISCUSSION

The pH titration curves showed that separation between the reference and experimental curves occurred above pH 7·0, 6·2, 6·0 and 4·5 for manganese, cobalt, nickel and copper, respectively. Above pH 10, precipitation of the metal sulphosalicylate started in the cell. The pk_2 (carboxyl group) of 5-sulphosalicylic acid obtained from the pH at half-neutralisation being 2·86 at 0·1*M* ionic strength, the chelating agent may be regarded as completely dissociated to the $HSSA^{2-}$ form in the pH range 5 to 10. The additional amount of alkali required in presence of added metal salt to give the same pH as the reference solution, is used up in neutralising the hydrogen ion produced by the dissociation of the phenolic group as a result of chelation.



(1)



(2)

The overall reaction is therefore,

$$M^{2+} + 2\,SSA^{3-} = M(SSA)_2^{2-}$$

and the overall stability constant, β_2, is obtained as

$$\beta_2 = [M(SSA)_2^{2-}]/[M^{2+}]\,[SSA^{3-}]^2 = K_1 \,.\, K_2,$$

where K_1 and K_2 are the equilibrium constants for the first and second stages. For evaluation of equilibrium constants of stepwise complex formation of this type, Bjerrum's method[7] could be employed very successfully. In this, a formation function $\bar{n}$ is defined as the average number of donor groups bound per metal ion present in any form. The function $\bar{n}$ was calculated from the additional amount of alkali required in presence of added metal to produce the same pH as in the blank titration (which is equivalent to the chelate formed) and the total concentration of metal ions at every stage of the titration. At any pH, the theoretical value of $[SSA^{3-}]$ was calculated from the value of k_3[9], the third dissociation constant of H_3SSA. Bjerrum has shown that, as a first approximation, when $\bar{n} = 0\cdot5$, $1/[SSA^{3-}]$ equals K_1 and at $\bar{n} = 1\cdot5$, $1/[SSA^{3-}]$ equals K_2; in the simple case of two steps only, at $\bar{n} = 1\cdot0$, $1/[SSA^{3-}]^2 = \beta_2$. These relationships are strictly valid only when the spreading factor, x, between the successive formation constants, is more than 100, in which case the plot of $\bar{n}$ *vs.* $-\log_{10}[SSA^{3-}]$ shows the two steps completely separated. In the present work the formation curves were mostly of this form showing two distinct steps (*cf.* Fig. 2). The values for K_1, K_2, and β_2 obtained by this method are given in Table I.

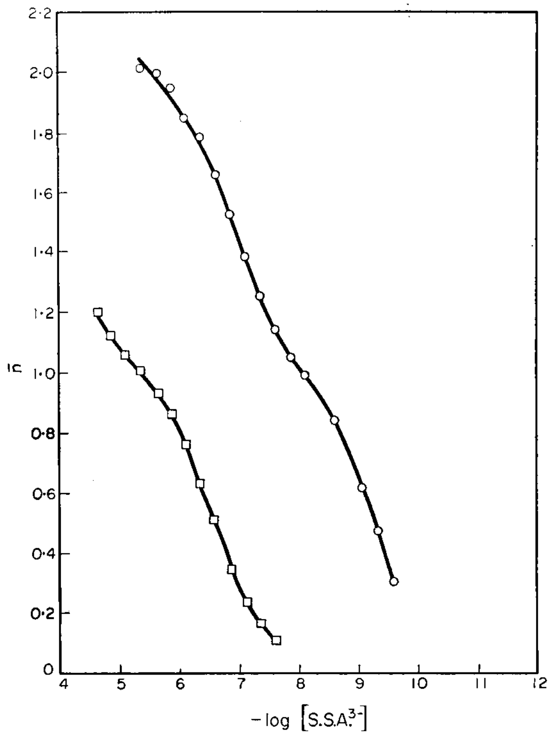


FIG. 2.—The formation curves for copper and nickel complexes, ○-Copper: □-Nickel.

TABLE I.—FORMATION CONSTANTS OF 5-SULPHOSALICYLATES OF TRANSITION METALS
(Ionic strength = 0·1)

Ion	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} \beta_2$	2nd overall ionisation potential[8] E_2, *kcal*	Ionic radius,[8] *Å*
Mn^{2+}	5·25	∼3·4	8·70	534·7	0·78
Co^{2+}	6·47	∼4·3	10·76	586·0	0·74
Ni^{2+}	6·61	∼4·2	10·80	599·0	0·73
Cu^{2+}	9·35	6·92	16·10	648·6	0·72

The K_2 values could not be determined directly except in the case of copper and may be slightly in error. No precipitation occurred in any of the experiments up to a pH of 10, but in the case of nickel the titration curve crossed that of cobalt at a pH of 8·5 and thereafter was between the manganese and cobalt titration curves. The K_2 values of cobalt and nickel are obtained very close to each other because of this. This is in apparent disagreement with the findings of Banks and Singh, who give the titration curves obtained with mixtures of $2{\cdot}5 \times 10^{-2}M$ H_3SSA and $2{\cdot}5 \times 10^{-3}M$ M^{2+}.

The $\log_{10}K_1$ and $\log_{10}\beta_2$ values increase in the order Mn, Co, Ni, Cu, in exactly the same way as have been found by Irving and Williams[8] for a number of neutral ligands, and for anions of weak acids complexing with the bivalent ions of the first transition series. Table I shows that this is the same order as is shown by the reciprocal of the cationic radius and by the second overall ionisation potential of the metals. These two parameters would be expected to determine the magnitudes of the electrostatic and covalent interactions, respectively. In those cases where the ligands interact with protons more strongly than does water, *i.e.* conjugate bases of weak acids, it may be assumed that the free energy of complex formation is dominated by the heat term in the relationship

$$\Delta G = \Delta H - T\Delta S$$

and that the entropy change would be of the same order for all the metal complexes in this series. It would, however, be desirable to determine the heat of complex formation, preferably by calorimetric methods, in order to obtain contribution to free energy from the entropy term, because of the partial charge neutralisation involved in complex formation between oppositely charged species.

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Zusammenfassung—Die Stabilitätskonstanten der 5-Sulfosalizylsäurekomplexe von Mangan, Cobalt, Nickel und Kupfer wurden bestimmt bei 25°C und konstanter Ionenstärke von 0.1. Eine Zelle ohne Salzbrücke wurde verwendet. Die folgenden log K-Werte wurden nach der Bjerrummethode erhalten: Mn: $pK_1 = 5{\cdot}25$; $pK_2 = 3{\cdot}4$. Co: $pK_1 = 6{\cdot}47$; $pK_2 = 4{\cdot}3$. Ni: $pK_1 = 6{\cdot}61$; $pK_2 = 4{\cdot}2$. Cu: $pK_1 = 9{\cdot}35$; $pK_2 = 6{\cdot}92$.

Résumé—Les stabilités des complexes 5-sulfosalicylique du manganèse, du cobalt, du nickel et du cuivre ont été étudiées à 25°C, à force ionique constante (I = 0,1), en utilisant une cellule sans jonction liquide. Les valeurs de log K obtenues par la méthode de Bjerrum sont; Mn: $pK_1 = 5{,}25$, $pK_2 = 3{,}4$; Co: $pK_1 = 6{,}47$, $pK_2 = 4{,}3$; Ni: $pK_1 = 6{,}61$, $pK_2 = 4{,}2$; Cu: $pK_1 = 9{,}35$, $pK_2 = 6{,}92$.

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RADIOCHEMICAL SEPARATION OF INDIUM BY AMALGAM-EXCHANGE

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Summary—The radiochemical separation of indium by an amalgam-exchange technique has been critically evaluated for the aqueous hydrogen bromide system. The efficiency and contamination of the separation has been studied using tracers of 19 different representative elements. Yields of contaminating elements are reduced in most cases to less than 0·1 %, and indium yields are usually above 95 %. The procedure requires no special equipment, and takes about 11 min overall. A number of factors affecting the separation have been studied and improved.

THE principle of isotopic exchange between a metal ion and an amalgam of the metal has been applied to cadmium[1,3] and zinc[5] with considerable success. Preliminary work[1] also indicated that indium could be readily adapted to this type of separation. Sunderman and others[6,8] have given extensive yield and concentration data on a number of radiochemical separations of indium which can form a solid basis for a general evaluation of this amalgam-exchange method *versus* standard separation techniques.

A procedure has been developed for the aqueous hydrogen bromide system, which gives high yields of indium with good decontamination. Many factors which affect the procedure, such as concentrations of reagents, interferences, time of agitation, *etc.*, have been studied and evaluated.

The total separation procedure involves two isotopic exchange steps. In the first exchange, radioactive indium selectively exchanges with inactive indium in the mercury phase:

$$\mathrm{In(Hg)} + \mathrm{In}^{*3+} \rightleftharpoons \mathrm{In}^{*}\mathrm{(Hg)} + \mathrm{In}^{3+}.$$

The requirement here is that the concentration of indium in the amalgam should be much greater than the concentration of indium in the aqueous phase. The mercury phase is then removed, and the radioactive indium is back-exchanged into the aqueous phase by contact with higher concentrations of indium ion. Cobalt$^{\mathrm{II}}$ ion was also used for a few experiments in this back-exchange process.

EXPERIMENTAL

Apparatus

The separations are made in a 1/2-oz Boston-round bottle with polyethylene insert screw cap (available from Plax Corp., Bloomfield, Conn.). This is clamped in a mechanical shaker (Burrell Wrist-Action Shaker, Model 33) manufactured by the Burrell Corporation, Pittsburgh, Pa., to which an extension arm of 12 inches has been connected to give added radial action.

All radioactivity measurements were made with a Nuclear-Chicago Model DS-3 scintillation well counter as described previously.[2,6]

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Reagents

Amalgams: These were prepared by adding (under water purged with nitrogen) the appropriate weight of indium foil to 10 g of reagent-grade mercury which had been further purified by shaking with dilute nitric acid and rinsing 3 to 4 times with distilled water. The indium foil had also been subjected to dilute nitric acid and distilled water rinses before weighing.

Cobalt eluent solution: 100 mg of cobalt (as cobalt chloride) per ml in 0·4N hydrochloric acid.

Indium eluent solution: 10 mg of indium (as indium nitrate) per ml in 0·4N nitric acid.

Indium metal foil: 99·9 % pure, Indium Corporation of America, Utica, New York.

Mercury: Baker and Adamson, triple distilled, analytical reagent.

Nitrogen gas: water-pumped, 99·99 % pure, Liquid Carbonic Co.

All other non-radioactive reagents were of C.P. or analysed reagent grade.

All tracers used in this work have been described previously (Table II[7] and Table I[2]).

Amalgam-exchange procedure

Place 2 ml of 0·1M hydrobromic acid solution, containing tracers of contaminating ions (10^5 to 10^6 cpm) plus microgram amounts of inactive indium in a bottle. Chemical contamination added by the aliquots of contaminating tracers is negligible. Radioactive indium and non-radioactive interferences are used for yield determinations. Mix well. Add 0·5 ml of mercury as scavenger, cap the bottle, and shake for 1 min. Remove the mercury layer. Purge the system (both liquid and air above it in bottle) with nitrogen gas for 1 min. Add 75 μl ($\sim$1·0 g) of indium amalgam containing 0·2 % of indium by weight ($\sim$2 mg). Quickly cap the bottle and shake mechanically for 4 min.

Decant the aqueous layer, transfer the amalgam to a new bottle, and wash twice with 2-ml portions of distilled water. Transfer the amalgam to a new bottle containing 2 ml of indium eluent solution. Add 0·5 ml of mercury to dilute the amalgam, cap the bottle, and shake mechanically for 5 min. Take a 100-μl aliquot of supernate for counting. The total time for separation is about 11 min.

Cobalt$^{\text{II}}$ ion back-exchange procedure

Decontamination studies were also made employing cobalt$^{\text{II}}$ ions as the eluent instead of indium. The procedure is the same as above except that a 2 % (instead of 0·2 %) indium amalgam was used and a 2-ml portion of the cobalt eluent solution was substituted in the final step for the indium eluent.

DISCUSSION AND RESULTS

A number of preliminary experiments were made to determine the optimum procedure to use for yield and contamination studies. Several solvent systems in addition to hydrobromic acid were investigated. For typical conditions 0·1M systems of HF, HCl, HBr, and HI gave yields of about 3 %, 91 %, 98 %, and 97 % respectively. The last two appear to give similarly high readings but the presence of free iodine in the HI system, as evidenced by discolouration, could lead to complications because of its oxidising character. Therefore hydrobromic acid was used.

Similar studies with different concentrations of HBr gave yields of 98 %, 98 %, and 79 % for procedures using 0·5M, 0·1M, and 0·01M HBr respectively. Higher concentrations of acid generally tend to decrease the yield, and thus 0·1M HBr was used for the standard procedure.*

Failure to purge the system with nitrogen leads to a noticeable decrease in yield. For a 0·2 % indium amalgam, however, only a fraction of a minute is required to rid the system of this oxygen effect. If no purging with nitrogen is performed, there is sufficient oxygen trapped in the bottle above the solution to oxidise indium from the amalgam into the aqueous phase on vigorous agitation, and thus to decrease the capacity of the amalgam for overall isotopic exchange.

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* The results of these and other specific runs will be included in our AEC Progress Report No. 10, November, 1961, edited by R. S. Maddock and W. W. Meinke.

In the amalgam-exchange procedure, the separation of the radioisotope takes place by virtue of the rapid exchange which is known to occur between an element in the form of a dilute amalgam and its ions in solution. If there are many more inactive atoms of the element in the amalgam than there are of its radioisotope in solution, the amalgam exchange will result in most of the activity being incorporated into the amalgam.

Since the conditions used for these separations are far from ideal, experiments using different amounts of indium in the amalgam and in the aqueous layer indicate the limiting practical conditions which should be applied to this separation. Procedures using a 2% amalgam gave yields of 94–96% for concentrations of 0·4–50 μg of indium per ml in the aqueous solution. A slight reduction in yield to 90% was observed when this aqueous concentration was increased to 500 μg/ml.

With an aqueous concentration of $\sim$2 μg of indium per ml, yields of about 97%, 96%, 90%, 44%, and 1% were obtained for amalgams containing 2%, 0·2%, 0·02%, 0·002%, and 0·0002% of indium, respectively. Since the results with 2% and 0·2% amalgams are about equally good, both have been used in some of the experiments.

Problems of air oxidation of the amalgam and of oxidation by microgram concentrations of the contaminants combine to reduce the yields at lower amalgam concentrations, so that it was felt that no smaller than 0·2% amalgam should be used for a general procedure.

Yields also depend upon the duration and type of agitation employed for the initial extraction and for the back-extraction. With the equipment mentioned above, yields increased regularly with time of shaking and levelled out after 3–4 min of agitation. In the back-extraction process there was a sharp rise until about 3 min with a gradual continuation of the rise after this time. Thus, the conditions chosen as optimum were a 4-min agitation for the initial extraction and a 5-min agitation for the back-extraction.

Methods other than shaking might be used to produce an intimate contact between the amalgam and the solution and thus to speed up this approach to equilibrium. Some preliminary studies have been made using an ultrasonic generator to disperse the drop of amalgam in the aqueous phase, but this method was so violent that it left some of the amalgam in suspension, and subsequent centrifuging was required to clear the solution.

The resultant optimum procedure has been outlined above. The degree of separation of indium obtained with this procedure from a number of elements representative of the periodic table is shown in Table I. For many of the elements the decontamination afforded was greater than could be measured with the levels of tracer used. It should be kept in mind, however, that these high decontamination values are in any case meant to give only a general indication of results, since at these levels, amounts of contaminants carried along are very dependent upon the techniques of manipulation.

These results are also plotted in Fig. 1 along with comparative values for decontamination by other methods such as bromide extraction, ion-exchange, and sulphide precipitation.[6] In general, the amalgam-exchange procedure gives somewhat better decontamination than the bromide extraction and considerably better than the other two methods. In addition, it is more convenient and less messy than the bromide extraction.

Some yield and decontamination values were also determined by the cobalt

TABLE I.—SEPARATION OF INDIUM AND CONTAMINANTS, AMALGAM EXCHANGE PROCEDURE[a]

Tracer[b]	Weight, μg[c]	Reduction potential, *volts*[d]	Separated, %
^{131}I	C.F.; I^-	[e]	<0·01
^{137}Cs	1	−2·92	<0·01
^{90}Sr-^{90}Y	C.F.	−2·89, −2·37	<0·01
^{144}Ce-^{144}Pr	C.F.	−2·48, −2·47	<0·01
^{95}Zr-^{95}Nb	C.F.	−1·53, −1·1	<0·01
^{182}Ta	970	−0·81	<0·01
^{65}Zn	200	−0·76	<0·01
^{51}Cr	2·5	−0·74	<0·01
^{115m}Cd	10	−0·40	0·7
^{204}Tl	420	−0·34	30
^{114m}In	3	−0·34	96·6 ± 0·5
^{60}Co	2	−0·28	<0·01
^{113}Sn	270	−0·14	28
^{124}Sb	3·5 (SbO^+)	+0·21	1
^{106}Ru-^{106}Rh	6 ($RuCl_5^{2-}$)	+0·60, +0·25	0·1
^{75}Se	11·5 (SeO_3^{2-})	+0·74	<0·01
^{192}Ir	1 ($IrCl_6^{2-}$)	+0·77	<0·01
^{203}Hg	140	+0·79	1
^{110}Ag	16	+0·80	0·04

[a] Average of duplicate runs except for indium, which is the average of five runs. Error is "standard deviation".

[b] Elements have been listed in order of their reduction potentials.

[c] Weight of inactive element present before separation. C.F. = carrier free.

[d] Standard reduction potential of lowest stable oxidation state to the elemental state. Data taken from Latimer.[4]

[e] Iodine is in its lowest reduced state.

eluent procedure. The indium and cobalt eluent systems appear to be comparable from the indium yield point of view but the indium eluent seems to give somewhat better decontamination for several of the elements.

The yield of the amalgam-exchange procedure can be affected by macro quantities of different reagents. The yield is quite insensitive to mineral acids, except for oxidising acids such as nitric acid in higher concentrations. Sulphates, phosphates, and alkaline materials decrease the yield considerably, as do oxidising agents in general. The fact that HBr is present in 0·1*M* amounts during the exchange procedure appears to "buffer out" some of the possible difficulties with certain reagents. For example, when HF is used alone at 0·1*M* concentration, a yield of only a few per cent is obtained whereas in the presence of 0·1*M* HBr the yield is above 90%. Some of these interference studies are summarised in Table II where the molarity of typical reagents is listed opposite the concentration near which the yield of indium appeared to drop below 85%.

Interferences from foreign cations appear to be small except where their reduction potential is such that they might be reduced by the amalgam or form precipitates with the reagents. When a cation is also an oxidising agent, additional problems are encountered and reduction to its lowest state by a reagent such as chromium$^{\mathrm{II}}$ sulphate is necessary before the exchange step should be attempted.[3]

The yield of selenium in Table I is surprisingly low in contrast to the 17% yields found in a study of the cadmium amalgam exchange procedure.[3] This discrepancy

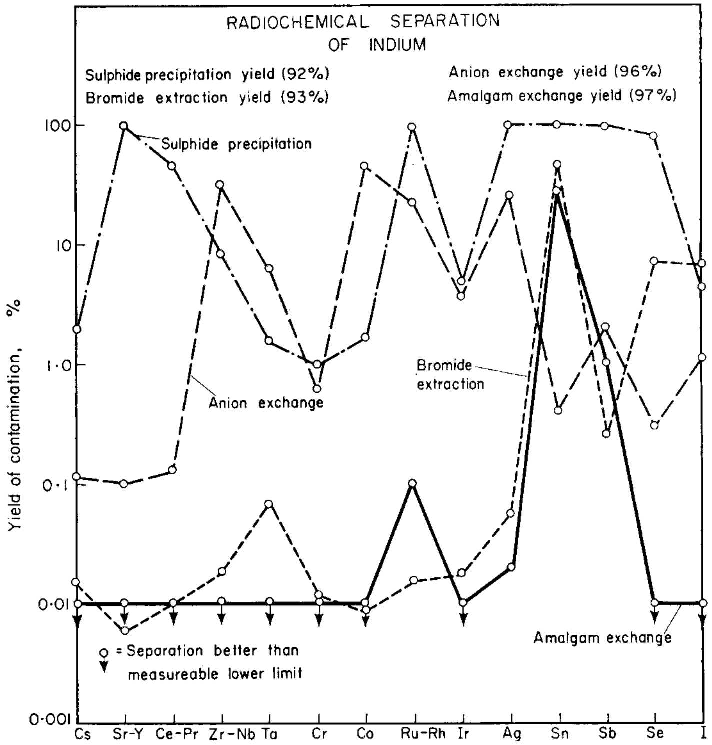

Fig. 1.—Experimental contamination for four types of indium separations.

is apparently caused by a difference in manipulation. In this indium work, the amalgam drop was brought into contact with an absorbent tissue to remove excess water after washing and before the back-extraction. At this point, the selenium, which upon reduction had formed a thin film on the surface of the mercury, mechanically rubs off on the tissue.

TABLE II.—INTERFERENCE SUMMARY, AMALGAM EXCHANGE PROCEDURE

(All taken in presence of 0.1*M* HBr)

Species	Molarity at which indium yield reduces below 85%
HF	2·5
HCl	10
HI	2
$HClO_4$	6
HNO_3	1·0
H_3PO_4	0·5
H_2SO_4	0·4
Na_2SO_4	0·25
NH_4NO_3	1·0
$NaClO_4$	0·25
Citric Acid	0·5
Sodium tartrate	0·05
Sodium acetate	1·0

The amalgam-exchange procedure for the separation of radioisotopes of indium is rapid and selective. It yields high decontamination from most elements and is relatively insensitive to interferences except for oxidising agents. It is somewhat better than the best previous radiochemical separation (bromide extraction) for this element and is more convenient to use since it avoids the necessity of working with inflammable ethers, and since the separation of phases is much more simple because of their high immiscibility.

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Zusammenfassung—Die radiochemische Abtrennung von Indium durch eine Methode mittels Amalgamaustausches wurde für das System Wasserstof-Bromid (in wasser) untersucht. Wirkungsgrad und Verunreinigungen der Trennung wurden studiert, wobei Tracer von 19 verschiedenen Elementen, verwendet wurden. Die Menge der Verunreinigung für die meisten Elemente wird auf 0·1 % reduziert während die Ausbeute an Indium für gewöhnlich über 90% bleibt. Die Methode benötigt keine besonderen Ausrüstungsgegenstände und der Zeitbedarf ist ungefähr 11 min. Eine Anzahl von Faktoren, welche die Trennung beeinflussen wurde studiert und die optimalen Bedingungen erarbeitet.

Résumé—La séparation radiochimique de l'indium par une technique d'échange sur amalgame a été examinée de façon critique pour le système aqueux hydrogène-bromure. L'efficacité et la contamination de la séparation ont été étudiées en utilisant des traceurs de 19 éléments représentatifs différents. Les rendements des éléments contaminants sont réduits dans la plupart des cas à moins de 0·1 %, cependant que les rendements d'indium sont d'habitude supérieurs à 95 %. La méthode ne nécessite pas d'équipement spécial et prend environ 11 minutes en tout. Un certain nombre de facteurs ayant une action sur la séparation ont été étudiés.

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STERIC EFFECT OF *ortho*-SUBSTITUTED ALKYL GROUPS ON CHROMATOGRAPHIC ADSORPTION OF ANILINE*

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Summary—*Ortho* substitution of aniline can produce a variety of effects which dictate the behaviour of the molecule in chromatographic adsorption. The alkyl group thus substituted is clearly the best one through which to isolate the effect of blocking adsorption while minimising or eliminating other factors.

STERIC hindrance of an alkyl substituent has been shown to exert a marked influence on the chromatographic adsorption of *ortho*-alkyl substituted phenols.[1] LeRosen and co-workers[2] chromatographed a series of *ortho*- and *para*-disubstituted benzene compounds, but the influence of the second substituent was such as to enhance or impair the normal adsorption affinity of the first functional group in such a manner as to preclude quantitative evaluation of the factors involved. Among the factors to which this abnormal behaviour was attributed were steric hindrance, internal hydrogen bonding, and resonance and inductive effects.

The study of alkyl substituted anilines was undertaken to determine to what extent steric hindrance was effective in blocking adsorption of the amino group in aniline. The basicity of the amino group and its possession of two hydrogen atoms present a functional group capable of strong adsorption. As in the phenol study, the alkyl group was chosen as substituent because it would contribute nothing but steric hindrance as a factor in altering the normal adsorption of aniline.

EXPERIMENTAL

Reagents

N,*N*-Dimethylaniline, *N*-methylaniline, 2,6-dimethylaniline, *p*-toluidine, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, *o*-phenylenediamine, *p*-phenylenediamine, *o*-chloroaniline, *m*-chloroaniline and *p*-chloroaniline were all Eastman White Label and were used without further purification. Aniline from open stock was purified by distillation from zinc dust at reduced pressure.

2,4,6-*Tri*-t-*butylaniline:* Prepared by the method of Bartlett, Roha and Stiles[3] from a sample of 1,3,5-tri-*t*-butylbenzene generously provided by Standard Oil of Indiana.

o-t-*Butylaniline and* p-t-*butylaniline:* The respective nitrobenzenes were prepared according to Craig[4] and reduced in the manner of Bartlett *et al.*[3]

o-*Isopropylaniline and* p-*isopropylaniline:* The respective nitrobenzenes were prepared by the method of Haworth and Barker[5] and reduced according to Bartlett *et al.*[3]

2,6-*Diethylaniline and* o-*ethylaniline:* Eastman Practical Grade reagent was dissolved in ether, precipitated with dry hydrogen chloride, and washed thoroughly with ether. The free amine was

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* Much of the experimental work reported herein was performed while the authors were colleagues in the Department of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.

liberated on dissolving in aqueous sodium hydroxide, then extracted into ether. After evaporation of ether the amine was distilled from zinc dust at reduced pressure.

o-*Toluidine:* Contaminating *p*-toluidine was removed by precipitation from ether solution with oxalic acid. After filtering, *o*-toluidine was precipitated with an excess of oxalic acid, washed thoroughly with ether, and finally liberated by the addition of aqueous sodium hydroxide. The free amine was isolated by ether extraction, the ether evaporated, and the amine distilled from zinc dust.

Solutions of the above anilines were prepared by weighing a small quantity of each amine into a glass-stoppered Erlenmeyer flask and adding sufficient benzene to make a $0{\cdot}01M$ solution.

Adsorbents: Merck reagent grade silicic acid, and Florisil kindly donated by the Floridin Company, Tallahassee, Fla., were ground separately in a ball mill for 3 hr, then dried for 30 hr at 145°. Predetermined amounts of silicic acid and water were mixed intimately in a horizontal rotating cylinder to produce an adsorbent containing 12·75 % water by weight. Florisil was treated similarly to bring its water content to 11·38 % by weight.

Streak reagents: Cerium^{IV} nitrate was prepared in the manner of LeRosen *et al.*[6] *p*-Nitrobenzenediazonium tetrafluoroborate was prepared according to the directions of Cheronis and Entrikin.[7] Fresh 1 % solutions in water were prepared daily.

Apparatus

Vacuum pump: Cenco Hyvac or any equivalent pump.

Chromatographic tubes: Number 1, precision bore, tapered tubes, 9 mm o.d. × 150 mm long, Scientific Glass Apparatus Co., Bloomfield, N.J.

Procedure

Adsorption columns were prepared by dry packing the chromatographic tube to a height of 75 ± 5 mm with adsorbent while applying full vacuum. Tapping the sides of the tube vigorously with a small wooden rod, and finally levelling the top of the adsorbent gently with the end of the rod, resulted in columns of sufficient reproducibility. A sample of 0·2 ml of the $0{\cdot}01M$ aniline solution in benzene was applied to the top of the column and was followed immediately by a few drops of benzene. Two or three additional increments of benzene were introduced, precaution being taken not to allow the top of the column to become dry. Having worked the sample onto the column the void above it was filled with benzene and the developing process allowed to continue until solvent reached the bottom of the column. The vacuum was then shut off to the column, the upper assembly disconnected from the lower, and the adsorption column extruded from the chromatographic tube. Streaking the column with the appropriate colour producing reagent revealed the location of colourless anilines. At least duplicate runs were made on each of the anilines, the R values averaged, with the deviation of a single run being no greater than 0·02 from the average. Cerium^{IV} nitrate and *p*-nitrobenzenediazonium tetrafluoroborate were employed as streak reagents on each column.

DISCUSSION OF RESULTS

In studying the effects of various substituents upon the chromatographic adsorption of aniline it should be expected that geometric location of the substituent would play a significant role. It should be expected further that with the possible exception of the alkyl group several factors come into play, all contributing to an alteration of the normal adsorption of the amino group. Thus a nitro group or a chloro group will alter the basicity of the amino group through resonance or inductive effects, or both. This substituent effect on base strength is not reflected in an orderly manner in the chromatographic adsorption of the molecule, as examination of Table I shows. Confining the comparison to only *para*-substituted anilines or *ortho*-substituted anilines does not improve the correlation.

One might suspect that dipoles produced or intensified through substitution would, by altering the solubility characteristics of the adsorptive molecule in the developing solvent, give rise to orderly changes in R values as dipole moments or dielectric constants change. This does not prove to be the case.

TABLE 1.—R VALUES AND SOME pK_a VALUES OF SUBSTITUTED ANILINES ON SILICIC ACID ADSORBENT

Compound	R	pK_a
Aniline	0·25	4·58[a], 4·14[b]
o-Toluidine	0·30	4·39[a]
p-Toluidine	0·20	5·12[a]
o-Ethylaniline	0·34	
p-Ethylaniline	0·21	
o-Isopropylaniline	0·37	
p-Isopropylaniline	0·25	
o-*t*-Butylaniline	0·55	3·78[a], 3·39[b]
p-*t*-Butylaniline	0·25	4·00[b]
2,6-Dimethylaniline	0·35	3·42[c]
2,6-Diethylaniline	0·51	
2,4,6-Tri-*t*-butylaniline	1·00	2·00[b]
o-Nitroaniline	0·50	
m-Nitroaniline	0·27	
p-Nitroaniline	0·20	2·00[a]
o-Phenylenediamine	0·04	4·52[a]
p-Phenylenediamine	0·08	
o-Chloroaniline	0·72	2·13[c]
m-Chloroaniline	0·50	2·93[c]
p-Chloroaniline	0·42	3·46[c]
N-Methylaniline	0·50	4·40[a]
N,N-Dimethylaniline	0·56	4·26[c]

[a] In water at 25°.
[b] In 90% methanol.
[c] In 50% aqueous ethanol.

Ortho substitution in aniline would bring additional factors into consideration. Internal hydrogen bonding and steric hindrance are important among these. Again, however, interplay of such a variety of factors complicates the identification of any one as being paramount. Earlier works discuss at greater length some of the above-mentioned substituent effects.[2,8]

The steric effect can be isolated from the others by choosing the appropriate substituent. The alkyl group serves to accomplish this. Table I indicates that the R values of all of the *para*-alkyl substituted anilines are essentially the same. The absence of appreciable inductive or resonance effects with *para* substitution of the alkyl group validates the assumption that with the alkyl group substituted in the ortho position these effects are negligible. Yet, with the alkyl group substituted *ortho* to the amino group the R values increase significantly as the size of the alkyl group increases. Steric hindrance becomes particularly effective when alkyl groups are substituted on both *ortho* positions, as in dimethylaniline, 2,6-diethylaniline, and 2,4,6-tri-*t*-butylaniline.

The effect of *ortho alkyl* substitution on the chromatographic adsorption of phenols produced results which were qualitatively the same as those obtained in this study in which aniline provided the active adsorbing functional group. With the mechanism of adsorption of many functional group-bearing organic compounds generally accepted to lie in hydrogen bond formation between adsorptive and adsorbent,[2,8,9,10] the amino group with two hydrogen atoms would appear to possess a greater facility than the phenol group to bond through active electron donor sites on the adsorbent. Compare the R values of the *ortho*-alkyl substituted anilines with those of the analogous phenols (Table II). The anilines are consistently more strongly adsorbed than the phenols.

TABLE 2.—R VALUES OF *ortho*-ALKYL SUBSTITUTED ANILINES AND ANALOGOUS PHENOLS

Substituent	R	
	Anilines	Phenols
o-Hydrogen	0·25	0·26
o-Methyl	0·30	0·37
o-Ethyl	0·34	0·43
o-Isopropyl	0·37	0·52
o-*t*-Butyl	0·55	0·74
2,6-Dimethyl	0·35	0·55

Regardless of the degree of coplanarity of the aniline molecule, some resonance energy has been gained at the expense of basicity by extending the resonance system of the ring to include the p_z electrons of the amino nitrogen. Thus a substituent which sterically hinders the coplanar arrangement of aniline would bring about a corresponding increase in the basicity of the molecule. Yet, basicity does not appear to be the over-riding factor. Consider the pK values and the R values of *o*-phenylenediamine, *p*-toluidine, and *N*-methylaniline in Table I. Although all are of approximately the same pK value, *o*-phenylenediamine exhibits a low R value consistent with the possession of a second active adsorbing group, *p*-toluidine exhibits an intermediate R value, and *N*-methylaniline exhibits a relatively high R value apparently as a result of substitution of an active hydrogen. Since the pK values and the R values of *N*-methylaniline and *N*,*N*-dimethylaniline are approximately the same it appears that both amino hydrogens are necessary for effective adsorption.

Zusammenfassung—Orthosubstitution von Anilin kann verschiedene Effekte verursachen, die für das Verhalten der Molekel bei chromatographischer Adsorption verantwortlich sind. Die Alkylgruppe ist klar die beste um den Effekt der Adsorptionblockierung zu isolieren, während andere Faktoren ausgeschlossen oder lediglich gemindert werden.

Résumé—On a examiné l'adsorption chromatographique de la molécule de l'aniline qui a été modifiée par l'ortho-substitution. Le groupe alkyl sert à distinguer entre les effets différents qui en resultent.

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EMISSION SPECTRA FROM HIGH-FREQUENCY EXCITATION—II

THE SPECTRA OF NITROGEN, HYDROGEN AND AMMONIA

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Summary—The spectra of rarified samples of N_2, H_2 and NH_3, excited by a Tesla discharge, have been studied and found to be composed of known molecular band systems, strong atomic lines of hydrogen and impurity band systems. The significance of the results with a view to the analytical possibilities of the technique is discussed.

INTRODUCTION

In the first publication in this series[1] the historical background to the use of a Tesla-type discharge for the excitation of spectra was discussed, and the development of a new apparatus and technique was outlined. This work has now been extended by an intensive study of the behaviour of a number of gases. In particular, this paper reports the results obtained using nitrogen, hydrogen and ammonia.

EXPERIMENTAL

Apparatus

High-frequency generator, vacuum train and sample cell: In this study the high-frequency generator, vacuum train and sample cell were similar to those previously described.[1] The Tesla-generator consisted of a radio-frequency transformer in a self-oscillating circuit at about 236 Kc/sec. with a Mullard QV06-20 valve. This generator produces an alternating voltage in the range 5–15 KV with low output power. The gases were energised by continuous excitation under low pressures.

The technique of sample introduction, pressure adjustment and control were also the same as described earlier.[1]

Measuring and recording instruments: Hilger Medium Quartz Spectrograph E498. Hilger Uvispek Photo-electric Spectrophotometer H700 with quartz prism. Hilger Non-recording Microphotometer L451 with Galvoscale ER300. Sunvic pen-recorder.

For qualitative or identification purposes, the plate from the spectrograph was run through the microphotometer attached directly to the recorder and a trace obtained which, when compared with a copper standard, enabled wavelengths to be assigned to peaks.

The microphotometer attached directly to the Galvoscale was used in the normal way for the quantitative estimation of the intensities of selected bands and lines.

The Uvispek spectrophotometer was used as a modified flame spectrophotometer with the flame source replaced by the glowing sample-tube. The responses were recorded on the Sunvic recorder.

Purification of gases: The gases were obtained from commercial cylinders, and had purity better than 99·9%. The gases were purified as far as possible, either by passing them through two liquid nitrogen traps or by condensing them in liquid nitrogen traps and re-distilling. This procedure was repeated twice.

Detection of spectra: In the procedure for the detection of the spectra, the sample-tube was attached to a vacuum train evacuated by a two-stage mercury diffusion pump backed by a rotary oil pump. The whole system was pumped out to a pressure of 10^{-4} mm of Hg, as measured on a Pirani gauge. The filling gas was allowed to sweep out the system, which was then pumped out again to 10^{-4} mm of Hg. The sample-tube was now isolated at 10^{-4} mm pressure, and the rest of the system was filled with the gas under examination. On opening the sample-tube to the system, the gas flowed into it. The pressure in the sample-tube was now reduced, the high-frequency generator was switched on, and the pressure was altered until maximum glow was obtained.

Spectrophotometric investigations

The spectra of the glowing gases were examined with the spectrophotometer used as a modified flame spectrophotometer in which the normal flame source was replaced by the glowing gas. With the recorder attached, the responses were traced on the chart. Slit widths varied from 0·20 mm to 0·05 mm. The range of wavelength over which the glow was studied was 6100 Å to 2000 Å. The results obtained for the three gases are shown in Table I.

To interpret the above results obtained with the spectrophotometer, the spectra of the glowing gases were examined with the spectrograph.

Spectrographic studies

The spectrum of each gas was photographed with a slit width of 0·03 mm at an exposure time of 15 min. Ilford Ordinary N.30 and Panchromatic H.P.3 plates were used to examine the ultraviolet and blue regions, and the red regions of the spectra, respectively. The copper arc was employed as standard. The spectra were examined with microphotometer and recorder attachment, and with the Galvoscale. Wavelengths were assigned to the band heads obtained on the recorder chart by measuring the dispersion of the standard copper spectrum and using the relationship for the unknown band system. The trace of the standard copper spectrum is shown in Fig. 1 and that of nitrogen in Fig. 2.

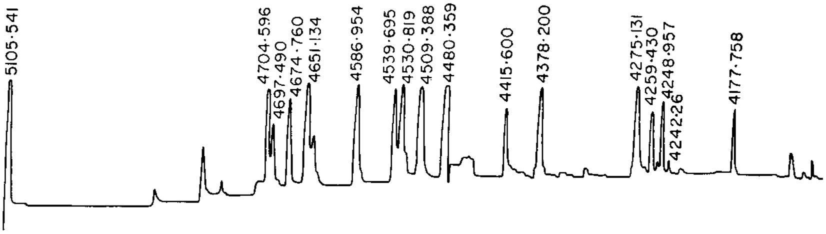

FIG. 1

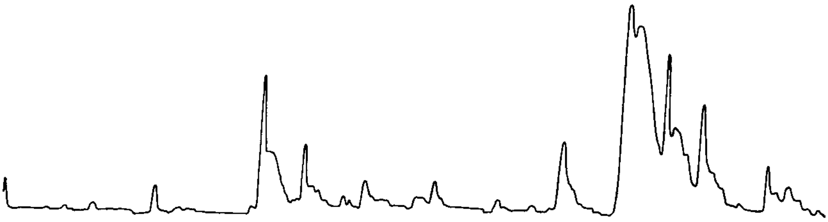

FIG. 2

RESULTS

In the method of measuring wavelengths by the procedure indicated above, there are experimental limitations so that an error of ±5 Å can arise. This, however, did not prevent the assignment of the bands to known molecular band systems, and the atomic lines to elements. In this assignment Pearse and Gaydon's book[2] was used as the principal reference source.

The results from a series of experiments with the three gases were examined. The band systems and atomic lines which occurred are shown in Table II.

TABLE I

Gases	Band heads, *Å* (± *5Å*)	Pressure, *mm of Hg*	Colour of glow	Nature of glow	Pressure for maximum intensity of glow, *mm of Hg*	Remarks
Ammonia	5430, 5380, 5260, *4860*, 4700 *4300*, 4280, 4060, *3910*, 3800, *3750*, *3580*, 3540, 3370, 3300, *3160*, 2980, 2820, 2420, 2300, 2190	0·5	Purple	Bright and stable	1·0–0·3	Glows down to a pressure of about 0·10 mm of Hg. The upper limit of pressure not determined. The most intense peaks are italicised.
Hydrogen	5610, 5200, *4860*, 4710, 4510, 4390, 4280, 4200, 4120, *3910*, 3710, 3640, *3370*, *3290*, 3130, 2980, 2880, 2820, 2300, 2190	0·4	Blue-violet	Bright and stable	1·5–0·3	Glows down to a pressure of about 0·15 mm of Hg. The upper limit of pressure not determined. The most intense peaks are italicised.
Nitrogen	5610, 5200, 4860, 4710, 4280, 4060, 4000, *3910*, 3800, *3760*, 3710, *3580*, 3540, *3370*, *3160*, 2980, 2880, 2300, 2190	0·4	Deep purple	Bright and stable	1·0–0·2	Glows down to a pressure of about 0·07 mm of Hg. The upper limit of pressure not determined. The most intense peaks are italicised.

Table II

Gas	Glow Pressure, *mm of Hg*	Observed molecular spectra and atomic lines
Ammonia	1·0–0·3	N_2 (second positive system); N_2^+ (main system); NH_2 (ammonia α bands); H_2 atomic line
Hydrogen	1·5–0·3	N_2 (second positive system); N_2^+ (main system); CN (violet system); CO (Angström system); CO^+ (first negative system); H_2 atomic line
Nitrogen	1·0–0·2	N_2 (second positive system); N_2^+ (main system); CN (violet system); CO (angstrom system); CO^+ (first negative system); H_2 atomic line

Interpretation of results

From the observations recorded in Table II, the results of Table I may be interpreted as follows:—

(1) *Ammonia.* The peaks at 5430 Å (5429·19 Å), 5380 Å (5384·64 Å) and 4700 Å (4702·18 Å; 4704·00 Å) are those of the NH_2 ammonia α-bands. That at 3370 Å is one of the NH bands. The strong peak at 4860 Å is that of the Hβ hydrogen line (4861·33 Å). All other peaks can be assigned to the other systems outlined in Table II.

The presence of the atomic line of hydrogen and the molecular bands of nitrogen would suggest the dissociation of ammonia into its components, nitrogen and hydrogen. They could possibly also arise from impurities. It is interesting to note that with time, the intensities of the NH_2 ammonia α-bands decreased, while those of nitrogen and hydrogen increased.

(2) The peaks in the hydrogen spectrum are from the strong atomic line of hydrogen 4860 Å (Hβ, 4861·33 Å) and those of the other systems indicated in Table II.

(3) The peaks of nitrogen are those of N_2 (second positive system), N_2^+ (main system), CN (violet system), CO (Angström system), CO^+ (first negative system).

DISCUSSION

From the results of this study, two significant points arise concerning the spectra produced by the Tesla-type discharge. The first is that the bands and lines which are excited can be ascribed to known systems. Thus, it can be shown that the results obtained by Given *et al.*,[1] arise in the main from well-known band spectra (*e.g.*, nitrogen) arising from impurities.

This leads to the second significant fact, which is that excitation of gaseous impurities is more readily achieved than excitation of the gas under study. In the present work, the occurrence of nitrogen band systems in the nitrogen and ammonia spectra are understandable, but their appearance in the hydrogen spectra can only be attributed to impurities. Experience has shown that heating an outgassed cell is sufficient to liberate impurities from the walls and give the characteristic nitrogen bands. In the first instance, the presence of the carbon monoxide and cyanogen bands was attributed to the black wax used to attach the quartz window to the sample cell, but later experiments with epoxy resin adhesive confirmed that these bands were caused by desorbed impurities from the walls. Adsorption and desorption processes play significant roles in this technique. Baking of the cell and the high vacuum train at 400° under a pressure of 10^{-4} mm of Hg greatly reduces the impurities, but even then they interfere with the analytical possibilities of the method.

A number of the bands and lines in the spectra of the three gases were examined for linearity with pressure but, over the short range of pressure (from 1·5 mm to 0·2 mm) used, the intensity did not vary linearly with pressure. It increased to a maximum over a very short pressure range, and then decreased again. The position and magnitude of the maximum varied with the nature of the diluent gas. This confirms the findings of Steinberg and Poulson[3] that the sensitivity-pressure curves are parabolic in shape.

The present study also confirms the recent work of Heath,[4] who studied the relative intensities of the spectra from mildly excited discharges in N_2, air, NO, O_2, and mixtures of these gases at high resolution, as a function of pressure (0·01–760 mm of Hg). The gases were excited by means of an oscillator with a 1 kW, 200 Mc/sec output. Heath found that the parameter which largely determined the spectral characteristics was the gas pressure. He further found that the intensity of the second positive group of N_2 bands was reduced by more than a factor of 20 in an air discharge at atmospheric pressure, when compared to a corresponding discharge in pure N_2, and that the first positive group of N_2 bands was weakened in an air discharge at reasonably high pressure. The significance of these findings is that the intensity of emission is sometimes dependent on pressure and diluent gas, and some bands and lines are more sensitive to pressure than others. Again, some bands and lines are independent of pressure. In the development of this technique as a quantitative analytical method all these factors must be taken into consideration.

CONCLUSION

This study has shown that gases and vapours which are excited can be readily detected and identified by this technique. It holds promise, therefore, as a qualitative analytical tool with the advantage of sensitivity. However, while the characteristic molecular bands and atomic lines on photographic plates are one of the best means of identifying the species that produced them, their quantitative application, depending as they do on many variables, *e.g.*, nature of excitation, design of cell, photographic plate, time of exposure, *etc.*, is far from simple. To place the technique on a quantitative basis, therefore, requires (1) elimination of the impurities or their effect; (2) elimination of the effect of variation of pressure and temperature. This may mean working at constant pressure and temperature, or the selection of such bands or lines as are independent of pressure; (3) selection of bands free from interference by other systems present, or elimination of the effects of other systems present by careful control of experimental conditions; (4) use of instruments for measurement of the spectra which are capable of measuring intensities directly, ensuring greater speed, precision and accuracy than obtainable from the photographic methods of spectroscopy; and (5) elimination of the effect of diluent gases by careful calibration with standard mixtures of gases.

The requirements of (3) and (4) can be fulfilled by preliminary examination of spectra with the spectrograph, followed by examination with the spectrophotometer. Besides giving greater speed, the latter instrument gives better accuracy and precision, since the spectrographic technique bases its accuracy and reproducibility on many variables, especially the behaviour of photographic emulsions.

At present, investigations are being carried out along these lines in this department. The results of this work will be communicated shortly.

Acknowledgement—One of us (C. L. C.) gratefully acknowledges the award of a research studentship from the Queen's University of Belfast which has made this work possible. Our thanks are also due to Dr. W. D. McGrath of this Department and Dr. W. F. Pickering of Newcastle University College, Technical University of New South Wales, at present working in this Department, for their advice on a number of matters, and for much helpful discussion.

Zusammenfassung—Die Spektren, angeregt durch eine Tesla-Entladung, von N_2, H_2 und NH_3 wurden studiert. Sie enthalten bekannte Molekülbanden, starke Atomlinien von Wasserstoff und Systeme von Verunreinigsbanden. Die Bedeutung der Befunde im Hinblick auf analytische Verwertung wird diskutiert.

Résumé—Les auteurs ont étudié les spectres d'échantillons raréfiés de N_2, H_2 et NH_3 excités par une décharge Tesla; ces spectres sont composés de systèmes de bandes moléculaires connues, de raies atomique intenses d'hydrogène et de systèmes de bandes d'impureté. La signafication des résultats est discutée; les auteurs donnent une idée des possibilités analytiques de la méthode.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—V

MAGNESIUM

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Summary—A method has been developed for the precipitation of magnesium 8-hydroxyquinolate from homogeneous solution with 8-acetoxyquinoline. Satisfactory separations from sodium, potassium, and barium were obtained.

INTRODUCTION

Magnesium 8-hydroxyquinolate was first precipitated in 1910 by Fox,[1] who added an aqueous solution of 8-hydroxyquinoline and sodium hydroxide to a neutral solution of magnesium acetate. Many investigators have subsequently recommended gravimetric methods in which 8-hydroxyquinoline is used to determine magnesium. The formula of the precipitate dried at 110 ± 10° is said to be $Mg(C_9H_6ON)_2 \cdot 2H_2O$. The anhydrous form is reported to exist above 130°; the usual recommended temperature for weighing the precipitate in this form is 150 ± 10°.[2,3]

The purpose of this investigation was to develop a method of precipitation from homogeneous solution for magnesium using 8-acetoxyquinoline and to determine the effect of some diverse ions.

EXPERIMENTAL

At temperatures above 5–10°, 8-acetoxyquinoline hydrolyzes too rapidly so that precipitation occurs almost instantly. When the pH is below 10·0, precipitation is incomplete (*cf.* Table I). The crystals formed at low pH values are darker in colour and coarser in texture.

Satisfactory results for analytical purpose were obtained by the dropwise addition of 2·1 ml of a solution containing 0·42 g of 8-acetoxyquinoline (20% excess over the stoichiometric quantity required for 25 mg of magnesium) to a cold, ammoniacal solution containing magnesium and allowing the reaction mixture to stand for 2·25 hr followed by a short warming period. Three to four min were required for the dropwise addition (burette with Teflon stopcock) of 8-acetoxyquinoline; initial precipitation of the magnesium would usually begin when the last of the reagent had been added. Other derivatives of 8-hydroxyquinoline were not tested for rate of hydrolysis; however, some related exploratory work was attempted with derivatives of 8-hydroxyquinaldine. Only one of the latter, 8-benzoxyquinaldine, was prepared in crystalline form but it was found to hydrolyse too slowly for precipitation purposes.

Reagents

Magnesium: Reagent grade $MgCl_2 \cdot 2H_2O$. (J. T. Baker Chemical Company, Phillipsburg, New Jersey). The concentration of the standard solution was determined by precipitation of the magnesium as the oxalate and titration with potassium permanganate.[4]

Calcium: Reagent grade $CaCl_2$. (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Barium: Reagent grade $BaCl_2 \cdot 2H_2O$. (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Sodium: Reagent grade NaCl. (Mallinckrodt Chemical Works, St. Louis, Missouri).

Potassium: Reagent grade KCl. (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

8-*Hydroxyquinoline:* (Matheson, Coleman, and Bell Division of Matheson Company, East Rutherford, New Jersey). An acetic acid solution of the reagent was used to precipitate magnesium in the conventional manner as described by Kolthoff and Sandell.[5]

8-*Acetoxyquinoline:* PFHS grade (Burdick and Jackson Laboratories, 1953 Harvey St., Muskegon, Michigan).

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TABLE I.—PRECIPITATION OF MAGNESIUM 8-HYDROXYQUINOLATE

Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Method of precipitation	conventional	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS
Modifications in precipitation procedure	a,h	b,h	c,h	i	h,i	h,i	h,i	h,i	h,i	h,i	h,i	h,i	h,i
Diverse element taken, *mg*	none	none	none	none	none	none	none	none	Na 1000	K 1000	Ba 200	Ba 50	Ba 15
Magnesium taken, *mg*	11·94	11·94	9·77	12·32	2·57	5·14	12·32	25·68	12·84	12·84	12·84	12·84	12·84
Difference, *mg*	−0·14 −0·07 −0·14	−0·11 −0·12 −0·14 +0·07 +0·14	−0·09 −0·09 −0·08	−1·58[d] −0·16[e] −0·54[f] −0·10[g]	+0·01 −0·03 0·00 −0·05	+0·01 −0·05	−0·04 −0·03 −0·06	−0·11 −0·15	+0·16 +0·13 +0·03	−0·05 −0·07	+1·48 +1·36 +1·96	+0·21 +0·42	−0·05 +0·06

[a] 4x stoichiometric quantity of 8-hydroxyquinoline added.
[b] 3x stoichiometric quantity of 8-acetoxyquinoline added.
[c] 2x stoichiometric quantity of 8-acetoxyquinoline added.
[d] pH 8.5
[e] pH 9.0
[f] pH 9.5
[g] pH 10.5
[h] pH 10.0
[i] 0.42 g of 8-acetoxyquinoline added = 1.2x stoichiometric quantity required for 25 mg of magnesium.

Procedure

Dilute a nearly neutral solution containing 5 to 25 mg of magnesium to approximately 125 ml with distilled water. Add 4 ml of 3*N* hydrochloric acid and adjust to pH 10·0 with filtered 1:1 ammonium hydroxide. Adjust the final volume to 150 ml. Cover the beaker with a watch glass and allow to stand in an ice bath for 15 min. Slowly add, with stirring, 2·1 ml of an acetone solution containing 1·0 gm of 8-acetoxyquinoline per 5·0 ml of acetone. Allow to stand at room temperature for 2·25 hr with occasional stirring. Heat the solution to 50–60° for 20 min before filtering through a medium-porosity filtering crucible. Wash the precipitate with a 1% ammonium hydroxide solution. Dry at 105° ± 1° for 2 hr and weigh as $Mg(C_9H_6ON)_2{\cdot}2H_2O$ or at 155° ± 1° for 2 hr and weigh as $Mg(C_9H_6ON)_2$; the gravimetric factors are 0·0698 and 0·0778, respectively.

RESULTS AND DISCUSSIONS

The results shown in Table I were obtained using the procedure given, concluding the determination by drying the precipitate at 105°. Although good results were obtained with less than 5 mg of magnesium present, *i.e.* with 2·57 mg, excess 8-hydroxyquinoline also tended to precipitate. The recommended procedure proved satisfactory for 5 to 25 mg of magnesium.

The drying temperature of 105 ± 1° for the dihydrate is somewhat critical. Precipitates dried at 110° gave low values for magnesium. Both a chemical analysis by bromination of the precipitate and thermal studies indicated that $Mg(C_9H_6ON)_2 \cdot 2H_2O$ loses some water at 110°. Further work showed that the precipitate could be weighed as the anhydrous material after drying at 155° for 2·5 hours.

Spectrophotometric determination of magnesium[6] in the filtrate and wash solution showed that the combined solubility loss is approximately 0·02 mg when 12·32 mg of magnesium were precipitated according to the procedure.

Table I shows that 12 mg of magnesium can easily be separated from 1000 mg of sodium or potassium and 15 mg of barium; a separation from 200 mg of calcium was not successful.

Acknowledgement—The authors acknowledge the support of this investigation by the United States Atomic Energy Commission under Contract AT(11-1)-582 and by the National Science Foundation.

Zusammenfassung—Eine Methode wurde entwickelt um Mg-oxinate aus homogener Lösung zu fällen, wobei 8-Acetoxychinolin verwendet wird. Zufriedenstellende Trennung von Na, K und Ba ist erzielbar.

Résumé—Les auteurs ont mis au point une méthode de précipitation du 8-hydroxyquinoléate de magnesium en solution homogène par la 8-acétoxyquinoléine. Des séparations satisfaisantes du sodium, du potassium et du baryum ont été obtenues.

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THE COMPLEXOMETRIC DETERMINATION OF PLUTONIUM IN REACTOR FUEL PROCESSING PLANT SOLUTIONS—I*

NITRIC ACID SOLUTIONS OF IRRADIATED URANIUM

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Summary—An accurate and precise method for the determination of plutonium in nitric acid solutions of irradiated uranium is described. $\text{Plutonium}^{\text{IV}}$ is extracted using the quaternary amine Hyamine 1622 dissolved in benzene; the benzene is removed by evaporation and, after dissolution of the residue in acetone, an excess of ethylenediaminetetra-acetic acid (EDTA) is added and the uncomplexed EDTA determined by photometric titration using standard zinc chloride solution and dithizone as indicator. The extraction is highly specific for plutonium and a two-stage cycle results in a decontamination factor of approximately 10^5 for mixed fission products and 10^2 for uranium. Under carefully controlled conditions the method yields a standard deviation of 0·4% for 10^2-μg amounts of plutonium.

INTRODUCTION

THE safe and efficient operation of a chemical process for the separation and purification of plutonium from irradiated uranium requires extensive analytical control. Of particular importance is the precise and accurate determination of plutonium at selected stages of the process. Inherently the most difficult problem is the determination of plutonium in nitric acid solutions of the fuel elements which constitutes the feed solution to the processing plant. Such solutions, which are considered in this paper, contain uranium in several thousand-fold excess of the plutonium, and fission product $\beta\gamma$-activity of approximately 15 mc per ml of solution. A second paper will deal with solutions arising after several stages of the separation process and which contain approximately equal amounts of plutonium, uranium, iron and chromium at much reduced levels of fission product radioactivity.

Methods for determining plutonium in impure solutions of this type fall into two main groups, radiometric and chemical. Radiometric methods usually involve the counting of α-particles from a suitably diluted portion of the sample.[1] This approach is virtually independent of the non-radioactive constituents of the sample unless these are present in sufficient concentration to lead to serious absorption of α-particles in the source prepared for counting. The technique has the disadvantage of requiring correction for the α-particle contributions from transplutonium elements (in particular americium-241 and curium-242) and also uranium if present in sufficient quantity, and these corrections must be separately determined. Further, the conversion of counting rate to mass of plutonium requires an ancillary determination of an accurate specific activity of the plutonium. Clearly this conversion can prove troublesome when processing fuel of widely varying irradiation history.

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Chemical methods such as absorptiometry,[2,3] coulometry[4,5,6] and redox titrimetry,[7] circumvent these difficulties but they require a much larger sample and in consequence necessitate fully or semi-remote handling, at least in the early stages of the procedures. In addition, when applied to impure solutions of the type under discussion they invariably require a complete preliminary separation of the plutonium. However, in view of their inherently greater accuracy considerable attention has been devoted to chemical methods in recent years. The isotope dilution method recently described by Webster *et al.*[8] offers an interesting alternative in which complete chemical isolation of the plutonium is not required.

In the Windscale laboratories the plutonium content of solutions of irradiated uranium has been determined absorptiometrically using the coloured complex formed by plutonium^{IV} with thoronol [1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid][9] and 50–100 μg of plutonium for each determination. The preliminary separation is achieved by extracting the plutonium from a 2–4*M* nitric acid into a solution of Hyamine 1622 in benzene. Hyamine 1622 is essentially *p*-di-isobutylphenoxyethoxyethylbenzyldimethylammonium chloride and its behaviour as an extractant has been studied in detail by Powell.[10] It extracts plutonium as the anionic species $Pu(NO_3)_6{}^{2-}$ and provides an extremely selective means of separating plutonium since few elements form anionic nitrates in 2–4*M* nitric acid. The complete method yields a standard deviation of 1·4% at the 100-μg plutonium level and thus compares favourably with other non-differential absorptiometric methods for other elements.

It was considered that improved precision would result by replacing the absorptiometric finish by a titrimetric one, whilst retaining the initial Hyamine 1622 separation. Ethylenediaminetetra-acetic acid (EDTA) was selected for study since it forms strong 1:1 complexes with all valency states of plutonium[11,12] thereby obviating a valency conditioning step. In addition it forms only weak complexes with the uranyl ion[13] and consequently the small amounts of uranium co-extracted with the plutonium should not interfere. Milner and Woodhead[14] have shown that milligram amounts of plutonium as plutonium^{III} can be successfully determined using EDTA. The present procedure has been developed to give precise and accurate results using 100–200 μg of plutonium contained in a solvent phase. It involves adding EDTA in excess of the plutonium to an acetone solution of the Hyamine 1622 extract and back-titrating with standard zinc solution to a dithizone end-point.

EXPERIMENTAL

Apparatus

Extraction apparatus: The extraction unit is shown in Fig. 1. It comprises two vessels attached to a manifold which enables them to be filled and emptied through a capillary swan-necked side-arm by applying suction or compressed air. Mixing of solutions in the vessels is promoted by drawing air through the capillary into the body of the vessel. The cone and socket joints are kept free of grease to avoid introducing titratable impurities into the system.

Photometric titration apparatus: This is shown diagrammatically in Fig. 2 and the titration cell is shown in detail in Fig. 3. The conical cell, fitted with a few coils of resistance wire to provide gentle heating for the evaporation stage, is situated between an ordinary filament lamp and a photoelectric cell connected to Cambridge galvanometer through a variable resistance. An Ilford 604 filter having maximum transmission at 510 mμ was placed between the titration cell and the photocell since the pink end-point colour of the zinc—EDTA titration shows maximum absorbance at this wavelength. The contents of the cell are stirred by means of compressed air bubbled through a glass dip tube drawn out to a fine jet.

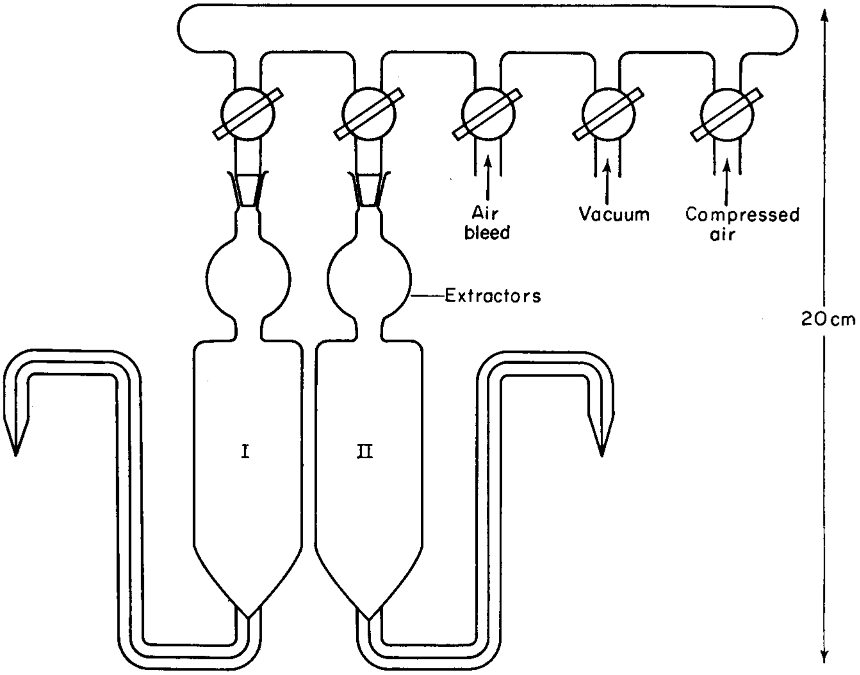

FIG. 1. Extraction apparatus.

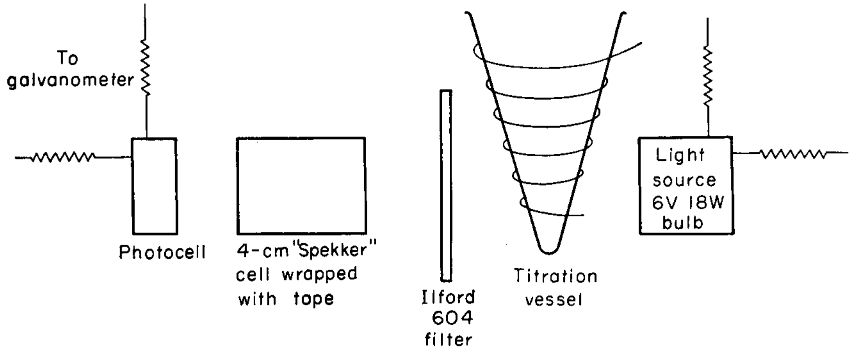

FIG. 2. Photometric titration assembly.

Remotely controlled pipette: For the remote handling of radioactive solutions a capillary pipette of the type shown in Fig. 4 was used. Application of suction draws the solution into the pipette until it just overflows the fine-capillary top. When the overflow ceases the measured volume is ejected. Two pipette washings were carried out for each sampling by drawing up and ejecting wash liquor in the same manner but not allowing it to overflow at the top.

Microburettes: Agla microburettes of 0·5-ml capacity were used. The one used to deliver standard zinc chloride solution was calibrated over the full range of drum readings. The second burette, used to deliver a fixed volume of EDTA solution was not calibrated, but always used over the same scale range.

Reagents

1% *w/v Hyamine* 1622 *solution in benzene:* 0·5 g of Hyamine 1622 (supplied by Rohm and Haas Co. Ltd.) was dissolved in 5 ml of water and the nitrate precipitated by adding 5 ml of 3*M* nitric acid.

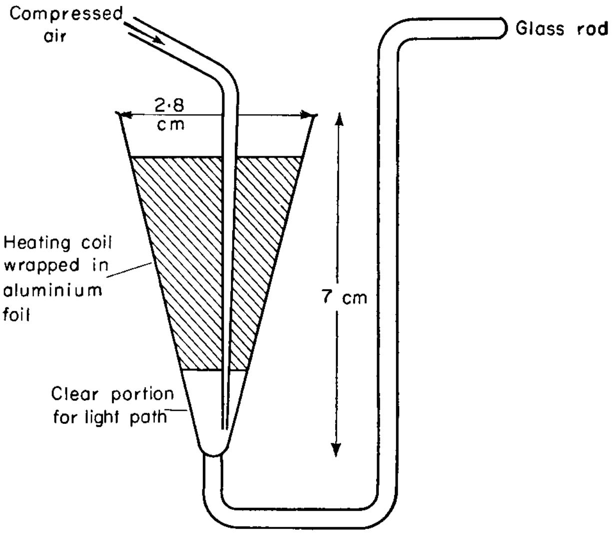

FIG. 3.—Titration cell.

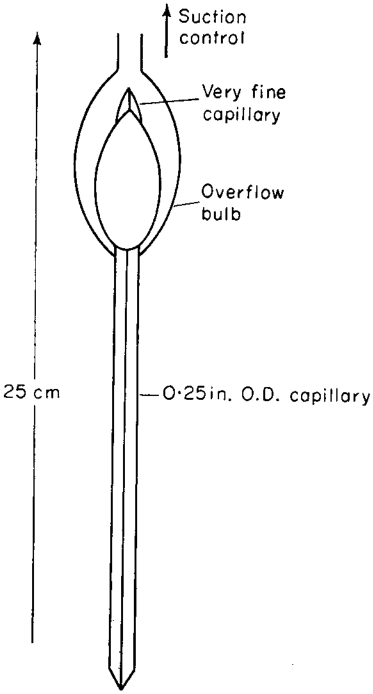

Fig. 4.—Remotely operated pipette, 2-ml capacity.

After decanting off the supernate the white curdy precipitate was dissolved in 50 ml of twice distilled benzene. The suspended aqueous phase was removed by filtration through a Whatman No. 41 filter paper moistened with benzene.

All other reagents were of AnalaR quality where possible. The standard 0·004*M* zinc chloride solution, the 0·04% w/v dithizone solution in acetone and the 10% iron^{II} ammonium sulphate solution (0·004*M* in sulphuric acid) were prepared freshly each day.

Extraction of plutonium by Hyamine 1622 *in benzene*

Plutonium^{IV} is the only valency state of plutonium efficiently extracted by this solvent, the approximate partition coefficients being greater than 200, 0·2 and very low for plutonium^{IV}, ^{VI} and ^{III} respectively. Consequently the success of the procedure depends on complete conditioning to plutonium^{IV} before extraction. The samples to be analysed comprised primarily plutonium^{IV} with some plutonium^{VI}. Iron^{II} ion was chosen as the reductant since it operates efficiently at room temperature. Hydrogen peroxide, demonstrated to be an efficient conditioning agent by Ockenden and Foreman,[15] was rejected for the present work since it involves prolonged heating in 7–8*M* nitric acid.

Optimum conditions for complete conversion to plutonium^{IV} were established using a synthetic solution containing approximately 10% of plutonium^{VI}, 90% of plutonium^{IV} (total concentration 88·2 μg/ml) in 3*M* nitric acid. The results quoted in Table I were derived by extracting a 2-ml portion of this solution twice with 2-ml volumes of 1% Hyamine 1622 in benzene for 1·5 min under the stated conditions and examining the aqueous phases from each extraction by α-counting. Essentially complete reduction of plutonium^{VI} to plutonium^{IV} occurred on adding 0·3 ml of freshly prepared 10% w/v iron^{II} ammonium sulphate before the first extraction. In the absence of nitrite ion, iron^{II} ion is capable of causing further reduction to inextractable plutonium^{III}. Normally, sufficient nitrite is present in nitric acid to stabilise plutonium^{IV} but occasionally poor extraction efficiencies were found (85–90%) and tentatively attributed to nitrite ion deficiency. In all subsequent analyses an adequate concentration of nitrite ion was ensured by adding 0·15 ml of 1*M* sodium nitrite solution together with the iron^{II} solution.

TABLE I.—CONDITIONING TO PLUTONIUM^{IV} USING IRON^{II}

All experiments performed on a solution containing 160 μg of plutonium^{IV} and 18·5 μg of plutonium^{VI} in 2 ml of 3*M* nitric acid

Experiment no.	Conditions	Plutonium in aqueous phase, μg	
		After one extraction	After two extractions
1	No Fe^{2+} present	13·5	10·5
2	No Fe^{2+} present	15·0	10·0
3	0·3 ml of 10% iron^{II} ammonium sulphate added before first extraction	6·9	0·2
4	0·3 ml of 10% iron^{II} ammonium sulphate added before first extraction	7.3	0·16
5	0·3 ml of 10% iron^{II} ammonium sulphate added after first extraction	14·0	2·4
6	0·3 ml of 10% iron^{II} ammonium sulphate added after first extraction	13·6	2·0
7	0·3 ml of 10% iron^{II} ammonium sulphate added after first extraction	14·0	(10·0)*
8	0·1 ml of 10% iron^{II} ammonium sulphate added before first extraction	14·0	3·0
9	0·5 ml of 10% iron^{II} ammonium sulphate added before first extraction	14·8	0·3

* High results caused by use of aged iron^{II} ammonium sulphate solution.

The most favourable acidity for extracting plutonium^{IV} from uranium-rich solutions is dependent upon the uranium concentration as illustrated in Table II. Throughout this work samples were adjusted to $2M$ nitric acid at 100–120 mg/ml of uranium by appropriate nitric acid addition. Some uranium is co-extracted with the plutonium but one wash of the solvent with $4M$ nitric acid reduces the uranium contamination of the solvent to an acceptable level; it also improves decontamination from fission product $\beta\gamma$-activity.

TABLE II. OPTIMUM NITRIC ACID MOLARITY FOR EXTRACTION OF PLUTONIUM^{IV} INTO 1% HYAMINE 1622/BENZENE AS A FUNCTION OF URANIUM CONCENTRATION

Uranium concentration, *mg/ml*	Optimum acidity	Plutonium extracted in a single stage, %
<10	4M	99·6
100	2M	98
300	1M	97

To test the overall performance of the optimised extraction procedure a number of synthetic 2-ml samples, initially 300 mg/ml of uranium, 50–150 μg/ml of plutonium, $3M$ nitric acid and containing added fission product activity, were conditioned with respect to plutonium valency and acidity as described above, then extracted twice with 1% Hyamine 1622 in benzene and the solvent washed once with 2 ml of $4M$ nitric acid. The plutonium contents of the aqueous phases from each extraction and of the $4M$ nitric acid wash were determined by α-counting, correcting for the presence of uranium where necessary. Plutonium losses are shown in Table III from which it is evident that an overall efficiency of 99·8% is achieved. The results also emphasise the necessity of the second extraction. The procedure gave decontamination factors of approximately 10^2 for uranium and 10^5 for fission products in agreement with the work of Powell.[10]

TABLE III. SUMMARY OF PLUTONIUM LOSSES IN THE EXTRACTION AND WASHING PROCEDURE

Solution	Aqueous after first extraction	Aqueous after two extractions	$4M$ nitric acid wash
Initial plutonium, %	1·5–2·0	<0·1	0·15–0·20

Determination of plutonium in the solvent extract

(a) *Evaporation and titration:* The Hyamine 1622 in benzene extract, together with Hyamine 1622 in benzene washings of the extractor, was transferred to the titration cell (Fig. 3) and the benzene removed by careful evaporation. Mechanical losses of up to 5% of the plutonium occurred when attempts were made to evaporate the entire volume (about 6 ml) at a single stage. Exhaustive trials using standard plutonium solutions showed that no loss of plutonium occurred when aliquots of about 1·5 ml were successively evaporated with gentle air stirring. Careful control of the heating was necessary to prevent charring of the non-volatile Hyamine 1622, an effect which causes undesirable masking of the end-point colour in the final titration.

After allowing the residue to cool, 0·05 ml of $4M$ nitric acid was added (to inhibit the formation of polymeric plutonium^{IV} species which do not react with EDTA) and the whole dissolved in acetone. A known volume of $0{\cdot}01M$ EDTA, in excess over the plutonium to be determined, was added, the solution buffered to pH 4·75 with ammonium acetate/acetic acid solution and sufficient further acetone added to yield a clear solution, followed by a fixed volume of 0·04 w/v % of dithizone. The volume of indicator added must be maintained constant[16] and for the most precise results the volume of buffer solution and acetone must also be controlled. The residual uncomplexed EDTA was titrated using $0{\cdot}004M$ zinc chloride solution, the green to pink end-point change being followed photometrically and the end-point taken as the point of inflexion of the graph of galvanometer reading against titre.

During the titration the tip of the microburette delivering the zinc chloride solution dipped just below the surface of the solution and to limit diffusion of Hyamine 1622 into the burette the aperture of the tip was reduced to approximately 0·006 inch. For the same reason, and to prevent gradual build-up of foam inside the microburette, the latter was completely emptied and refilled with fresh zinc chloride solution after each titration.

(b) *The blank titre:* A blank titre can arise from three sources, benzene, Hyamine 1622 and uranium co-extracted with the plutonium. The magnitude of the effect for the appropriate quantities of benzene and Hyamine 1622 is shown in Table IV. This compares the blank values with standardisation titres of zinc chloride against the normal volume of EDTA used per determination, benzene, Hyamine 1622 and uranium all being absent. Table IV, in which each figure is the mean of several determinations, indicates that double distillation of the benzene (Analytical Grade) sufficed to eliminate any effect from it. The Hyamine 1622 contribution could not be reduced, even by exhaustive washing with EDTA. Nevertheless the blank titre caused by 60 mg of Hyamine 1622 (the amount used per determination) is seen to be only 1 % of the total standardisation titre.

TABLE IV. CONTRIBUTION OF REAGENTS TO THE BLANK TITRE

Conditions	Hyamine and benzene absent	6 ml of benzene present		6 ml of hyamine 1622/ benzene present		60 mg of hyamine present
		As received	Twice distilled	Benzene as received	Benzene twice distilled	
Titre (micro-burette units)*	15·00	14·84	14·98	14·70	14·85	14·86

* 1 microburette unit = 0·020 ml.

To assess the blank contribution from uranium, sample analyses were simulated in the absence of plutonium by taking 2 ml of a solution of 3*M* nitric acid containing 300 mg/ml of uranium through the complete extraction, evaporation and titration procedure. Typical titres so obtained, which represent the total blank from benzene, Hyamine 1622 and uranium, are given in Table V, and comparison with Table IV shows the uranium contribution to be approximately equal to that from Hyamine 1622.

TABLE V. DETERMINATIONS OF TOTAL BLANK TITRE (REAGENTS + URANIUM)

	Laboratory solutions of uranium in nitric acid							Process plant solution after removal of plutonium				
Standardisation titre (micro-burette units)	15·10	15·05	15·10	15·12	15·10	15·10	15·10	15·03	15·05	15·02	15·10	15·01
Blank titre (microburette units)	14·76	14·75	14·80	14·84	14·83	14·80	14·78	14·71	14·75	14·64	14·74	14·62
Difference	0·34	0·30	0·30	0·28	0·27	0·30	0·32	0·32	0·30	0·38	0·36	0·39

Under the extraction conditions described some 5 to 6 mg of uranium enters the titration cell and since further experiments showed that the uranium blank was constant within the limit of experimental error over the range of 3 to 15 mg of uranium it is evident that this is not a source of bias in the method.

Further independent checks on the uranium blank (the constancy of which is difficult to explain) were performed by extracting process plant sample solutions with Hyamine 1622/benzene to remove plutonium, then submitting the uranium-bearing aqueous phase to the full extraction and titration procedure. The results obtained are also shown in Table V, and are seen to be in good agreement with those from laboratory uranium solutions.

Interferences

The Hyamine 1622 in benzene extractant is almost completely selective for plutonium and the method suffers little interference from foreign ions. Only those ions which co-extract with plutonium and react with EDTA or affect the end-point will give rise to interference. Foreign ions may be present as impurities in the reagents used and in the uranium, or as fission products and transuranic elements formed during irradiation of the uranium.

Reagent impurities are compensated for in the blank titration, where, as stated above, the only contribution observed is from the Hyamine 1622. Impurities in the uranium should be similarly accounted for, but since their level may vary from one source of uranium to another the effect of several commonly occurring impurities has been examined. Chromium and nickel do not interfere up to the 0·5 mg/ml level, which exceeds the impurity variation normally anticipated.

Fission product elements were examined collectively by making up a non-radioactive solution approximately simulating normal sample conditions and taking a number of 2-ml aliquots through the entire procedure. This solution, which had the following composition:

Element	Sr	Zr	Mo	Ru	Cs	La	Ba	Ce
Concn., *µg/ml*	5	15	12	7	15	25	5	10

produced no interference in either blank or plutonium titrations. A further solution was then prepared containing each element at a concentration of 1 mg/ml. Two-ml volumes of this solution (which represents fission product levels far in excess of normal circumstances) when subjected to the full procedure yielded a positive interference equivalent to 4 µg of plutonium.

Of the transuranic elements only neptunium-237 is produced in sufficient quantity to interfere. In the presence of the iron^{II} ammonium sulphate conditioner this will be present as neptunium^{IV} which readily extracts into the solvent and will probably interfere quantitatively. The bias so produced is normally much less than 1 % of the plutonium concentration. For accurate work this can be eliminated by performing the method against an external plutonium standard containing an appropriate concentration of neptunium, or with the aid of a correction graph of neptunium concentration against irradiation level.

Certain oxidising agents destroy the dithizone colour by oxidising the indicator to diphenylthiocarbadiazone.[17] Cerium^{IV} is the only such oxidant likely to be present in the sample solutions and this will be reduced to cerium^{III} by the iron^{II} ion conditioner.

Method

(a) *Safety considerations:* The procedure is carried out in a suitably shielded cubicle divided into two sections, a remote-handling section for the solvent extraction of the highly $\beta\gamma$-active sample and a semi-remote unit for the subsequent evaporation and titration of the extract, which is only slightly radioactive.

(b) *Standardisation:* To the clean, dry titration cell, arranged as in Fig. 2, add 2 ml of acetone and 1 ml of buffer solution. From an Agla microburette add an accurately measured volume (about 0·12 ml) of 0·01M EDTA solution, washing the tip of the microburette with a few drops of acetone before withdrawing it. Add 0·15 ml of 0·04% dithizone solution and titrate the solution with 0·004M zinc chloride solution from a second microburette, the tip of which should be immersed just below the surface of the solution. Stir the solution by a gentle flow of air between successive additions of titrant. As the end-point is approached make additions of 0·002 ml and record the galvanometer reading after each addition. Derive the end-point from the point of inflection of the plot of galvanometer reading against the titre. Carry out at least two standardisations to establish the satisfactory functioning of the burettes before commencing the analysis of a batch of samples. Table V shows the order of reproducibility which should be achieved.

(c) *Sample analysis:* Take an aliquot of the sample containing 100–200 µg of plutonium using the remotely controlled pipette (Fig. 4) and transfer it to extractor I of the solvent extraction unit (Fig. 1) using a 3-ml polythene cup as the transfer vessel. By the same means add sufficient dilute nitric acid to yield a final acidity of 2M and a uranium concentration between 100 and 150 mg/ml. Mix the contents of the extractor and add 0·3 ml of 10% iron^{II} ammonium sulphate, 0·15 ml of 1M sodium nitrite and

2 ml of 1 % Hyamine 1622 in benzene via the polythene cup. Mix the phases for 90 sec, allow them to separate, eject the aqueous layer into a second 3-ml polythene cup and transfer this solution into extractor II. Wash the cup with 2 ml of 1 % Hyamine 1622 in benzene solution and draw this into extractor II. Mix the phases and allow to separate as described above and eject the aqueous phase to the radioactive drain. Transfer the solvent in extractor II to extractor I, again using a polythene cup for the transference. Wash extractor II with 2 ml of 4*M* nitric acid and combine this solution with the bulked solvent extracts in extractor I. Mix the phases for 90 sec, allow them to separate, and reject the aqueous layer. A trace of the aqueous phase (about 10 μl) should be left with the solvent because it is essential that recovery of the solvent should be quantitative. Eject the solvent into a 5-ml polythene cup. Wash extractor I with 1 ml of 1 % Hyamine 1622 in benzene solution and eject this into a 3-ml polythene cup.

Using a glass tube drawn to a fine capillary bore at one end and with a rubber teat attached to the other, transfer 1 ml of the solvent from the 5-ml cup to the clean, dry titration vessel. Apply the heating current and stir the solution carefully with a gentle stream of air. Transfer the remaining solvent in small volumes, maintaining the volume of solution in the titration vessel at about 1·5 ml. Use the solvent in the 3-ml cup to wash the 5-ml one and finally use 1 ml of fresh solvent to wash both cups and the transfer tube. After the final addition of solvent to the titration cell allow the solution to evaporate to about 0·7 ml, switch off the heating current and remove the final traces of benzene by gentle air stirring. Allow the residue to cool, add 50 μl of 4*M* nitric acid and stir for 1 min. Add 1 ml of acetone followed by the appropriate accurately measured volume (normally 0·12 ml) of 0·01*M* EDTA delivered from a microburette. Stir gently, add 1 ml of ammonium acetate/acetic acid buffer solution (pH 4·75) and acetone to clarify the solution. Add 0·15 ml of 0·04 % dithizone solution and titrate the excess of EDTA using 0·004*M* zinc chloride solution according to the "standardisation" procedure.

(d) ***Blank determinations:*** Take a suitable aliquot of a solution of similar acidity and uranium concentration to the sample and carry this through the operations of section (c) above.

(e) ***Calculation of result:*** The concentration C of plutonium (μg/ml) of sample solution is given by:

$$C = 1000 \frac{W(v_2 - v_1)}{V} M$$

where v_1 and v_2 are the sample and blank titres (ml) V is the volume of the initial sample aliquot, M the molarity of the zinc chloride solution and W is the atomic weight of plutonium. W is not a fixed quantity since it depends upon the isotopic composition of the plutonium under examination, and this is a function of the irradiation dosage. For work requiring the highest accuracy it is necessary to run the sample analysis against an external plutonium standard of similar isotopic composition.

RESULTS

The accuracy and precision of the method have been extensively tested using both standard plutonium solutions containing a large excess of uranium, and on a homogenised volume of process solution. In the latter case standard additions of plutonium

TABLE VI.—PERFORMANCE OF METHOD ON STANDARD PLUTONIUM SOLUTIONS

Plutonium present in standard, *μg/ml*	Plutonium found, *μg/ml*	Standard deviation, σ
98·5	98·5, 98·9, 98·2, 98·3 98·2, 98·5, 98·9, 98·4 Mean value = 98·5	0·23 %
99·9	100·2, 100·5, 100·3, 99·5 100·8, 99·5, 100·3, 99·5 99·0, 99·6 Mean value = 99·9	0·43 %

TABLE VII. PERFORMANCE OF METHOD ON A BULKED PROCESS SOLUTION

Plutonium by Hyamine 1622/EDTA, *µg/ml*	Standard Deviation, σ	Plutonium by check method, *µg/ml*	Process solution + 98·5 µg of plutonium by Hyamine 1622/EDTA, *µg/ml*	Recovery, %
95·0, 95·0, 94·5				
95·5, 95·0, 94·6	0·37%	96·5[a]	194·2	100·6
95·5, 94·9, 95·6		94·8[b]	193·0	99·3
95·1		95·1[b]	193·2	99·5
Mean value = 95·1				

Notes [a] = radiometric method
[b] = absorptiometric method[9]

were made in some instances as a further check on its recovery and check analyses by α-counting and the Hyamine 1622/thoronol absorptiometric method[9] were carried out. Typical results are shown in Tables VI and VII. The method is capable of a standard deviation of 0·3–0·4% with an accuracy of about ±0·3% at the 100-µg plutonium level.

Zusammenfassung—Ein genaue und reproduzierbare Methode zur Bestimmung von Plutonium in einer salpetersauren Lösung der Produkte einer Uraniumbestrahlung ist beschrieben. Pu(IV) wird extrahiert unter Verwendung einer benzolischen Lösung des quaternären Amines, Hyamine 1622. Das Benzol wird durch Verdampfen entfernt; nach Lösen des Verdampfungsrückstandes in Aceton wird EDTA im gemessenen Überschuss zugesetzt und der Überschuss mit zink zurücktitriert. Dithizon dient als Indicator; der Endpunkt wird photometrisch festgestellt. Die Extraktion ist hochselektiv für Pu. In einem zweistufigen Cyklus ist der Decontaminierungsfaktor 10^5 für Fissionsprodukten und 100 für Uran. Unter gut kontrollierten Bedingungen beträgt die Standardabweichung der Methode 0.4% für 100 µg Pu.

Résumé—Les auteurs décrivent une méthode précise de dosage de plutonium dans des solutions dans l'acid nitrique, d'uranium irradié. Le plutonium(IV) est extrait par une amine quaternaire: hyamine 1622 dissoute dans le benzène; le benzène est séparé par évaporation et, après dissolution du résidu dans l'acétone, un excès d'EDTA est ajouté; l'EDTA non complexé est titré par photométrie avec une solution de chlorure de zinc étalon et la dithizone comme indicateur. L'estraction est spécifique du plutonium, et il résulte d'une opération en deux étapes un facteur de décontamination approximativement de 10^5 pour les produits de fission mélangés et de 100 pour l'uranium. Dans des conditions soigneusement controlées, la méthode conduit à un écart standard de 0,4% pour des quantités de 100 µg de plutonium.

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THE REGENERATION OF SPENT MAGNESIUM PERCHLORATE DESICCANT

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Summary—The regeneration of spent magnesium perchlorate is described.

Directions are given for the purification of perchlorate for recovery. Exfoliated vermiculite is employed as carrier base. A description is given of the compounding of a carrier-based granular product by absorption of a saturated aqueous solution of magnesium perchlorate and the dehydration to form a finished product of bulk density 20·5 lb per cu ft. The fraction retained on a 10-mesh sieve and passing through a 5-mesh sieve is approximately 75% anhydrous magnesium perchlorate in a highly dispersed condition.

The testing of carrier-based anhydrous magnesium perchlorate for drying efficiency is described.

GENERAL CONSIDERATIONS

DEHYDRATED magnesium perchlorate for use as a desiccant was first studied by Willard and Smith in 1922.[1] In the form of $Mg(ClO_4)_2{\cdot}3H_2O$ it was proposed as a desiccant for use in organic combustion analyses in the determination of carbon and hydrogen, and for the determination of carbon in steel by combustion in oxygen. Vacuum drying equipment in the manufacture of the anhydrous material, for use in general analytical applications, was described by Smith and Rees.[2] A thorough study of the properties of magnesium perchlorate in the form of its hexa-, tetra-, and dihydrates as well as in the anhydrous granular porous form was made by Smith, Rees and Hardy.[3] Their studies were reprinted in a booklet by Smith[4] which includes a study of the use of anhydrous magnesium perchlorate in the dehydration of air for liquifaction and fractionation to prepare high pressure tank oxygen. For this purpose it was successfully applied[5] for a period of six months in a study of the efficiency attained in plant practice. An increase in plant yield of oxygen and a material saving in power consumption were demonstrated. Anhydrous magnesium perchlorate is now a standard desiccant, commercially available under the trade names *Dehydrite* and *Anhydrone* as well as under its chemical designation. Its use in laboratory desiccators was described by Smith, Bernhart and Wiederkehr.[6] Its use in the preparation of anhydrous perchloric acid, through dehydration of the aqueous acid and vacuum distillation, was described by Smith.[7] The American Chemical Society Reagent Specifications[8] require the maximum water content to be less than 10%. Commercially available "anhydrous" magnesium perchlorate is manufactured to contain approximately 5% of residual water. A rapid test for its water content has been described by Smith.[9]

According to data published by Bower at the U.S. Bureau of Standards,[10] anhydrous magnesium perchlorate would appear to be less efficient in the absorption of water than phosphorus pentoxide. This is, however, incorrect, since it has been shown[3] that phosphorus pentoxide is ineffective in the dehydration of magnesium perchlorate dihydrate to the anhydrous product at any temperature up to over 100°, or, indeed, at any higher temperature at which phosphorus pentoxide may be effectively employed. An exhaustive study by Diehl and his associates[11] shows that anhydrous magnesium perchlorate leaves in a gas stream only one twentieth of the amount of water left by phosphorus pentoxide at its best performance. The capacity for the absorption and adsorption of water by anhydrous magnesium perchlorate is roughly 35 % of the weight of the starting product. An industrial supply of anhydrous magnesium perchlorate has been provided, following a complete description of the operations involved.[4] The dew point of air, dried by anhydrous magnesium perchlorate, is approximately the same as that at the temperature of liquid air.

The statement is often made that a given desiccant is highly efficient but that it may be readily regenerated. Such statements have no justification. The more efficient a desiccant is the more difficult is its regeneration. The object of the present work is to describe a practical method for the regeneration of anhydrous magnesium perchlorate.

One of the most outstanding properties of anhydrous magnesium perchlorate is its high temperature coefficient in the absorption of water vapour. It has been shown to absorb water efficiently at temperatures in excess of 150°. It reacts with ammonia quantitatively to form di-, tetra-, and hexammoniates.[12] Magnesium perchlorate diammoniate retains its absorbed ammonium at temperatures in excess of 175°. Anhydrous magnesium perchlorate is stable at 290°, at or below which temperature no dissociation with the evolution of oxygen can be observed. It has been prepared in 95 % yield by the dry reaction of mixtures of ammonium perchlorate and magnesium oxide heated in vacuo to 250–260°.[13] As a result of the preparation of anhydrous magnesium perchlorate by high vacuum dissociation of its hexahydrate, unaccompanied by fusion, the finished desiccant has an exceptionally high porosity caused by capillary voids. By virtue of this property, alcohol vapours, and a number of other volatile organic vapours, are readily adsorbed quantitatively. This has been employed analytically. It is also of great importance when magnesium perchlorate is used for the dehydration of air in the manufacture of liquid air. The contamination by cracked hydrocarbons from oil lubricated pressure pumps of the air being liquified does not pass into the liquid oxygen of the fractionation column used to separate oxygen from nitrogen. Thus explosion hazards from contact of the oxygen with an accumulation of organic matter are eliminated.

Granular anhydrous magnesium perchlorate, with added colour to indicate its exhaustion as desiccant by a colour change, has been described by Smith.[14] As shown by Nemeth,[15] this has a very valuable advantage when using Pregl tubes for micro carbon and hydrogen determination in organic combustion analyses. This indicating desiccant was prepared at the request of Lieb.

REGENERATION OF SPENT MAGNESIUM PERCHLORATE DESICCANT

Spent magnesium perchlorate desiccant is unsuited for immediate regeneration, since it may be contaminated by impurities such as organic matter which, at the temperatures required, would be objectionably reactive. The first step should be the dissolution of the spent reagent in water, followed by filtration and boiling to volatilise organic impurities. The boiling, which occurs at a temperature of 130–135°, followed by slow cooling, causes the deposition of large crystals of the hexahydrate. The cooled crystals and accompanying saturated aqueous solution are centrifuged to separate off the crystals, and the residual solution is mixed with further solutions which are then subjected to similar crystallisation processes. The hexahydrate may then be dehydrated in stepwise fashion in electrically heated vacuum ovens to form, successively, the tetrahydrate, then the dihydrate, and finally the anhydrous finished product. These operations must be carried out at predetermined maximum temperatures for each stage of the dehydration as described previously.[4] This process is unsuited to small-scale regeneration of spent desiccant, but has been used by the manufacturers for large-scale regeneration in applications such as that described previously.[5] For small-scale regeneration of spent magnesium perchlorate desiccant a practical procedure involves the addition of a supporting base or carrier. By proper selection of carrier, the recovered reagent can be compounded in granular form to give a product with a high surface of contact which is not dependent upon dehydration without fusion, as is the case when starting with crystals of the hexahydrate.

EXPANDED VERMICULITE AS A GRANULATED DESICCANT CARRIER

Expanded vermiculite, which is a bulk material now commercially available, is sold under various trade names one of which is *Zonolite*. This product is commonly supplied for use as an insulating material for air-conditioning household insulation or for use as aggregate in the compounding of light weight "concrete" in combination with cement and other ingredients. Another extensive use of expanded vermiculite is as absorbent packing material for transportation of corrosive liquids in glass; the packing material serves as cushioning material to protect against breakage with rough handling or to serve as a non-reacting absorbent in case of breakage of containers in transit. Expanded vermiculite has a bulk density of approximately 6·5 lb per cu ft. The average analysis of seven different samples of mined vermiculite is given in Table I.

Vermiculite occurs in broad crystals or crystalline flakes with a yellowish-brown, greenish-black, or greenish-yellow colour. It has a soapy graphitic feel. Deposits of vermiculite are found in many parts of the world. The American deposits are located in Montana, Colorado, and Wyoming. At 110°, with gradual heating, half of the water content is expelled without distortion of the original physical conglomerate.

TABLE 1. AVERAGE ANALYSIS OF SEVEN NATURALLY OCCURRING VERMICULITES, SP.GR.APP. 2·13.

Unit Cell—4 Moles-$[(OH)_2(Mg,Fe)_3(Si,Al,Fe)_4O_{10}\cdot 4H_2O]$

	Analysis, %	Theoretical	Composition
SiO_2	35·04	36·71	22 SiO_2
Al_2O_3	14·55	14·15	5 Al_2O_3
Fe_2O_3	5·13	4·43	Fe_2O_3
FeO	0·59		
NiO	2·44		
MgO	21·71	24·62	22 MgO
CaO	0·46		
H_2O	19·99	20·09	40 H_2O

Average Formula: $22\ MgO\cdot 5\ Al_2O_3\cdot Fe_2O_3\cdot 22\ SiO_2\cdot 40\ H_2O$

EXFOLIATION OF VERMICULITE AT 1000–1100°

The most outstanding properties of vermiculite are its exfoliation when exposed to elevated temperatures and its chemical inertness in the heat-expanded form. The surface of a sample of vermiculite, as mined, was measured by Brunauer, Emmett, and Teller[16] by nitrogen adsorption at $-195°$, and was found to be 0·52 m^2 per g. The platelet thickness calculated from this is 1·8 μ when the theoretical density of 2·13 is assumed. This indicates that vermiculite is extensively fissured before exfoliation. The same sample of vermiculite was exfoliated by heating for 5 min at 950°. There resulted a silvery-white accordion-like structure, and the change was associated with a loss in weight of 19·6%. The surface area of the exfoliated sample was 10·35 m^2 per g, and the calculated platelet thickness was 0·091 μ.

Vermiculite consists of sheets of magnesium aluminum silicate of 9·26 Å thickness with alternate layers of 8 H_2O spaced at about 4·8 Å.[17] The exfoliated vermiculite has platelets 200 times this thickness; Gruner[17] suggests that this is because of structure collapse above 750°, and that it indicates that exfoliation is a mechanical process consequent on the formation of steam.

It is claimed that a modified procedure for exfoliation[18] produces a much greater surface.

PREPARATION OF EXPANDED VERMICULITE AS CARRIER-BASE MATERIAL

Expanded vermiculite, as supplied to the building trade, is granular, with a maximum particle size of 10–12 mm. This material is sifted to any suitable intermediate granular size and is ready for impregnation. A particle size passing 5-mesh and retained on a 10-mesh screen* is appropriate for use in the process described below.

IMPREGNATION OF EXPANDED VERMICULITE WITH AQUEOUS MAGNESIUM PERCHLORATE AND DEHYDRATION

The saturated aqueous solution of magnesium perchlorate recovered as described above, and at ordinary temperature, is placed in a large vacuum desiccator. The vermiculite carrier, contained in a wire basket with a wire screen closure at the top, is completely immersed in the perchlorate solution. Vacuum is then applied followed by release to ordinary pressure, and this operation is repeated a number of times. By this procedure the carrier absorbs the maximum amount of the hydrated desiccant and excess solvent. Upon removal from the saturating solution, the product is allowed to drain for a few min and is then ready for dehydration to carrier-based anhydrous magnesium perchlorate desiccant. The material thus formed does not "weep", either in the original saturated form or during the subsequent dehydration.

An electric muffle furnace is suitable for the dehydration. The impregnated carrier-based product is spread on trays made of nichrome gauze or a substitute material to a depth of 1–2 cm. Wire mesh trays with 2–3-cm sides, which stack one upon the other leaving ample space between the layers of material to be dehydrated, are used. The muffle furnace should be set to give a maximum temperature of 230 to 250°. The product can be placed in the muffle at this temperature. No bleeding of the carrier granules will result. Drying under atmospheric pressure is continued for 24–48 hr or to constant weight of the finished product. (For the commercial preparation of carrier-based anhydrous magnesium perchlorate, specially constructed high-vacuum drying ovens are used.)

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* This sifted product constitutes approximately 35–45% by weight of a starting material which is commercially available at $0·50–0·60 per cu ft.

PHYSICAL CONSTANTS OF CARRIER-BASED ANHYDROUS MAGNESIUM PERCHLORATE

The physical constants of the desiccant prepared as described are as follows:

Bulk density: 328 g per 1000 ml or 9287 g (20·5 lb) per cu ft.

Carrier weight: 23·75 % or 4·86 lb per cu ft.

Anhydrous magnesium perchlorate: 76·25 % or 15·62 lb per cu ft.

TESTING OF DRYING EFFICIENCY AND CAPACITY

A cylindrical drying tower constructed of stainless steel, 200 mm (8 in.) in diameter and 600 mm (24 in.) high, was employed. This was fitted with a tube passing from the top to the bottom for the admission of moist air, a pressure gauge of range 0–100 psi, and a discharge vent at the top with needle-valve control. The total volume was 19,060 ml (0·673 cu ft.). The air intake was connected to the laboratory compressed air line through an open valve. The pressure in the drying tower ranged from 60 to 68 psi, and was mostly, during the off-peak load demand, at the higher pressure. The air supply was saturated with water vapour at the ambient temperature and the pressure prevailing.

The rate of flow of gas from the drying power was measured by a standard wet-test meter and was adjusted to 1 cu ft (28317 ml) per min, continuously operated.

The effluent line was sampled at 24-hr intervals. A Pregl micro-combustion absorption tube charged with anhydrous granular Indicator Anhydrone[14] was used for this operation. The rate of gas flow through the Pregl tube was approximately 150 ml per min, and 5000 ml of withdrawn dehydrated air was passed for each test to determine drying efficiency. The performance of this test for 12 consecutive days is shown in Fig. 1.

EFFICIENCY OF DEHYDRATION

Fig. 1 shows that after the passage of more than 10,000 cu ft of air the complete removal of water was attained over a period of 7 days. By direct determination each

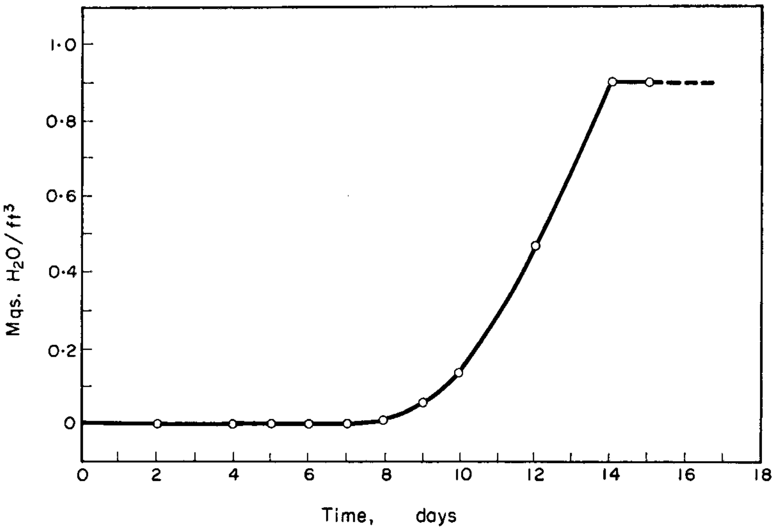

FIG. 1

cu ft of dried air contained 0·1507 g of water vapour or 3·548 lb of water in 10,000 cu ft. The carrier-based anhydrous magnesium perchlorate in the 8 × 24 inch absorption tower weighed 13·8 lb. Therefore the capacity of the desiccant for perfect absorption of water under the conditions described was 25·71 % of the original weight of desiccant. The anhydrous magnesium perchlorate content of the carrier-based desiccant was 10·32 lb. Thus the perchlorate desiccant adsorbed 34·4 % of its weight, which corresponds to the capacity of granular, porous anhydrous magnesium perchlorate employed without added carrier-base. The second stage of dehydration efficiency involves the absorption of water by conversion of $Mg(ClO_4)\cdot 2H_2O$ to the tetrahydrate. The absorption of water at this stage is inefficient to the extent of 0·85 mg per litre of air dried, or approximately 16 mg per cu ft.

Zusammenfassung—Die Regenerierung von verbrauchtem Magnesiumperchlorat wird beschrieben. Anweisung zur Reinigung des Perchlorates werden mitgeteilt. Vermiculit wird als Träger verwendet. Magnesiumperchlorat wird als gesättigte, wässrige Lösung auf den Träger gebracht; nach Dehydratation erhält man ein granuliertes Endprodukt. Die Schüttdichte des Produktes is 20.5 Pfund per Kubikfuss. Die Teilchengrösse entspricht 75 % zwischen 10-Maschensieb und 5-Maschensieb. Die Wirksamkeit des auf dem Träger befindlichen Perchlorates wurde überprüft und als zufriedenstellend gefunden.

Résumé—L'auteur décrit la régénération de perchlorate de magnésium. Des directives pour la purification du perchlorate à récupérer sont données. La vermiculite exfoliée est utilisée comme entraineur. La combinaison de l'entraîneur à base de produit granulaire par absorption d'une solution aqueuse saturée de perchlorate de magnésium et la déshydratation pour former le produit final sont décrites. On obtient ainsi un produit fini de densité: 20,5 livres par pied cubique. Le produit fini de dimension particulaire, retenu sur un tamis de 10 mesh et passant à travers un tamis de 5 mesh, contient approximativement 75 % de perchlorate de magnesium anhydre sous forme très dispersée. Le pouvoir desséchant du perchlorate de magnésium anhydre est contrôlé.

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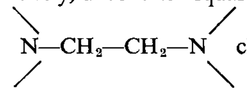
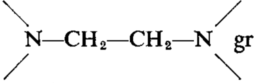
PRELIMINARY COMMUNICATIONS

Selective chelatometry of copper^{II} with ethylenediamine-*N,N,N',N'*-tetra-n-propionic acid

(*Received* 26 *October* 1961)

In a recent review of some aspects of the selectivity of chelatometric titrations it has been indicated that, without recourse to auxiliary complexing agents, selectivity of titration with reagents of the complexan group is only possible by the simultaneous availability of selective chelating agent *and* selective pM indicator.[1] In the same paper, the high selectivity of ethylenediamine-*N,N,N',N'*-tetra-n-propionic acid, referred to subsequently as EDTP, and the -*N,N'*-di-n-propionic acid (EDDP) towards copper^{II} ion[2] was stressed. The strength of the copper^{II} chelates of these reagents relative to their chelates with magnesium, cadmium, *etc.* was attributed to the (relatively) uncommon square-coplanar habit of the copper^{II} ion and the presence in both reagents of the  $>N-CH_2-CH_2-N<$ chain. The replacement of acetic acid groups (EDTA) by n-propionic acid groups critically weakens the strength of the primary chelate ring for most metal ions and results in low stability constants for the EDTP and EDDP chelates of magnesium ($10^{1.8}$, $10^{1.6}$), cadmium ($10^{6.0}$, $10^{5.6}$), *etc.*,[2] whereas the steric disposition of the copper^{II} bonding and its well known tendency to react well with molecules containing  $>N-CH_2-CH_2-N<$ groups ensures efficient chelation of copper ($10^{15.4}$ $10^{15.1}$).

The above findings suggested to us that these reagents should serve as useful titrants for copper^{II} in the presence of several other ions; but such a reagent is of no avail with conventional metallochromic indicators since these will respond to the presence of other metal ions such as magnesium, *etc.* However, two virtually specific indicators for copper^{II} have been described previously *viz.* Fast Sulphon Black F[3] and Ponceau 3R.[4] The first of these indicators responds only to copper^{II} and nickel and the second also to copper and nickel. In both cases the quality of the nickel end-point is poor.

In our preliminary experiments, of which this communication is a brief report, the EDTP/Ponceau 3R system was explored using $10^{-2}M$ solutions of copper^{II}, other metals and the complexan. The titrations were carried out using an Agla micrometer syringe burette, with a total volume of titration medium of approximately 1 ml. Ponceau 3R works most effectively at pH $\approx$ 9 in an ammoniacal medium, when the colour change is from yellow to red. The quality of the end-point in the EDTP titration of copper^{II} is only slightly inferior to that with the considerably stronger complexan EDTA. Interference studies were carried out with *ca.* 60 μg of copper^{II} and varying concentrations of magnesium, calcium, barium, strontium, cadmium, manganese, zinc, lead, cobalt, nickel and aluminium. When EDTA was used as titrant all of these titrated additively with the copper. With EDTP, however, no interference was found from 10 molar ratios of magnesium or calcium or from 5 molar ratios of strontium, barium and cadmium. No attempt was made to find the upper limit of non-interference of these five ions. Manganese^{II} did not interfere up to a 2 molar ratio, but larger amounts promoted sluggish end-points and low copper recoveries, presumably caused by coprecipitation of some copper with manganese hydroxide. Cobalt interfered, of course, by virtue of its colour and zinc and lead could not be held in solution at pH 9. A slight raising of the pH to 10 allowed the titration of copper in the presence of a 1 molar ratio of zinc, though the quality of the end-point was considerably impaired at this pH. Nickel titrated as copper with a sluggish end-point while aluminium could be maintained harmlessly in solution by the addition of fluoride ion.

The procedure was applied successfully to the small-scale analysis of copper in a standard brass sample (70.8% of Cu, 24.17% of Zn, 1.85% of Sn, 2.52% of Pb, 0.31% of Fe, 0.12% of Mn, 0.17% of Ni). The brass was dissolved in the usual way, the solution diluted, the pH adjusted to 9-10 and the copper titrated directly with EDTP without significant interference from the other elements present.

Further more detailed experiments will shortly be initiated with Fast Sulphon Black F[3] as indicator. This indicator functions at pH $\approx$ 11 where aluminium, lead, zinc, *etc.* can be held in solution. The indicator action of Ponceau 3R is rather dependent on electrolyte concentrations and pH; but it was used in these preliminary small-scale experiments because it is rather more sensitive.

EXPERIMENTAL

Reagents

$10^{-2}M$ *EDTP:* Prepared by condensation of 3-chloro-n-propionic acid with ethylenediamine.

$10^{-2}M$ $CuSO_4$*:* Standardised against EDTA.

Indicator: 0.25% aqueous Ponceau 3R.

Buffer: 54 g of NH_4Cl plus 22 ml of NH_3 solution (sp. gr. 0.88), diluted to 1 litre.

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Summary—A highly selective complexometric titration of copper^{II} is reported using the complexan ethylenediamine-*N,N,N′,N′*-tetra-n-propionic acid and a selective metallochromic indicator.

Zusammenfassung—Es wird eine Methode fur eine hoch-selektive complexometrische Titrierung von Kupfer(II) mittels. Athylendiamin-*N,N′*-tetra-n-propionsaüre und ein selektives metallochromisches Indikator angelgeben.

Résumé—On décrit une méthode complexométrique pour le dosage de cuivre (II) par l'acide ethylénediamine-*N,N,N′,N′*-tétra-n-propionique avec un indicateur métallochromique.

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Analytical aspects of the oxidation of organic nitrogen compounds with chromic acid

(*Received* 4 *September* 1961.)

THE oxidation of a series of organic nitrogen compounds from different classes with chromic acid in a medium of dilute sulphuric acid has been systematically investigated. From the consumption of the oxidising agent, oxidation numbers have been calculated and defined as the amount of oxygen in grams consumed by the oxidation of 100 grams of the substance. The oxidation numbers calculated from the experimental data have been compared with the theoretical ones that had been calculated from the oxidation equations for the tested compounds. In most cases a good agreement was found, the following processes being taken into consideration:

Carbon and hydrogen are oxidised to carbon dioxide and water, respectively, nitro and nitroso groups (attached to carbon, nitrogen or oxygen) being oxidised to nitric acid; two nitrogen atoms attached to each other as in azo compounds, hydrazines, pyrazoles, *etc.*, are split off in the form of elementary nitrogen and aromatic amino groups are converted into ammonia. From halogen compounds, chlorine and bromine are liberated in the form of the elements, while iodine is oxidised to iodic acid. All groups containing sulphur are ultimately oxidised to sulphuric acid.

The oxidation numbers of oximes were, however, lower or higher than the theoretical values when considering the quantitative conversion of the isonitroso group into nitric acid or, alternatively, elementary nitrogen. Amino groups containing one or two methyl groups attached to nitrogen gave lower oxidation numbers than would be expected in the case of quantitative formation of ammonia. This is apparently caused by the partial splitting off of nitrogen as methylamine or dimethylamine, which are relatively stable to the oxidising agent. The oxidation number of a nitrogen compound, however, in connection with its molecular formula, may provide the first information of the nature of the nitrogen functional groups present in the substance under investigation.

Because of the different behaviour of various nitrogen functional groups to chromic acid, new semimicro methods for the selective determination of some forms of nitrogen in organic compounds either separated or combined have been worked out. The elementary nitrogen, split off during the heating of the reaction mixture from groups containing the N—N bond, is collected and measured in a nitrometer. After reducing the chromic acid with iron^{II} sulphate and rendering the reaction mixture alkaline, the ammonia, formed from most types of amino groups, is distilled off and titrated in the usual way. Methylamine or dimethylamine, originating from N-methyl groups which may be present, are distilled off and titrated together with ammonia. The nitric acid formed from the nitro or nitroso groups is then reduced in an alkaline medium with Devarda's alloy to ammonia, which is determined as mentioned above.

The selective determination of various forms of nitrogen and their ratio to the total nitrogen may be of considerable importance for solving problems of constitution.

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Summary—The oxidation of a series of organic nitrogen compounds of different types with chromic acid in dilute sulphuric acid has been examined. The method can provide useful information about the nature of the compound.

Zusammenfassung—Die mit Chromsäure in verdunnte Schwefelsäure Oxydation einer Reihe von organischen Stickstoff-verbindungen underen Arten wird untersucht. Die methode befert wertvolle Auskunft über der Natur der Verbindung.

Résumé—On a examiné l'oxydation d'une série de composés organiques d'azote de types divers, utilisant l'acide chromique dans l'acide sulfurique dilué. Cethe méthode fournit des indications utiles sur la nature des composés.

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SHORT COMMUNICATIONS

Coulometric titration by electrogenerated tin^{II} ion

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THE electrogenerated reducing agents titanium^{III},[1] iron^{II},[2] chromium^{II},[3] uranium^{IV} [4] and copper^{I} [5] have been used for the application of the coulometric titration in chemical analysis. Strong reducing agents have low standard oxidation-reduction potentials, so that the electrolytic generation of hydrogen takes place easily on the surface of the cathode, favouring the use of the less versatile mercury cathode of large hydrogen over-potential rather than a solid cathode. Although tin^{II} ion has long been known as a reducing reagent in conventional titrations, it is very unstable to the action of oxygen in air or water and therefore needs to be stored in the absence of air and restandarised each time it is used. This defect may be overcome by using electrogenerated tin^{II} ion in a coulometric titration. The standard oxidation-reduction potential of tin^{II} ion is $+0{\cdot}05$ V *vs.* N.H.E. and its reducing power is weaker than that of titanium^{III} or of chromium^{II}, but stronger than that of iron^{II} or of ferrocyanide.

During the course of the present study, Bard and Lingane[6] published a coulometric titration method using tin^{II}. According to their work, from the standpoint of the current efficiency bromide solution is more favourable than chloride solution as a supporting electrolyte and also a gold electrode or platinum electrode with tin oxide film on its surface gives about 100% current efficiency.

EXPERIMENTAL

Apparatus and reagents

A constant current source, titration cell, potentiometer for end-point detection, time measuring apparatus and stirrer form the coulometric apparatus.[7] The present titration was carried out in a current of nitrogen gas, because tin^{II} ion is readily oxidised in air.

All of the reagents were of commercial special grade, and water was purified by ion-exchange, then boiled and cooled. Nitrogen was purified by passing it through pyrogallol-sodium hydroxide solution followed by water.

DISCUSSION AND RESULTS

The current efficiency was investigated at various compositions of the electrolytic solution by titrating cerium^{IV} sulphate solution with electrogenerated tin^{II} ion. In the electrolyte solution, hydrochloric acid, sulphuric acid, potassium chloride solution as well as hydrochloric acid-potassium chloride solution were employed. Tin^{IV} chloride was dissolved to give a $0{\cdot}2M$ solution. The generating cathode was a platinum plate (2×2 cm^2). In the coulometric titration of $0{\cdot}01N$ cerium^{IV} sulphate solution at a current of 5 mA, only potassium chloride solution could be used, because at the concentrations employed with the other electrolytes hydrogen gas was evolved on the surface of the generating cathode, resulting in markedly low current efficiencies. Further, the hydrogen gas absorbed on the surface of the indicating platinum electrode disturbs the potential indicator system. The evolution of hydrogen gas increased with the concentration of acid. On the contrary, it was observed that the electrolytic solution became turbid or produced a white precipitate instantaneously or sometimes when tin^{IV} chloride was dissolved in hydrochloric acid ($<0{\cdot}1N$), sulphuric acid ($<0{\cdot}6N$) or potassium chloride solution ($<0{\cdot}2M$).

In the following experiment, $3M$ potassium chloride, ammonium chloride or $3N$ hydrochloric acid was employed for the electrolyte solution. The results are summarised in Table I. According to Table I, potassium chloride solution gives the highest current efficiency. The results obtained at an electrolytic current of 5 mA indicated current efficiencies which were, respectively, about 80% and 60% in ammonum chloride solution and hydrochloric acid.

TABLE I. COULOMETRIC TITRATION OF CERIUM^{IV} BY ELECTROGENERATED TIN^{II} IN VARIOUS ELECTROLYTIC SOLUTIONS

Electrolyte solution	Ce^{IV} taken, *mequiv.*	Electrolytic current, *mA*	No. of expt.	Electrolytic time, *sec*	Std. devn., *sec*
3*M* KCl	0.01824	10.005	5	187·5	1·83
3*M* KCl	0·03648	9·975	5	372·3	3·90
3*M* NH_4Cl	0·01824	10·000	4	200·7	2·07
3*N* HCl	0·01824	9·986	3	417·4	58·2

Although the current efficiency for 3*M* potassium chloride solution does not exceed 95%, the standard deviation is about 1%, so that 3*M* potassium chloride solution can be employed as an electrolyte for tin^{II} coulometry.

Next, the effect of the concentration of tin^{IV} on the current efficiency was examined. The electrolytic solution was composed of 0·5, 0·3, 0·2, 0·1, 0·05 or 0·015*M* tin^{IV} chloride and 3*M* potassium chloride solution. One ml of 0·015*N* cerium^{IV} sulphate solution was titrated with electrogenerated tin^{II} at a current of 5 mA. The current efficiency increases with the concentration of tin^{IV} chloride up to 0·2*M* when it reaches a maximum of 94 ~ 96%.

The effect of the concentration of potassium chloride was then studied. The coulometric titrations of 1 ml of 0·015*N* cerium^{IV} sulphate were carried out with electrogenerated tin^{II} at a current of 5 mA in potassium chloride solutions of concentrations varying from 0·2 to 3*M*. The current efficiency is not less than 95% above a concentration of 2*M* potassium chloride, but falls off below this concentration of potassium chloride.

Summarising the results obtained, the mixture of 0·3*M* tin^{IV} chloride and 3*M* potassium chloride is considered to be the most suitable for the present coulometric titration. Cerium^{IV} ion, free iodine and bromine can be reduced instantly and quantitatively by tin^{II} ion, so that the tin^{II} coulometric titration method can be applied to the determination of these substances. One hundred ml of 0·3*M* tin^{IV} chloride and 3*M* potassium chloride solution were employed, tin^{II} being electrogenerated at a current of 10 mA. After passing nitrogen gas through the solution for about 10 min to remove the dissolved oxygen, the sample solution was introduced, then titration commenced in the nitrogen atmosphere. The end-point was detected either potentiometrically or amperometrically. In Table II,

TABLE II. COULOMETRIC TITRATION OF CERIUM^{IV}, BROMINE AND IODINE

Sample taken, *mequiv.* ($\times 10^{-2}$)	Electrolytic current, *mA*	No. of expts.	Electrolytic time, sec	Sample found, *mequiv.* ($\times 10^{-2}$)	Error, %
Ce^{IV} 0·814	5·097	2	156·3	0·829	2·0
Ce^{IV} 1·628	5·096	2	318·6	1·683	2·4
Ce^{IV} 2·452	5·099	2	485·4	2·565	4·6
Ce^{IV} 4·070	10·076	4	412·2	4·302	5·8
Ce^{IV} 8·140	10·094	4	820·8	8·586	5·5
Ce^{IV} 21·275	14·707	2	1428·4	21·771	2·1
Iodine 2·084	10·055	5	212·4	2·217	6·4
Iodine 5·210	10·055	3	523·1	5.446	4·5
Iodine 20·84	10·160	3	2039·5	21·309	2·3
Bromine 1·010	10·036	5	104·4	1.085	7·4
Bromine 2·020	10·030	5	206·6	2·147	6·3
Bromine 5·050	10·046	4	511·7	5·327	5·5
Bromine 10·10	10·030	4	997·0	10·359	2·6
Bromine 20·20	10·030	3	1963·3	20·559	1·8

the coulometric titration of cerium^{IV} ion and iodine used the potentiometric method and that of bromine used the amperometric method. In the amperometric detection, the indicating current was expressed with the voltage drop measured through the definite resistance, when the voltage 0·3 $\sim$ 0·4 V was applied between the two platinum electrodes through 100 kΩ resistance.

In conclusion, the coulometric method with tin^{II} ion is considered to be more versatile using a solid electrode such as platinum than that with titanium^{III} or chromium^{II} ions in which cases the mercury electrode is forced to be employed in place of the solid electrode.

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Summary—The coulometric method of electrogenerated tin^{II} ion using the platinum electrode as a generating cathode has been investigated. The electrolytic solution comprising 3*M* potassium chloride and 0·3*M* tin^{IV} chloride has been found to be satisfactory for the determination of cerium^{IV} ion, iodine and bromine with an error of only a few percent provided suitable conditions are employed.

Zusammenfassung—Coulometrie mit Zinn(II)-ionen (an einer Platinelektrode erzeugt) wurde untersucht. Eine elektrolyt welcher 3M in Kaliumchlorid und 0,3M in Stannichlorid ist wurde für die Titration von Cer(IV), Jod und Brom geeignet gefunden.

Résumé—Les auteurs ont étudié la coulométrie à l'aide de l'ion stanneux préparé par électrolyse, en utilisant une cathode de platine. Ils ont trouvé qu'une solution contenant du chlorure de potassium 3 M et du chlorure stannique 0,3 M convenait pour le dosage du cérium (IV), de l'iode et du brome.

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Photometric titrations-IV:* The chelometric titration of cadmium in the presence of zinc

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Sweetser and Bricker[1] described the EDTA titration of cadmium in the presence of zinc, with a photometric end-point at 236 mμ. The titration is performed in strongly alkaline medium where zinc is present as unreactive zincate, and cadmium is kept in solution by the addition of a small amount of cyanide. The disadvantages of this procedure are: operating at a very short wavelength, the high alkalinity, and the fact that the amount of cyanide added is critical. It therefore seemed worthwhile to search for a possibility of performing such a determination under more favourable conditions.

The numerical values of the stability constants of cadmium-chelonates are always very close to those of the corresponding zinc complexes with only one remarkable exception, namely, EGTA [ethyleneglycol-bis(aminoethyl)-tetra-acetic acid]. The logarithms of the stability constants of the EGTA complexes of cadmium and zinc are 16·7 and 12·8, respectively.[2] This difference of 3·9 logarithmic units refers to the absolute constants. In a practical titration the apparent stability constants have to be taken into account, and their difference can be increased by the use of an appropriate medium, such as an ammonia buffer. The logarithms of the β-factors of cadmium and zinc in an ammonia-ammonium chloride buffer pH 10 (total concentration 0·1*M*) are 3·9 and 8·6 respectively.[3] Hence the difference in the apparent stability constants under these conditions is 4·7 logarithmic units. This difference should be sufficient to permit the potentiometric titration of

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* Part III—see *Talanta*, 1961, **8**, 885.

cadmium in the presence of zinc employing the mercury drop electrode.[4] This approach is at present under investigation in the authors' laboratory.

The difference of barely five logarithmic units represents a border-line case for a visual titration when a complex-forming indicator is employed. In addition to this, there is no indicator known which reacts specifically with cadmium, and the hope of ever finding one seems to be very slight.

The difference of 4·7 log-units is more than sufficient for a photometric end-point, provided that either of the two metal-systems is self-indicating.[5] This, however, is not the case, since all species involved are colourless. A possibility may exist in the ultraviolet region, but this has not been investigated. Theoretical considerations indicate the possibility of placing a self-indicating system having an appropriate stability constant between that of the cadmium and zinc. For example, Underwood used copper as photometric indicator in the EDTA titration of bismuth.[6] Copper is especially suitable for this purpose because of the relatively large difference of the extinction coefficients of the free copper ion or its amino complex and any chelon complex. The stability constant of the copper-EGTA complex has not yet been reported in the literature. It is, however, reasonable to assume that it will be of the same order as, or even somewhat greater than, that of the cadmium complex. Fortunately the logarithm of the β-factor for copper in an ammonia buffer as specified above is 8·3.[3] This makes it possible to arrange the apparent stability constants in the order Cd $>$ Cu $\geqslant$ Zn. Experiments verified this assumption. Thus, a titration of cadmium in the presence of zinc is possible with copper as the photometric indicator.

EXPERIMENTAL

Apparatus

The photometric titrator used was described in an earlier paper in this series.[7] Cuvettes with a light path of 3 and 10 cm and a capacity of about 100–200 ml were employed. A Sargent automatic burette was used.

Reagents

Solutions of metals ions and complexing reagent were prepared from Reagent Grade material and standardised according to well-established chelometric procedures.[8,9] The buffer, pH 10, was prepared by dissolving 70 g of ammonium chloride and 570 ml of conc. ammonia in de-ionised water and diluting to 1 litre.

Absorbance curves of copper in solutions containing buffer (pH 10) in the absence of EGTA and in the presence of excess EGTA show that the most suitable wavelength for the titration is between 700 and 750 mμ. A 742-mμ interference filter was used.

Procedure

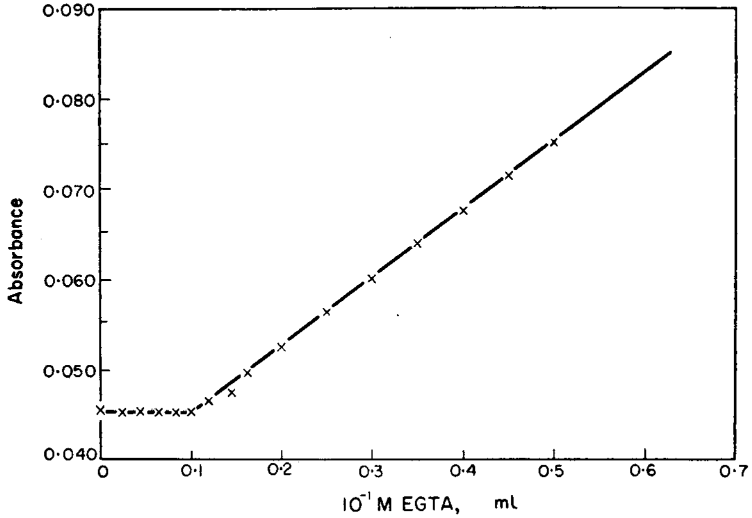
Accurately measured amounts of cadmium and zinc solutions were pipetted into the titration cell, 10 ml of buffer, pH 10 (the amount of buffer is not critical), and 5 ml of 0·1*M* solution of copper sulphate were added, and diluted to about 150 ml with de-ionised water. The cell was placed in the phototitrator, and the titration was performed in the usual manner. The transmittance readings were plotted on semi-log paper or, in the case of small changes, more conveniently transformed to absorbance and plotted on linear paper.

RESULTS

A representative curve is shown in Fig. 1. The results of some titrations are presented in Table I.

When the concentration of zinc is not exceedingly high the titration can be extended to a second, but less sharp, end-point thus permitting the determination of cadmium *and* copper in the presence of zinc.

Iron and aluminium in moderate amounts, when masked with tartrate, do not interfere. Magnesium can be present in considerable quantities. Most of the other ions interfere as in other chelometric procedures; they are either co-titrated, *e.g.*, lead and calcium, or cause a decrease in the slope difference, *e.g.*, nickel. This, however, is no serious drawback, since the separation of cadmium and zinc from most other elements can readily be effected by ion-exchange methods.[10] On the other hand, some multicomponent systems can be resolved by chelometric titrations involving operation with aliquots and employing different masking reagents, titrants and indicators. Where up till now the sum of cadmium plus zinc has been determined, the cadmium may be determined in a further step incorporating the new method.



0.1M Zn (total volume about 150 ml; cell length 10 cm; 742 mμ).

FIG. 1.—Titration curve for the determination of 2·00 ml of 5 × $10^{-3}M$ Cd in the presence of 50 ml of 0·1M Zn (total volume about 150 ml; cell length 10 cm; 742 mμ).

TABLE I. TITRATION OF CADMIUM WITH 0·1M EGTA IN THE PRESENCE OF ZINC, 742 mμ

Cd			Zn, *ml*		Cd:Zn *Ratio*
Taken, *ml*	Found, *ml*				
4·00	4·00	0·1M 3-cm cell	0	0·1M	—
9·90	9·94		25		1:25
4·00	4·02		5		1:1·25
4·00	3·95		100		1:25
2·03	2·06	5 × $10^{-3}M$ 10-cm cell	0		—
10·00	10·00		25		1:50
2·03	2·00		10		1:100
3·56	3·64		50		1:260
1·01	1·04		15		1:300
2·03	2·08		50	0·2M	1:500

The following example may show the principle of this approach. The sample contained the following ions: Pb, Zn, Cd and Cu.

In the first aliquot Pb was titrated with EDTA (Eriochrome Black T as indicator) in the presence of tartrate and cyanide. After selective demasking of Zn and Cd with formaldehyde, the titration was continued to obtain the sum Zn + Cd. In a second aliquot the sum Pb + Cd was obtained employing the new method. In a third aliquot the sum of all metals present was obtained by an EDTA titration at pH 6 using PAN as indicator.

The following results were obtained; the first figure is the calculated value, the second figure the experimental one.

Pb: 3·82; 3·80. Cd: 1·05; 1·08. Zn: 5·45; 5·40. Cu: 2·18; 2·26.

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Summary—A new method for the photometric titration of cadmium in the presence of zinc using ethyleneglycol-bis(aminoethyl)-tetra-acetic acid is described. Copper ion in ammonical solution serves as photometric indicator. One ml of 0·01 Cd solution in a total volume of about 150 ml was determined in the presence of a 500-fold excess of zinc.

Zusammenfassung—Eine neue Methode zur photometrischen Titration von Cadmium neben Zink mit Äthylenglocol-bis(aminoäthyl) tetressigsäure wird beschrieben. Kupferion in ammoniakalischer Lösung dient als photometrischer Indicator. 1 ml 0·01 m Cd-Lösung in 150 ml Titrationsvolum konnte neben der 500 fachen Menge Zink bestimmt werden.

Résumé—Les auteurs décrivent une nouvelle méthode de dosage photométrique du cadmium, en présence de zinc, par l'acide éthylène-glycol-bis(aminoéthyl) tétracétique. L'ion cuivre en solution ammoniacale sert d'indicateur photométrique. Un ml de solution de cadmium 0,01 M dans un volume total d'environ 150 ml a été dosé en présence d'un excès de zinc 500 fois plus important.

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Semimicro determination of strontium and calcium in mixtures*

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INTRODUCTION

THE determination of strontium and calcium in a mixture is one of the most difficult and troublesome problems in analytical chemistry, because of the similarity of their properties. The gravimetric procedures described are not free from co-precipitation and therefore if a quantitative determination is needed, several precipitations must be effected. The commonly used procedure is by precipitating strontium nitrate in a mixture of alcohol-ether[1] thus separating it from calcium, followed by the gravimetric determination of the strontium as sulphate, or oxide, and the determination of calcium as oxide, or titrimetrically. Weiss and Shipman[2] used potassium rhodizonate in a gravimetric method for the separation of strontium-90 from calcium. According to their paper, about 80 to 90% strontium can be recovered when the ratio Ca:Sr is as high as 50, using a four-fold excess of rhodizonate. Lieser and Hild[3] determined the solubility of strontium rhodizonate in solution. Their results show that under appropriate conditions the separation between calcium and strontium can be effected quantitatively by this reagent. In the present study we attempted to find suitable conditions for (*a*) a quantitative separation of strontium and calcium by rhodizonate; (*b*) a rapid determination of both ions, without using radiochemical techniques.

Calcium and strontium were determined by a complexometric method.[4] To permit this the rhodizonate had to be eliminated, because its presence interfered in the titrations. The conditions for this elimination were also studied.

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EXPERIMENTAL

Reagents

The reagents used were all of analytical grade. The aqueous rhodizonate solution (0·2%) was always freshly prepared from the sodium rhodizonate salt (B.D.H.). The EDTA solution was standardised by titration against a standard solution of strontium or calcium nitrate. The complexometric indicator, which was not stable for more than 2–3 days, was prepared by dissolving 0·1 g of *o*-cresolphthaleincomplexone (B.D.H.), 0·05 g of methyl red and 0·05 g of bromocresol green in a few drops of concentrated ammonia and diluting to 100 ml with water.[5]

Procedure

(*a*) *Separation of strontium and calcium:* The pH of the solutions with appropriate contents of calcium and strontium is adjusted to a value between 6–7. If the solutions to be analysed are acid, neutralisation can only be effected by potassium hydroxide. The volume of the solution should be about 15 ml. A two-fold excess of rhodizonate to strontium is added, with continuous stirring. After 5 min standing, the precipitate is filtered through Whatman No. 42 filter paper. The precipitate is washed on the filter with small amounts of water (10–15 ml) and dissolved in 15 ml of 0·5*N* HNO_3. This solution is used for the determination of strontium after the elimination of the rhodizonate. The rhodizonate must also be removed from the filtrate for the determination of calcium.

(*b*) *Elimination of rhodizonate:* The acid solution of strontium and rhodizonate is neutralised with a few drops of 1*N* NaOH until a brown-reddish colour appears. The solution is passed through a column, 16 mm in diameter and 180 mm long, filled to 3/4 of its length with the anion-exchange resin Amberlite IRA 410 Cl-technical, and the resin is then washed with 50 ml of water, the washings being added to the eluate. The solution of calcium is passed through the same column without neutralisation.

To save time, the precipitate of strontium rhodizonate is filtered through a filter funnel which is placed directly above the ion-exchange column. By this procedure, the filtrate containing the calcium has the rhodizonate removed immediately.

(*c*) *Complexometric titrations:* (*i*) *Titration of calcium:* 15–20 ml of saturated NH_4Cl, 5 ml of conc. NH_4OH, 10–15 ml of alcohol and 5–6 drops of the indicator are added to the solution. The solution is titrated with 0·02*N* EDTA until the red colour disappears abruptly. (*ii*) *Titration of strontium:* 5 ml of conc. NH_4OH, 40–50 ml of alcohol and 5–6 drops of the indicator are added to the solution. The titration is carried out with 0·05*N* EDTA, to the same end-point.

RESULTS AND DISCUSSION

The conditions for the quantitative precipitation of strontium rhodizonate without the coprecipitation of calcium were studied. As the presence of sodium and ammonium ions interfere with the precipitation by rhodizonate, acid solutions can only be brought to the required pH by neutralisation with potassium hydroxide. As can be seen from the results (Table I) the greatest accuracy was obtained with mixtures containing about 5 mg of strontium and 0–5 mg of calcium in about 10–15 ml solution. Only a twofold excess of rhodizonate to the strontium was needed, and the precipitate obtained could be filtered after a few min. Under these conditions the coprecipitation of calcium was avoided.

The rhodizonate could be eliminated in two different ways:

(a) heating to dryness,

(b) ion exchange.

The first procedure prolonged the time needed for the determination by 3–12 hr, and therefore, the ion-exchange method was used. It was found that by using a small column, filled with anion-exchanger in the chloride form, the rhodizonate from the solutions was removed in about 15 min. The optimum pH for the exchange was found to be 6, and acid solutions of strontium rhodizonate were adjusted to this pH with a sodium hydroxide solution. It was also found that the removal of rhodizonate occurred more easily when the precipitate was dissolved in nitric acid than in hydrochloric acid.

The solutions containing calcium and strontium were titrated with EDTA after the addition of alcohol, ammonia, ammonium chloride and *o*-cresolphthaleincomplexone. The quantity of alcohol added influenced the end-point in the case of strontium. It was found that 40–50 ml of alcohol

TABLE I.—ANALYSIS OF MIXTURES OF CALCIUM AND STRONTIUM

Taken, *mg*		Found, *mg*		Deviation, *mg*		Deviation, %		No. of determns.
Sr	Ca	Sr	Ca	Sr	Ca	Sr	Ca	
4·99	—	5·00	—	+0·01	—	0·2	—	4
—	5·02	—	5·10	—	−0·08	—	1·5	4
4·99	2·51	5·00	2·53	+0·01	+0·02	0·2	0·8	6
5·00	5·02	5·10	4·88	+0·10	−0·14	2·0	2·8	4
9·99	5·15	10·98	4·70	+0·99	−0·45	10·0	8·0	4
4·99	~0·6	5·04	0·56	+0·05		1·0		4

were necessary for reproducible results. Titration effected with 0·01*N* EDTA showed no clear end-points. It was found that for calcium 0·02–0·1*N* EDTA could be used, while for strontium the smallest usable normality was 0·05. Complexometric titrations with other indicators were attempted but the best results were obtained by the *o*-cresolphthaleincomplexone mixture described above although the end-point was not very sharp.

Summary—A method is described for the quantitative separation and determination of about 5 mg of strontium and 0·5–5 mg of calcium, by precipitation of strontium at pH ~ 6 with sodium rhodizonate, and determination of both ions by complexometric titrations.

Zusammenfassung—Eine Methode zur quantitativen Trennung und Bestimmung von etwa 5 mg Strontium und 0·5–5 mg Calcium durch Fällung von Strontium mit Natrium-Rhodizonat bei pH ~6 und komplexometrische Titrierung der beiden Ionen wird beschrieben.

Résumé—Les auteurs décrivent une méthode de séparation et de dosage d'environ 5 mg strontium et de 0,5–5 mg calcium par précipitation du strontium par le rhodizonate de sodium à pH ~6 et dosage des deux ions par titrages complexométriques.

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A spot test for uranium^{VI} with resacetophenone-oxime

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RESACETOPHENONE-OXIME was recommended by Neelakantam and co-workers[1,2] for the colorimetric determination of iron^{III} and uranium^{VI}. A reddish-brown colour was developed on the addition of the reagent to uranium^{VI} in a weak mineral acid medium. The intensity of the colour was found to increase with an increase in pH of the solution. This paper presents the results of the experiments carried out to establish the limit of identification of uranium^{VI} using resacetophenone-oxime.

EXPERIMENTAL

Reagents

Uranium^{VI} nitrate: AnalaR uranium^{VI} nitrate was dissolved in water. This solution was standardised by gravimetric[3] and titrimetric[4] methods. It was suitably diluted for spot-test analysis.

Resacetophenone-oxime: A 0·5% solution of this reagent in alcohol.

Procedure for the spot test

0·05 Ml of the uranium^{VI} nitrate solution was taken on a spot plate and 0·05 ml of the reagent solution was added to this and the two were thoroughly mixed. The observations were made after 30 sec. It was found that the red-brown colour of the uranium^{VI}-resacetophenone-oxime complex could be perceived with $5 \cdot 0 \times 10^{-5}$ *M* uranium^{VI} solution. With lower concentrations of uranium^{VI}, no colour could be observed.

Effect of pH

The effect of pH was studied using $5 \cdot 5 \times 10^{-5}$ *M* uranium^{VI} solution. It was noticed that lowering of the pH below 5·6 adversely affected the colour development whereas increase in pH by the addition of ammonia enhanced the intensity of the colour appreciably. When 0·05 ml of uranium^{VI}, 0·05 ml of the reagent solutions and 0·1 ml of 1*N*–11*N* ammonia were mixed, it was found that the brown colour could be observed using even $1 \cdot 25 \times 10^{-5}$ *M* uranium^{VI} solution.

Limit of identification = 0·595 μg
Dilution limit = 1:3,400,000

Interferences

Over a wide range of pH the reagent did not give any colour with uranium^{IV} even on keeping for long periods. Aluminium, zirconium and thorium did not interfere with the test. Iron^{III} was found to give a deep purple colour with the reagent and this reaction enables one to detect 1·2 μg of iron^{III}.

Application to titrations

Resacetophenone-oxime can be used as an external indicator in the titration of orthophosphate solution with uranium^{VI}. Interferences are the same as when conventional indicators are used. The recommended procedure is as follows:

A known volume of standard potassium dihydrogen phosphate solution is taken in a beaker, and 5 ml of acetic acid–sodium acetate buffer solution (pH, during titration, could be varied between 3·6 and 5·6) per 50 ml of titration mixture are added. The mixture is heated to 80° and titrated with uranium^{VI} solution. The end-point, which is very distinct, is indicated by the appearance of a reddish-brown colour when one drop of the titration mixture is mixed thoroughly with two drops of the resacetophenone-oxime solution and two drops of ammonia on a spot plate.

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Summary—A spot test for the detection of uranium^{VI} using resacetophenone-oxime is developed. It is found that a reddish brown colour develops when solutions of uranium^{VI} and resacetophenone-oxime are mixed in ammoniacal medium. The limit of identification is 0·595 μg.

Zusammenfassung—Ein Tüpfelnachweis für Uran(VI) mit Resacetophenonoxim wird beschrieben. Eine rötlichbraune Färbung entsteht in ammoniakalischem Medium. Die Nachweisgrenze beträgt 0·595 μg.

Résumé—L'auteur met au point un essai par touches pour déceler l'uranium(VI) en utilisant le resacétophénone-oxime. Une couleur brun rougeâtre se forme quand des solutions d'uranium (VI) et

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de resacétophénone-oxime sont mélangées en milieu ammoniacal. La limite d'identification trouvée est de 0.595 μg.

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A qualitative test for detection of ferrocenes

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THE value of a diagnostic test for the detection of the ferrocene nucleus in reaction mixtures resulting from attempted "sandwiching" reactions to prepare ferrocene derivatives has been pointed out by Goldberg[1] in his report of such a test. A similar test method has also been applied to the separation and detection of ferrocenes.[2] We now wish to report an alternative test based on an original observation which is believed to provide a simpler procedure.

The previous method[1] involved separating the ferrocene constituent in the sample which was suspected of containing a ferrocene derivative from the materials in the reaction mixture on a paper chromatogram, treating the chromatogram with hydrogen peroxide to destroy the ferrocene nucleus and to oxidise the iron^{II} to iron^{III} and then detecting the iron^{III} as a red thiocyanate complex.* The method now being reported is based on the observation that various ferrocene derivatives, when dissolved in glacial acetic acid and treated directly with aqueous potassium cyanoferrate^{III}, gave an immediate colour change somewhat similar to that obtained with iron^{II} ion.

The present test method involves simply extracting, with chloroform, a small sample of a reaction mixture previously made aqueous, placing 2 drops of the chloroform extract in approximately 3 ml of glacial acetic acid, and treating with 2 drops of aqueous potassium cyanoferrate^{III} (approximately 1 g/10 ml). In dilute solutions the presence of a ferrocene derivative is indicated by the appearance of a clear green colour, whereas in more concentrated solutions a deep blue precipitate separates.

Results obtained in applying the cyanoferrate^{III} test to a number of different ferrocene derivatives are shown in Table 1. Although colour changes were obtained with all of these derivatives some minor deviations from the general behaviour noted above were observed. The difference in colour observed with 1,1′-dibenzoylferrocene may result from the original deep red colour of the solution of this compound, which undoubtedly masks the true colour change. The mono- and diethyl-esters of ferrocene dicarboxylic acid gave unusually weak responses to this test compared with the other derivatives. Although the quantitative sensitivity of this test was not established, a positive test was obtained with the parent compound, ferrocene, using as little as 1 drop of solution containing 0·1 g of ferrocene in 100 ml of chloroform.

This test is believed to have advantages over the previously described methods for detection of the ferrocene nucleus in that it is simpler and more rapid. It requires no chromatogram or separate step to oxidise and destroy the ferrocene nucleus, and it provides an immediate answer with only a few drops of test solution. The test can be carried out in a test tube or on a spot-test plate. The chloroform extraction required for the test can be part of the normal working up of the reaction mixture, or it may be carried out on a small sample withdrawn from the reaction mixture by shaking with an aqueous-chloroform mixture in a test tube. The nature of the chemical change which occurs in the cyanoferrate^{III} test is at present under investigation; the results of this study will be reported upon at a later date.

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* It is apparently not necessary to destroy completely the ferrocene nucleus since it has recently been reported[3] that the ferricinium ion also provides a colored complex with thiocyanate.

TABLE I. FERROCENES (4,5) TESTED WITH $K_3Fe(CN)_6$*

Compound tested	Observed change	
	Dil. soln.	Conc. soln.
Ferrocene	Green colour	Blue ppt.
Benzoylferrocene	Green colour	Blue ppt.
1,1′-Dibenzoylferrocene	Yellow-green colour	Green-brown ppt.
2-Hydroxybenzoylferrocene	Blue ppt.	Blue ppt.
2-Methoxybenzoylferrocene	Green colour	Blue ppt.
2,4-Dihydroxybenzoylferrocene	Green colour	Blue ppt.
2-Hydroxy-4-methoxybenzoylferrocene	Green colour	Blue ppt.
2,4-Dimethoxybenzoylferrocene	Green colour	Blue ppt.
Ferrocenemonocarboxylic acid	Green colour	Blue ppt.
Ethyl ferrocenemonocarboxylate	Green colour	Blue ppt.
1-Carboxy-1′-carbethoxyferrocene	V. lt. green colour	Lt. green colour
1,1′-Diethyl ferrocenedicarboxylate	V. lt. green colour	Lt. green colour
1,1′-Bis(α-hydroxyethyl)-ferrocene	Green colour	Blue ppt.
Diferrocenyl ketone	Green colour	Blue ppt.
1,1′-Bis(chloromethyldimethylsilyl)ferrocene	Green colour	Blue ppt.

* To determine whether iron^{II}, which is employed in the "sandwiching" reactions, or iron^{III} which might be present, could interfere with this test, both aqueous and aqueous-tetrahydrofuran solutions of iron^{II} and iron^{III} chlorides were extracted with chloroform and the extracts were subjected to the test. None of these extracts provided a positive test.

Acknowledgements—With the exception of the parent compound, ferrocene, which was a recrystallised sample of material purchased from Ethyl Corporation, all of the ferrocene derivatives listed in Table I were analytically pure samples prepared and purified by Robert L. Schaaf[4,5] under contract with Materials Central, Wright Air Development Division.

Summary—The detection of the ferrocene nucleus of various substituted ferrocenes by a colour reaction with cyanoferrate^{III} ion is reported.

Zusammenfassung—Ein neuer Test wird mitgeteilt um Nachweis von Ferrozinkerne hingewiesen.

Résumé—L'auteur décrit un essai pour la detéction des ferrocènes.

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A phosphorus pentoxide desiccant employing exfoliated vermiculite as carrier

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INTRODUCTION

PHOSPHORUS pentoxide has been consistently employed as a desiccant for dehydration of air and other gases. It has been popularly considered to be as near perfect in drying efficiency as any form of solid material.

Unfortunately, it exhibits many objectionable properties. It is a powder, acid in reaction and low in drying capacity; and it is extremely difficult to handle, except by employing dry-box manipulative techniques. In "drying pistols" for desiccation of chemicals at controlled temperatures, surface incrustations of spent desiccant soon form. The reagent reservoir is thus prematurely and effectively inactivated.

An inert carrier-base, exfoliated vermiculite of high porosity, has been found to correct most of these faults.

EXFOLIATED VERMICULITE AS CARRIER

Exfoliated vermiculite has been previously described[1] for use as a carrier-base absorbent for the preparation of granular anhydrous magnesium perchlorate as desiccant. Sifted samples were prepared. Mesh sizes passing 8 and retained by 12, and passing 12 and retained by 20, were employed. The bulk density was found to be 0·17 and 0·21 g per ml, respectively. Exfoliated vermiculite is a common product of the building trades. It is employed as a free-flowing thermal insulator, and costs only a few pence per pound.

PREPARATION OF CARRIER-BASED DESICCANT

A weighed amount of carrier is placed in a dry 1000-ml screw-top bottle. An equal weight of P_2O_5 is quickly added and the bottle is closed. The bottle and contents (only half full) are then shaken vigorously for 5 min. The powdered P_2O_5 is thus incorporated completely within the voids of the exfoliated carrier. The bulk density of the finished product is thereby doubled. The finished product is a dust-free and free-flowing granular product.

DESICCANT CAPACITY OF CARRIER-BASED PHOSPHORUS PENTOXIDE

An absorption tube (25 × 350 mm) charged with 8–12 mesh granules, contained 28·2 g of desiccant. When saturated with water from a continuous flow of air of high humidity, its capacity was found to be 5·15 g of water or 18·3 % of its original weight. The spent reagent is free flowing and alters in colour from grey to that of the untreated carrier base, a colour transition which is readily observed.

The University of Illinois, Urbana, U.S.A. G. Frederick Smith
Iowa State University, Ames, U.S.A. Harvey Diehl

Summary—A granular carrier based phosphorus pentoxide of selective mesh sieve size aggregates is described. The water absorption capacity at maximum efficiency is 18·3 percent of reagent weight. This desiccant, as compounded, and as the spent material, is simple to prepare from commercially available materials and free flowing.

Zusammenfassung—Phosphorpentoxyd als Trockenmittel auf einem Träger und in bestimmter Korngrösse wird beschrieben. Die Absorptionskapazität in Bezug auf Wasser beträgt maximal 18·3 % des Reagensgewichtes. Das vor und nach Absorption frei schüttbare Granulat ist leicht aus käuflich erhältlichen Materialien herstellbar.

Résumé—Les auteurs décrivent un support granulaire à base de pentoxyde de phosphore, en agrégats de dimension sélectionnée. La capacité d'absorption de l'eau, pour une efficacité maximum, est de 18,3 pour cent du poids du réactif. Ce desséchant est simple à préparer à partir de produits disponibles dans le commerce.

REFERENCE

[1] G. Frederick Smith and Harvey Diehl. *Talanta*, in the press.

Talanta, 1962, Vol. 9, pp. 86 to 88. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

The determination of tantalum, niobium and titanium by precipitation from homogeneous solution

Sir,

As was already shown in a previous article,[1] tungsten can be successfully determined by precipitation from a homogeneous hydrogen peroxide-nitric acid solution. The same procedure is readily adaptable to the determination of niobium and tantalum. After a potassium bisulphate fusion, the melt is dissolved in hydrogen peroxide and nitric acid, and subjected to thermal decomposition of the soluble peroxides. Tracer techniques showed that the recovery is better than 99.8%, whereas the co-precipitation of titanium is negligible.

Precipitation from homogeneous solution of niobium, tantalum and titanium is also possible by thermal decomposition of their peroxides from a slightly alkaline medium (pH = 7–8), with low tungsten co-precipitation.

By alternative precipitation from homogeneous solution in a nitric acid and an alkaline medium, it thus becomes possible to determine the tungsten, niobium + tantalum and titanium contents of a sample after a titanium and tungsten determination in the respective filtrates.

The co-precipitation distribution constants of titanium and tungsten for both procedures were determined. They appeared to follow Riehl's law.

A full account of this work will be published in due course.

Laboratory for Analytical Chemistry
Ghent University, Belgium
22 *August* 1961

R. Dams
J. Hoste

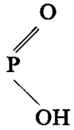
REFERENCES

[1] R. Dams and J. Hoste, *Talanta*, 1961, **8**, 664.

Infrared spectra of some organophosphorus extractants

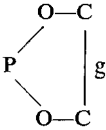
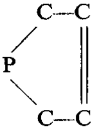
Sir,

The recent paper by Horton and White[1] contains errors in the assignment of absorption bands which should be corrected to prevent their perpetuation by future workers. The authors do not appear to have realised the danger of the application of published correlations without due regard to the chemistry and constitution of the compounds being examined. Typical examples are the assignment of a band in the spectrum of capryl phenylphosphonic acid[2] to a P-O-(aryl) vibration, when the molecule contains a P-aryl rather than a P-O-(aryl) bond, and the comment on the strength of the P-H absorption band in trialkyl phosphites,[3] which contain no P-H bonds.

The attribution throughout the paper of absorption in the region of 2400 cm^{-1} to P-H impurities, is also open to criticism. Absorption due to the P-H valence vibration undoubtedly occurs in this region but the P-H bands are sharp, are of medium intensity, and are invariably accompanied by a sharp, medium to strong, band, in the region of 1100 cm^{-1}, which is assigned[4] to the P-H deformation vibration. Inspection of the published spectra strongly suggests that the absorption near 2400 cm^{-1} is caused by the second of the three bands, characteristic of the  $\mathrm{P}(=\mathrm{O})\mathrm{OH}$ group[5,6] arising from the presence of an acidic impurity.

Similarly, the absorption bands reported[7] in the region 3300–3700 cm^{-1} may have a common source. Experience has shown that it is difficult to prepare organo-phosphorus compounds completely free of water and to exclude all water during subsequent storage and the handling stages preparatory to running a spectrum. The reported bands are probably caused by a trace of adsorbed water. The exact position of the band will vary both with the concentration of the water in the phosphorus compound and with the dilution of the latter in the solvent. The band detected at 3500 cm^{-1} in dibutyl hydrogenphosphonate is certainly not due to hydrogen bonded hydroxyl connected with the postulated dimeric structure, since this contains no hydroxyl groups. Also the observed phosphoryl frequency is somewhat higher than the calculated value, indicating that the P=O bond is not involved in hydrogen bonding. Furthermore, it has been shown by Fox,[8] as quoted by Doak and Freedman,[9] that the concentration of the phosphite isomer in dibutyl hydrogenphosphonate is about 10^{-4}%. At this level it is not surprising that the (P)—O—H absorption band has not been detected spectroscopically.

The use of empirical formulae[10] to calculate the approximate frequency of the phosphoryl band can be helpful in interpretation provided that due care is taken. We have found that the formula gives reliable results, usually within 10 cm^{-1} of the observed frequency, except in the case of acids where the variable hydrogen bonding makes the assignment of an "electronegativity" to the OH group impracticable. The calculation must, however, be performed accurately if the result is to be useful. The value obtained from the formula for tricapryl phosphate is 1289 cm^{-1}, not 1176 as quoted.[2] For di-sec-butylphenylphosphonate it is 1266 cm^{-1} rather than 1307.[11]

Care should also be taken in applying correlations developed by other workers, particularly in ensuring that the original assignment is clearly understood. For example, the assignment of a band at 1375 cm^{-1} to an R—O—P vibration[12] on the stated authority of McIvor *et al.*[13] is unacceptable as there is no reason to vary McIvor's assignment of this band to a C—H deformation mode. Similarly the assignment of the 926 cm^{-1} band[14] to a ring vibration by analogy with the work of Cason *et al.*[15] cannot be justified, since Cason's assignment is for rings involving  groups and the band used is due to a P—O—(C) vibration perturbed by the variation of bond angles on ring formation This correlation will obviously not be applicable to a ring such as  , with no P—O—C bonds. Again, instead of attributing bands in the 715–770 cm^{-1} region to P—C vibrations as stated, Thomas[5] stated that this assignment[16] should be regarded with grave suspicion. There are further errors of this type in the paper, but to enumerate them in detail would be needlessly repetitious.

Differences between the authors' spectra and other published spectra may indeed in some cases be caused by variation in the impurity content. However, when making such comparisons, it must be realised that it can be misleading to compare spectra obtained from different physical forms of the material, *e.g.*, solutions and capillary films, since band positions and relative intensities vary unpredictably in solution, and even more markedly when a change of state is involved. Care should also be taken to ensure the chemical validity of the comparison, *e.g.*, the Sadtler[17] spectrum (No. 9041), quoted as a comparison for dibutyl hydrogenphosphonate, is, in fact, that of dibutyl hydrogen phosphate.

Finally, a word of warning should be given to other chemists who may be tempted to interpret infrared spectra solely on the basis of correlation tables. Correlations are derived by spectroscopists as a guide to the region in which absorption bands should appear if a specific group is present in the molecule. The reliability of a correlation will depend on the number of compounds on which it was based and on their variety. At best it will only be a guide to a region, at worst it may be a frequency for a single compound. It should always be applied logically. Because P—H compounds absorb in the region of 2400 cm^{-1} it does not follow[18] that all absorptions in this region must be due to P—H vibrations. In general, it is impossible to assign all the absorption bands of any complex organic molecule.

The recording of spectra under conditions designed to accentuate weak bands increases the difficulty of interpretation in many cases. Because an absorption band is weak it is not necessarily caused by an impurity; it may be an overtone or combination band. Unless a spectrum of the compound is available, taken under identical conditions, in which a particular band is absent, there is no certain way of identifying that band as being due to an impurity. If a specific impurity is suspected of being present, then its whole spectrum should be considered in relation to that of the material in which it is occurring. Thus, the assignment of the 2380 cm^{-1} band in tricapryl phosphate[2] to unreacted capryl alcohol is obviously incorrect if the relative intensity of this band and the OH band in the spectra of capryl alcohol are considered. In addition, visual estimation of the absorption intensity of this band would have shown that the intensity is greater in the spectrum of a 0·05-mm film of the phosphate, in which it is stated to be an impurity, than in a 0·2-mm film of the alcohol.

War Department
C.D.E.E.
Porton Down, Wilts., England
25 *September* 1961

L. C. THOMAS
ROSEMARY A. CHITTENDEN

REFERENCES

[1] C. A. Horton and J. C. White, *Talanta*, 1961, **7**, 215.
[2] *Idem, loc. cit.*, 218.
[3] *Idem, loc. cit.*, 222.
[4] L. C. Thomas and Rosemary A. Chittenden, in press.
[5] L. C. Thomas, *Chem. and Ind.*, 1957, 198.
[6] L. C. Thomas, Rosemary A. Chittenden and H. E. R. Hartley, in the press.
[7] C. A. Horton and J. C. White, *loc. cit.*, 217, 219, 220, 226, 229.
[8] R. B. Fox, U.S. Naval Research Lab., NRL 5242, 1959.
[9] G. O. Doak and L. D. Freedman, *Chem. Revs.*, 1961, **61**, 31.
[10] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.
[11] C. A. Horton and J. C. White, *loc. cit.*, 219.
[12] *Idem, loc. cit.*, 220.
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[14] C. A. Horton and J. C. White, *loc. cit.*, 225.
[15] J. Cason, W. N. Baxter and W. DeAcetis, *J. Org. Chem.*, 1959, **23**, 247.
[16] D. E. C. Corbridge, *J. Appl. Chem.*, 1956, **6**, 456.
[17] S. P. Sadtler, *Infrared Spectra*. Sadtler and Sons, Philadelphia.
[18] Aristotle, *Prior Analytics*, Book 1, Ch. 3 ^{a}40–^{b}3, *circa* 350 B.C.

Talanta, 1962, Vol. 9, pp. 89 to 91. Pergamon Press Ltd. Printed in Northern Ireland

EDITORIAL NOTE

SOME months ago we promised to give a brief account of our editorial and refereeing policy, and considerable interest has been expressed in this.

As is implied in our Notes for Contributors, our aim is to provide a journal in which the standard of the contributions is very high, giving satisfaction at the same time to our subscribers and our contributors. The methods which we use to attain this end will perhaps be best indicated by describing the processing of a typical contribution from receipt to publication.

On receipt, either by the Editor-in-Chief or one of the Regional Editors, a paper is acknowledged formally, and is sent with as little delay as possible (aiming at an interval of a few days at most) to a suitable referee. The Editor-in-Chief and the Regional Editors are all experienced analytical chemists, who are concerned to make the right choice of referee in the light of their familiarity with the field and their acquaintance with a wide circle of experts. This choice is dictated solely by the subject of the paper, and the aim is to choose an undoubted authority in the field, without regard to whether he is "academic" or "industrial." The referee form which accompanies the paper carries the following extracts from *Notes to Contributors*, as a guide to the quality to be looked for by the referee:

> "Contributions may deal with any aspect of analytical chemistry, although papers concerned exclusively 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 announcements and reviews will be published. 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, but should be critical.
>
> "Original papers, short communications and reviews will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication."

The questions asked of the referee are six in number, as follows:

1. Is the paper of sufficient interest and originality and is its subject matter suitable for it to be published in the Journal (subject to the alterations suggested in the following sections)
    (*a*) in the form of an original paper (or review)?
    (*b*) as a short communication?
2. If the paper is generally acceptable, are there any obvious errors of fact or logic—as distinct from points of scientific controversy or literary style—which need correction?
3. If the paper is too long, what sections could be abbreviated?
4. If the paper is obscure in any respect, what alterations or additions would remove the obscurity?
5. Have you any further suggestions for improvement?
6. Are there any parts of the paper to which you have been unable to give adequate consideration?

The referee is asked to report within two weeks, and, on the whole, referees are very co-operative in this respect—indeed, in all respects.

When the referee's report is received, any points of substance which he has made are forwarded to the author for his consideration. On the whole, the editorial view is that one of the principal functions of the referee (after the primary one of deciding the over-all value of the paper, of course) is to draw attention to matters which, in his view, may be the result of author-blindness. In many cases, therefore, it is regarded as sufficient if the criticisms of the referee are brought to the notice of the author, whether he accepts them or not. Often the author may be as eminent in his field of research as the referee, and in the event of disagreement, one is as likely to be correct as the other. The editor who would venture to assert that all his referees are right all the time, and that all his authors are wrong all the time, would indeed be bold (and, we suspect, unsuccessful).

It may well be that more than one triangular exchange of correspondence between editor and author and editor and referee is necessary before the paper is finally accepted for publication, but on the whole, where the paper has been regarded as worthy of publication, we have found a ready (and indeed grateful) acceptance by authors of the referee's criticisms, and an equally ready approval by referees of the author's revisions—or of his objections to the criticisms.

On acceptance, the paper is now ready to be prepared for the press. Diagrams must go to the publishers, in many cases for re-drawing, and thence to the block-makers. Copies of the summary must go to the translators. The manuscript must be corrected and marked up for press by the Editor-in-Chief or the Assistant Editor. This, we must sorrowfully note, is in many instances made no easier by the form in which the authors have submitted manuscripts. Papers often have to be cut in pieces and stuck together again to transfer summaries from end to beginning (or, in the case of short communications, *vice versa*). Lists of references frequently have to be retyped to transform them to the conventional form used by TALANTA. On the other hand, we must admit that a few of our contributors are so good in this respect that we suspect they have actually studied the Journal before preparing their manuscripts! These, alas, are still too much in the minority.

While on this topic, we would also beg contributors who are writing in a language not their own to have their papers checked before submission, if possible, by a technical colleague who writes the language fluently. This, we think, would often save the editors a considerable amount of re-writing, and the printers a considerable amount of heart-burning at the futuristic mixture of red and black which is presented to them. In all justice to our printers, it is very rarely that they have admitted defeat; and the number of times that the editor has been complimented by authors on the "clean" proofs is a clear indication of how successfully the printers are doing their job.

In order to save time, papers are normally now set directly in page form. It is, therefore, no help if an author decides at this stage that two paragraphs of additional explanation or a new Table are necessary. Alterations, in fact, should be kept to the bare minimum. Even the addition of a footnote may alter the pagination of the whole paper.

By the time that the proofs are received from the printer, the block proofs should also be ready. Once again, any alteration may and indeed almost certainly will involve time and money in the preparation of a new block. Proofs are corrected by a team of voluntary readers in addition to the author. Most authors having returned a proof marked "No corrections are necessary," would probably be surprised to find how many errors or inconsistencies they have missed, and how much red ink is on the proof by the time that it goes to the printers for final correction before printing.

Finally, we would point out that we have a "deadline" with the printers, a date by which the corrected and made up proofs must be returned. If the proof of your paper sits on your desk for a week, this may make all the difference between appearing in the forthcoming issue or being held over to the next.

The first issue of TALANTA appeared in mid-1958. We think we have learned (the hard way) many of the snags in editing and producing it. We are grateful to those authors and referees whose patience, in our teething stage, have made us feel that this is a worthwhile venture, and we look forward to repaying this patience by providing the best possible service both for our contributors and our readers.

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PUBLISHER'S ANNOUNCEMENT

Special Subscription Rate for Students

THE publishers are pleased to announce a special Student's Rate for *Talanta. Bona fide* students will be able to obtain the Journal for £3.10.0. (U.S.A. $10) per annum. This offer is intended to encourage young people to follow the latest literature and to start building their personal libraries.

Students wishing to take advantage of this special subscription rate should send their application, with their remittance, to the Subscription Department of either the Oxford or New York Office of Pergamon Press (addresses are given on the inside cover of the Journal). The application should be accompanied by a brief note from their professor or tutor to the effect that the individual is a *bona fide* student.

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NOTICES

The Commission on *Microchemical Techniques, Section of Analytical Chemistry*, **International Union of Pure and Applied Chemistry**, has recently recommended a series of test substances for the microdetermination of nitrogen in organic compounds (see *Pure and Applied Chemistry*, 1961, **3**, 513).

FRANCE

Les conférences suivantes auront lieu à la Faculté de Pharmacie, Paris, à l'amphithéâtre Bourquelot, à 17 h 45, sous la direction des Professeurs J. A. Guatier et P. Malangeau:

Mardi 13 *février* 1962: **Les anthocyanes des fruits—méthodes d'identification et applications:** Professeur P. Ribereau-Gayon.

Mardi 27 *février* 1962: **De la distillation à la chromatographie:** Professeur P. Jaulmes.

Jeudi 15 *mars* 1962: **Les réactions électrochimiques dans l'acétonitrile—aspects récents de l'oxydation à une électrode de platine:** Mme. J. Badoz-Lambling.

Mardi 27 *mars* 1962: **La diazocpulation en analyse organique:** M. J. Bartos.

UNITED KINGDOM

Thursday 18 *January* 1962: **Polarography of Carbon Dioxide:** Professor J. Jordan: *Polarographic Society.* Biochemical Department, Institute for Diseases of Chest, Brompton Road, London, S.W.3. 5.00 p.m.

Thursday 8 *February* 1962: **New Analytical Reagents in Colorimetric Analysis:** *Society for Analytical Chemistry.* London 2.30 p.m.

Wednesday 14 *February* 1962: **Automatic Methods in the Analytical Laboratory:** Dr. I. D. P. Wootton and Dr. G. Mattock: *Society for Analytical Chemistry, Midlands Section and Association of Clinical Biochemists.* University, Edgbaston, Birmingham, 15. 6.30 p.m.

Wednesday 21 *February* 1962: **Assessment of Antibiotics in Animal Feeds:** *Society for Analytical Chemistry, Biological Methods Group.* Burlington House, London, W.1. 7.00 p.m.

Thursday 22 *February* 1962: **Analytical Research:** Dr. J. Haslam: *Society for Analytical Chemistry, Midlands Section.* Technical College, Luton. 6.30 p.m.

Friday 23 *February* 1962: **Annual General Meeting** followed by reading of Original Papers: *Society for Analytical Chemistry, Microchemistry Group.* Burlington House, London, W.1. 6.45 p.m.

Friday 23 *February* 1962: **Death from Poison,** Dr. A. C. Hunt, and **Scientific Aspects of Crime Detection,** Detective Supt. J. K. McLellan: *Society for Analytical Chemistry, Scottish Section.* Royal Society of Edinburgh, George Street, Edinburgh. 7.15 p.m.

Tuesday 27 *February* 1962: **Some Surface Effects in Electro-analytical Chemistry:** Professor H. A. Laitinen: *Society for Analytical Chemistry, Physical Methods Group* and *Polarographic Society.* School of Pharmacy, London, W.C.1. 6.30 p.m.

Wednesday-Saturday 28–31 *March* 1962: **Conference on Molecular Spectroscopy:** *Institute of Petroleum, Hydrocarbon Research Group.* William Beveridge Hall, Senate House, University of London, W.C.1 (see also *Talanta*, 1961, **8**, 695).

The provisional programme is as follows:

Wednesday 28 *March*

H. W. Thompson (University of Oxford, U.K.)	*Trends in Chemical Applications of Spectroscopy.*
A. Walsh (C.S.I.R.O., Melbourne, Australia)	*Atomic Absorption Spectroscopy.*

Thursday 29 *March*	
R. E. Richards (University of Oxford, U.K.)	*New Development in Magnetic Resonance Spectroscopy.*
R. B. Williams (Humble Oil & Refining Co. Texas, U.S.A.)	*A study of Nuclear Magnetic Resonance Performance Parameters.*
D. J. E. Ingram (University College of North Staffs., U.K.)	*The Method and Technique of Electron Resonance, and its Application to Metal Complexes.*
D. H. Whiffen (N.P.L., U.K.)	*A Review of Electron Spin Resonance of Organic Radicals.*
R. N. Dixon (University of Sheffield, U.K.)	*Free Radical Spectroscopy.*
T. M. Sugden (University of Cambridge, U.K.)	*Spectrophotometry of Free Radicals in Flames.*
Friday 30 *March*	
G. R. Wilkinson (University of London, U.K.)	*Spectroscopy in the Far Infrared.*
N. Sheppard (University of Cambridge, U.K.)	*Infrared Spectra of Molecular Rotations in Condensed States.*
L. J. Bellamy (ERDE, Waltham Abbey, U.K.	*The Effect of Internal Environment on Group Frequencies.*
H. W. Thompson (University of Oxford, U.K.)	*Factors Affecting Characteristics of Infared and Raman Vibrational Bands.*
Van Zandt Williams (Perkin-Elmer Corpn., U.S.A.)	*Developments in Applied Spectroscopy.*
H. E. Hallam (University College of Swansea, U.K.)	*Solvent Effects in Infrared Spectra.*
Saturday 31 *March*	
W. C. Price (University of London, U.K.)	*Vacuum Ultraviolet Spectra and Photoionisation of Molecules and Radicals.*
A. D. Walsh (University of St. Andrews, U.K.)	*Electronic Spectra of Small Polyatomic Molecules.*

Contributions to the conference will also be given by:

C. W. Chantry (N.P.L., U.K.)	*Optical Absorption Spectra of Orientated Free Radicals.*
R. L. Warren (Middlesex Hospital, U.K.)	*A Versatile Micro-sample Flame Spectrophotometer.*
D. M. Adams (I.C.I. Ltd., The Frythe, U.K.)	*Solvent Effects on the Infrared Spectra of Inorganic Complexes.*

It is also intended, during the conference, to discuss other topics, such as X-ray fluorescence.

April or May 1963: **Symposium on the Analysis of Calcareous Materials:** *Society of Chemical Industry, Road and Building Materials Group,* London.

It will include analytical procedures, using either chemical or physical methods for the determination of elements, radicals or compounds in naturally occurring or artificially made materials consisting to a large extent of calcium compounds. Thus, it will cover the analysis of calcareous rocks and minerals, hydraulic cements, lime, whiting, gypsum plasters, slags, calcareous building materials and some ceramic products. Papers will be contributed on physical methods of analysis such as spectrometry, flame photometry, X-ray fluorescence, X-ray diffraction, and mass spectrometry as well as chemical methods.

It is intended that the Proceedings of the Symposium shall be in such a form as to serve as a text book of analysis for this field. Authors who wish to contribute papers on appropriate topics for this Symposium are invited to write for further information to the Symposium Secretary: Mr. G. E. Bessey, Chalk Lime and Allied Industries Research Association, Church Street, Welwyn, Herts., England. It will be necessary for manuscripts to be available by October, 1962.

The *Annual General Meeting* of the *Physical Methods Group of the Society for Analytical Chemistry* was held at Burlington House, London, W.1, on Tuesday, 21 November, 1961. The Chairman of the Group, Dr. G. W. C. Milner, presided.

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

Chairman: Dr. W. Cule Davies
Vice-Chairman: Mr. L. Brealey
Hon. Secretary and Treasurer: Dr. T. L. Parkinson, Product Research Division, Beecham Foods Ltd., Harpenden Rise, Harpenden, Herts.

The following new British Standards have recently been announced (see *B.S.I. News*, 1961, December):

B.S. 3420: 1961: *Sealed glass cells for photometric haemoglobinometry.* This specifies requirements for sealed glass cells with suitable solutions for the accurate determination of haemoglobin concentration of blood samples, and describes the methods of using such samples to calibrate clinical instruments for the estimation of haemoglobin. (*Price* 4s.)

B.S. 3430: 1961: *Method for the sampling of paper for testing.* This specifies a method of obtaining a representative sample of a lot of paper for most test purposes. It applies to substances below 250 g/m^2 and is identical, except for editorial adjustments, with ISO Recommendation R 186. (*Price* 4s.6d.)

B.S. 3431: 1961: *Method for the conditioning of paper and board test samples.* This defines the conditioning atmosphere and the method of conditioning paper and board before and during testing. Except for minor (chiefly editorial) adjustments it is identical with ISO Recommendation R 187. (*Price* 3s.)

B.S. 3432: 1961: *Method for the determination of paper substance.* This specifies methods for determining the substance (*i.e.* weight of a specified area) of paper, under three different conditions, *viz.* 'as taken', 'after conditioning' and 'on the oven dry basis'. (*Price* 4s.6d.)

B.S. 3433: 1961: *Methods for the sampling and testing of paper for moisture content.* This specifies two methods of determining moisture content. Part I deals with the oven drying method and applies to papers that do not contain appreciable quantities of materials, other than water, which will escape from the paper at the test temperature. Part 2 specifies an entrainment distillation method for materials which cannot be tested by the oven-drying method owing to the probable loss of volatile or fusible constituents. (*Price* 5s.)

The following Amendment Slips are also announced;

B.S. 700: 1952: *Graduated pipettes and one-mark cylindrical pipettes.* Amendment No. 3: PD 4325.

B.S. 1017: *The sampling of coal and coke: Part* 2: 1960: *Sampling of coke.* Amendment No. I: PD 3266.

B.S. 1428: *Microchemical apparatus: Part JI:* 1954: *Micro-electrolytic apparatus.* Amendment No. I: PD 4350.

B.S. 2782: *Methods of testing plastics: Part* 4: *Analytical methods and viscosity in solution.* Amendment No. 7: PD 4364: Methods 402: Analysis of water extract of phenolic mouldings.

UNITED STATES OF AMERICA

Thursday–Friday 25–26 *January* 1962: **Ninth Annual Western Spectroscopy Conference.** Asilomar, Pacific Grove, Calif.

Monday 29 *January–Thursday* 1 February 1962: **Fifteenth Annual Symposium on Modern Methods of Analytical Chemistry.** Louisiana State University, Baton Rouge, La.

The following programme of invited speakers has been arranged:

EPR in investigation of Electrode Processes.	Ralph Adams (University of Kansas, U.S.A.)
The Electron Probe.	L. S. Birks (Naval Research Laboratory, U.S.A.)
Chronopotentiometry.	Donald Davis (Louisiana State University, U.S.A.)
Fusion Reactions and Morphological Structure of Precipitates.	L. Erdey (Technical University of Budapest, Hungary)
Raman Spectroscopy and Infrared Spectroscopy.	R. Norman Jones (National Research Council, Canada)
Detector Systems for GLC.	Kurt Kraus (Oak Ridge National Laboratories, U.S.A.)
Analysis of High Polymers.	John Mitchell (E.I. du Pont de Nemours & Co. Ltd., U.S.A.)
Activation Analysis.	W. W. Meinke (University of Michigan, U.S.A.)
Atomic Absorption Spectroscopy.	Alan Walsh (C.S.I.R.O., Australia)

Monday–Friday 5–9 *February* 1962: **A.S.T.M. Committee Week.** Statler Hilton and Sheraton-Dallas Hotels, Texas.

Talanta, 1962, Vol. 9, p. 96. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

An investigation of 5-(3-nitrophenylazo)-salicylic acid (Na salt) as a spectrophotometric reagent for magnesium. D. Betteridge and John H. Yoe. (30 *October* 1961).

The flame photometric determination of titanium. C. L. Chakribarti, W. F. Pickering and C. L. Wilson. (30 *October* 1961).

Titrimetric determination of vanadium^{IV} with cerium^{IV} sulphate at room temperature, using rhodamine 6G as fluorescent indicator. G. Gopala Rao and L. S. A. Dikshitulu. (3 *November* 1961)

Reductometric titration by ferrous sulphate in a medium of triethanolamine—I. Determination of manganese. Jan Dolezal, Stanislav Rossler and Jaroslav Zyka. (7 *November* 1961)

Über die analytische Gruppe fur Ti(IV) in organischen Reagentien. L. Sommer. (10 *November* 1961).

Analytical potential of separations by liquid ion-exchange. C. F. Coleman, C. A. Blake, Jr., and K. B. Brown. (13 *November* (1961).

The use of oxycellulose for the collection of traces of metals. E. Schulek, Zs. Remport-Horvath and A. Lasztity. (14 *November* 1961).

Mixed chemiluminescent indicators. L. Erdey, W. F. Pickering and C. L. Wilson. (20 *November* 1961).

Some observations on the precipitation of niobium and tantalum from homogeneous solution. T. H. Richert and Louis Gordon. (20 *November* 1961).

Ion-exchange separations using sulphosalicylic acid. James S. Fritz and Thomas A. Palmer. (20 *November* 1961).

Some consideration on masking effectiveness. Adam Hulanicki. (23 *November* 1961).

The analytical use of a standard solution of iodine trichloride. E. Schulek and L. Ladanyi. (23 *November* 1961).

Thiourea and its organic derivatives—I: Oxidimetric determination with potassium iodate. Balwant Singh and Balbir Chand Verma. (23 *November* 1961).

The determination of gallium. G. R. E. C. Gregory and P. G. Jeffery. (29 *November* 1961).

The colorimetric determination of molybdenum with polyhydric phenols. H. Buchwald and E. Richardson. (28 *November* 1961).

Emission spectra from high-frequency excitation—III: A study of argon-carbon dioxide mixtures. C. L. Chakribarti, R. J. Magee and C. L. Wilson. (28 *November* 1961).

Analytical rapid methods for the determination of metals and inorganic materials—XIII: The determination of tin in metallic antimony. Zdeněk Šulcek, Jan Doležal, Jan Michal, Văclav Sychra. (29 *November* 1961).

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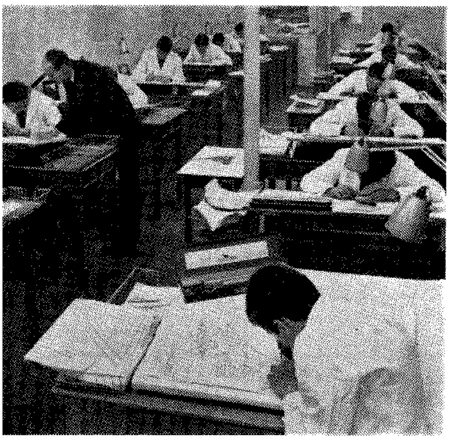

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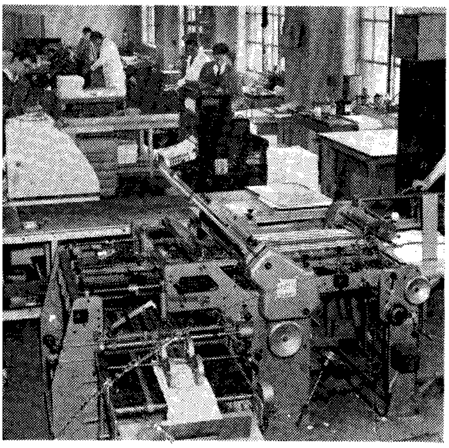

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